



Colloidal behavior of aqueous montmorillonite suspensions: the specific role of pH in the presence of indifferent electrolytes

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Abstract

Montmorillonite is the most often studied swelling clay mineral. The layers have permanent negative charges due to isomorphous substitutions, and pH-dependent charges develop on the surface hydroxyls at the edges. Wyoming montmorillonite samples with different extents of isomorphous substitutions (Swy-1 and Swy-2) were studied. The acid–base titration of Na-montmorillonite suspensions between pH 4 and 9 at 0.01, 0.1 and 1 M NaCl was used to characterize pH-dependent charge development on amphoteric edge sites and to determine the point of zero charge (PZC) of edges. The evaluation of reversible net proton surface excess vs. pH functions revealed that the OH groups at edges having PZC at pH \sim 6.5 are less basic than the Al-OH and less acidic than the Si-OH groups. Positive charges can develop in a protonation reaction of Al-OH sites at edges only at pHs below \sim 6.5, and deprotonation of Si-OH then that of the Al-OH sites takes place with increasing pH of solution resulting in negative charges at edges. Therefore, patch-wise charge heterogeneity of montmorillonite, i.e. oppositely charged surface parts of layers, exists only under acidic conditions. Coagulation kinetics measurements resulted in reliable stability ratio data for fine montmorillonite sols at different pHs, and provided undisputable characterization of hetero- and homoaggregation. Edge-to-face heteroaggregation occurs above NaCl concentration 25–26 mmol l^{-1} at pH \sim 4, where the hidden electric double layer (edl) of positively charged edge region has emerged. Edge-to-face attraction between the poorly charged edges and negatively charged faces of platelets around the pH of PZC of edges ($\text{pH}_{\text{PZC, edge}} \sim$ 6.5) in relatively low concentration of the indifferent electrolytes (typically around 50 mmol l^{-1} NaCl) is probable. The homoaggregation of uniformly charged lamellae at pH 8–8.5, formation of face-to-face aggregates requires much higher salt concentration (typically around 100 mmol l^{-1} NaCl) to compress the dominant edl on the highly charged faces of particles. XRD patterns of montmorillonite films prepared from slightly acidic suspensions proved that formation of well-ordered layer packages is hindered by the attraction between edges and faces. Characteristic changes in gel formation and in rheological properties induced by decreasing pH in dense suspensions containing 0.01 M NaCl provided experimental evidence for the structure of particle network. A significant increase in thixotropy and yield values, and also the formation of viscoelastic gels only below pH \sim 6.5 verify that attractive interaction exists between oppositely charged parts of lamellar particles.

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1. Introduction

Although the pH-dependent colloidal behavior and several properties of montmorillonite suspen-

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sions are well-known for decades, the unique charge heterogeneity of montmorillonite platelets, the different modes of association between asymmetric particles, i.e. edge-to-face, face-to-face, edge-to-edge, which result in particular properties and applications of suspensions, are still in the focus of clay research and the subject of even recent papers (Ramos-Tejeda et al., 2001, 2003; Janek and Lagaly, 2001; Penner and Lagaly, 2000, 2001; Bergaya and Lagaly, 2001; Abend and Lagaly, 2000; Durán et al., 2000; Benna et al., 1999; Yildiz et al., 1999; Altin et al., 1999; de Kretser et al., 1998).

The pH and indifferent electrolytes influence simultaneously the colloidal behavior of montmorillonite suspensions, but their effects may not be differentiated appropriately. While the specific effect of dispersing anions like carbonates (Yildiz et al., 1999), phosphates (Penner and Lagaly, 2000; 2001), silicates or organic polyanions (Ramos-Tejeda et al., 2001, 2003; Tombácz, 2003) is interpreted on the same theoretical basis, it seems the effect of pH and indifferent electrolytes is still the subject of scientific discussion. The effect of H^+ ions has to be distinguished from the simple charge neutralization of indifferent ions. The specific role of pH is not often emphasized even in good papers. For example, a noteworthy paper was published (de Kretser et al., 1998) about the surface chemistry–rheology inter-relationships in clay suspensions, in which the effect of added salt could be adequately explained by a combination of random coagulation and particle orientation effects as authors wrote “without restoring to the traditional edge-face heterocoagulation model” of Van Olphen (1963). Although it was stated in this paper that the suspension pH must be lower than the isoelectric point of the edges estimated pH between 7 and 8 for edge-to-face interaction in principle, the authors did not consider that the pH in all of their suspensions was above 9, where edge-to-face attraction does not exist at all. In an other recently issued excellent paper (Penner and Lagaly, 2001), the liquefying effect of different anions was investigated in such a way that sodium salts and acids were added to clay suspensions in parallel. The measured pHs were significantly different in the suspensions, the protons were considered only as stronger coagulating cations, and the lower coagulating values in acidic suspensions re-

lated to that in homoionic sodium systems were explained with their stronger adsorption on clay surface. A study on the pH-dependent rheological properties of montmorillonite suspensions (Benna et al., 1999) overvalued the role of pH with making a decision to prepare suspensions without any electrolyte addition in order to detect only the effect of pH variation without changing the salt concentration, meanwhile the pH adjustment in concentrated suspensions resulted in the undefined amounts of salt.

The effect of pH and indifferent electrolytes is mutual; none of them can be interpreted alone. We attempted to outline schematically how the material characteristics of montmorillonite govern the formation of local electrostatic field around the highly asymmetric clay platelet (in respect of both the aspect ratio and surface charge density of edge and face) in aqueous medium containing indifferent electrolytes besides the autoprotolytic products of water in Figs. 1 and 2.

The main contribution to the surface charge of montmorillonite layers is the permanent negative charge on the basal planes due to the isomorphic substitutions (Van Olphen, 1963). A negative charge associated with cation replacement in the tetrahedral sheet (e.g. Al^{3+} for Si^{4+}) results in localized charge distribution, whereas much more diffuse negative charge comes from cation replacement in the octahedral sheet (e.g. Mg^{2+} for Al^{3+}) (Johnston and Tombácz, 2002). This excess of negative lattice charge is compensated by the exchangeable cations in the diffuse part of the dominant electric double layer (edl) on faces (Fig. 2). Additional polar sites, mainly octahedral $Al-OH$ and tetrahedral $Si-OH$ groups, are situated at the broken edges (Johnston and Tombácz, 2002). These amphoteric sites are conditionally charged, and so variable (either positive or negative) charges can develop at the edges by direct H^+ or OH^- transfer from aqueous phase depending on the pH as shown in Fig. 1. The variable edge charges are compensated by a cloud of counter ions in a hidden edl, into which the dominant edl extending from the particle faces probable spills over at low concentration of indifferent electrolytes (top of Fig. 2). This last is probable, if the thickness of edl (Debye length, e.g. ~ 3 nm at 0.01 M) is larger than that of the

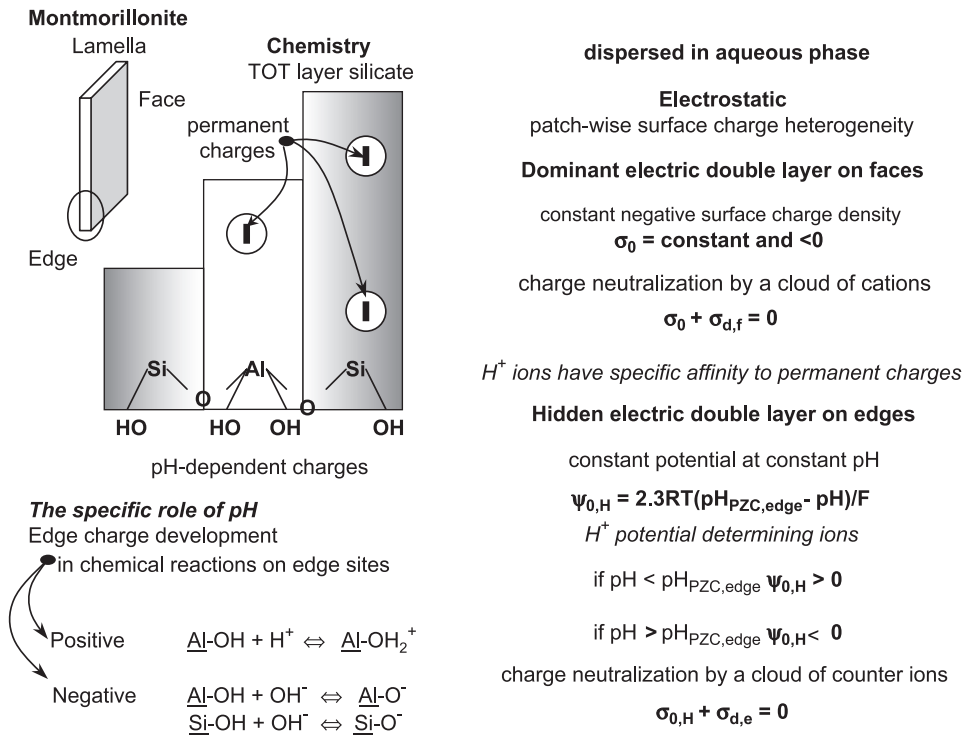


Fig. 1. Development of patch-wise surface charge heterogeneity on montmorillonite particles dispersed in aqueous solutions due to crystal lattice imperfections (permanent negative charges on faces) and surface protolytic reactions of edge OH groups (pH-dependent charges on edges). A dominant electric double layer (edl) with constant charge density (σ_0) on the face of lamella while a hidden edl with constant potential at constant pH ($\Psi_{0,H}$) on its edge are formed, and both are neutralized by the clouds of counter ions (charge densities of diffuse layers, $\sigma_{d,f}$ and $\sigma_{d,e}$, for faces and edges, respectively).

thin lamella (less than 1 nm as estimated from crystallographic data (Van Olphen, 1963)). As shown in the bottom of Fig. 2, the hidden edl at the edge region can emerge above a threshold of electrolyte concentration estimated between 0.01 and 0.1 M on the basis of numerical solution of Poisson–Boltzmann equation for a disk shape particle (Secor and Radke, 1985).

The surface charge characterization of clay minerals, when permanent charges from isomorphous substitutions of ions in a clay crystal lattice are present besides the variable edge charges, is more complicated than that of metal oxides (James and Parks, 1982). In this case, the intrinsic surface charge density (σ_{in}) can be defined as the sum of the net permanent structural charge density (σ_0), and the net proton surface charge density ($\sigma_{0,H}$), i.e. $\sigma_{in} \equiv \sigma_0 + \sigma_{0,H}$ (Sposito, 1984, 1992; Johnston and Tombácz,

2002; Tombácz, 2002). The term point of zero charge (PZC) defined as a unique pH, where the net surface charge is zero for amphoteric oxides bearing only pH-dependent charges, is not appropriate for clay minerals with both permanent and pH-dependent charges. Additional point of zero charge definitions have to be introduced. The point of zero net proton charge (PZNPC) for $\sigma_{0,H}=0$, and the point of zero net charge (PZNC) for $\sigma_{in}=0$ have been introduced by Sposito (1984, 1992). Unfortunately, consistent terminology for points of zero charge has not been used in the literature yet, but nobody argues against their general importance to particle surface characterization. The PZNPC seems to be correct for the unique case of surface charge heterogeneity on montmorillonite platelets, however, protons have specific affinity to the permanent charges (Janek and Lagaly, 2001; Penner and Lagaly,

The role of pH and indifferent electrolytes in the structure of

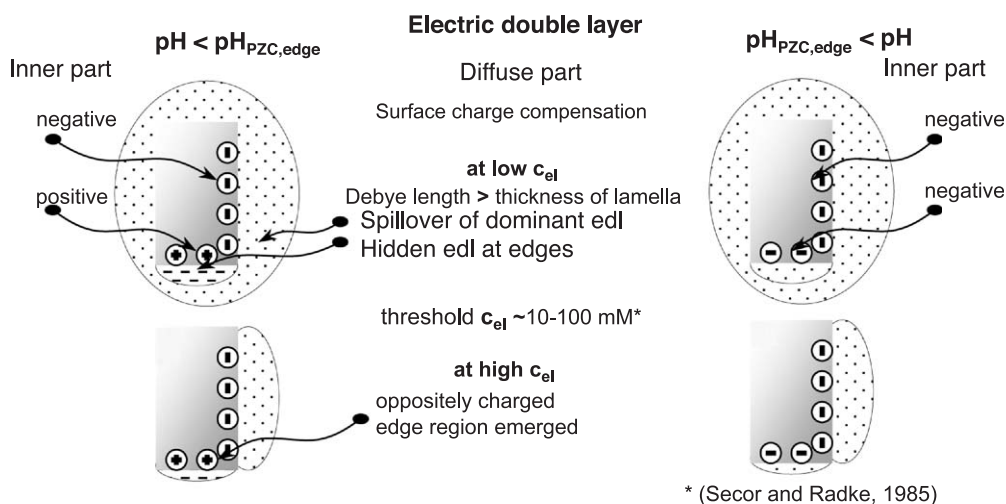


Fig. 2. Schematic representation of the dominant and hidden electric double layers forming around the montmorillonite lamellae under different solution conditions. The effect of indifferent electrolytes on particle charge heterogeneity besides the specific role of pH.

2001; Tombácz et al., 1990), and so the use of $\text{pH}_{\text{PZC,edge}}$, i.e. the pH of the PZC belonging to the amphoteric edge sites, is unambiguous.

To date, potentiometric titration is still a main approach to study the surface acid–base chemistry of clay minerals. One of the problems is to find a reference state (like the PZC of oxides), or at least a definite initial state. It seems a good solution to titrate proton-saturated montmorillonite prepared by Barshad method (Barshad, 1969). This approach resulted in reliable proton affinity constants related to the stronger and weaker surface sites in some cases (e.g. Janek and Lagaly, 2001; Tombácz et al., 1990). Only some papers deal with the dissolution of solid matrix resulting in various hydrolyzed aluminum species, silicic acid and their product—hydrrous aluminosilicates, though their interaction with clay surface should be considered in the modeling description. The surface complexation model (SCM) was successfully applied in a recent paper (Liu, 2001) to interpret surface acid–base reactions involving the dissolution of illite clays during the prolonged titration. A consistent thermodynamic model (called as clay model) was developed for metal ion adsorption on swelling 2:1 layer clays such as montmorillonite (Kraepiel et al., 1998, 1999).

The above discussed surface charge heterogeneity of clay minerals presented originally by Van Olphen (1963), then supported and elaborated further in many subsequent and recent investigations (Tombácz et al., 1990; Zhao et al., 1991; Thompson and Butterworth, 1992; Zhou and Gunter, 1992; Heil and Sposito, 1993; Keren and Sparks, 1995; Sondi et al., 1997; Schroth and Sposito, 1997; Tombácz, 2003), governs the particle interactions in clay mineral suspensions. Although the overall particle charge is always negative, both negatively and positively charged parts on the surface of clay mineral particles exist simultaneously under acidic conditions ($\text{pH} < \text{pH}_{\text{PZC, edge}}$). However, the positive double layer near the edge of plates is hidden at low concentration of indifferent electrolytes (top of Fig. 2), and so a second approaching particle cannot see it. The attraction between the oppositely charged parts results in aggregates with edge-to-face heterocoagulated structure below the pH of edge PZC (~ 7), only if the positive edge region is emerged above a threshold of electrolyte concentration (bottom of Fig. 2). Not too much work has been published on the theoretical prediction (using DLVO theory) of the pH-dependent stability of montmorillonite sols. Significant pH dependence was found experimentally and explained in theoretical point of

view for an edge-recharged (phosphate treated) H-montmorillonite sample (Tombácz et al., 1990), where only the surface charge suppression on faces was considered. The effect of pH and permanent charges on the sensitivity of swelling clays to electrolytes was explained (Mohan and Fogler, 1997) on the basis of a theoretical concept similar to that in paper (Tombácz et al., 1990). This approach proved to be effective to predict permeability reduction in porous media containing swelling clays (Mohan and Fogler, 1997). Although a successful application of the DLVO theory for mutual contribution of electric double layers on the face and edge of montmorillonite plates was published almost 20 years ago (Secor and Radke, 1985), the capability of the DLVO theory for description of such kind of patch-wise heterogeneity has been questioned in a recent work (Missana and Adell, 2000). An extended DLVO model was used to calculate the pH-dependence of face-to-face, edge-to-face and edge-to-edge interactions, which includes a repulsive short range interaction due to structural or hydration forces, the so-called polar acid–base contribution besides the electrostatic and van der Waals contributions (Durán et al., 2000). The theoretical prediction correlated well with the experimental results, however, a questionable assumption was made for edges, since their material constants were calculated as a weighted mean of those of SiO_2 and Al_2O_3 .

In any colloidally stable suspensions, the overall particle interaction is repulsive, while more or less loose physical network of adhered particles forms in the unstable suspensions. Whatever the reason, the formation of particle networks strongly affects the mechanical, flow properties of clay suspensions. In general, stable suspensions show liquid-like (viscous) Newtonian flow behavior with shear thinning or thickening character, while the appearance of plastic character frequently together with thixotropy refers to the network formation of aggregated particles. The rheology of clay suspensions is the subject of tremendous works for several decades, especially because of the wide-ranging practical application. The effects of several variables, i.e. suspension concentration, the quality and quantity of added salts, as well as the effect of thinning agents on the flow properties have been investigated as seen, e.g. in the excellent recent papers (Abend and Lagaly, 2000; Ramos-Tejeda et al.,

2001; 2003) and that for pH-dependence (Janek and Lagaly, 2001; Penner and Lagaly, 2001; Durán et al., 2000; Yildiz et al., 1999; Benna et al., 1999; Heath and Tadros, 1983).

The objective of present work is to show the specific effect of pH on surface charging of montmorillonite dispersed in indifferent electrolyte solutions using dilute and concentrated suspensions under simultaneously controlled pH and ionic strength conditions. A prudent determination of pH-dependent charging allowed us to model charge development at edges, and to interpret pH-dependent surface charge heterogeneity of montmorillonite, which influences the particle interactions in suspensions, the sensitivity to electrolytes, the spontaneous ordering of lamellae, and the structure formation in montmorillonite gels at different pHs and ionic strengths.

2. Experimental

2.1. Preparation of montmorillonite suspensions

Montmorillonite was obtained from Wyoming bentonite (Swy-1 and Swy-2 samples). Cation exchange capacity (CEC) values are 76 and 105 meq/100 g of Swy-1 (Van Olphen and Fripiat, 1979) and Swy-2 (Grim and Güven, 1978), respectively. Clay mineral fraction smaller than $1 \mu\text{m}$ was prepared by allowing the larger particles to settle down in a dilute (10 g/l) suspension and then decanting. About 10% of bentonite was discarded. To obtain the monocationic Na-montmorillonite, a calculated amount of NaCl was added to the remaining suspension to adjust salt concentration 1 M. After centrifugation of the suspensions at 3600 RPM, the supernatant solution was discarded and replaced with fresh 1 M NaCl solution. The procedure was repeated three times. The ionic strength of suspension was progressively lowered, first by washing with Millipore water and then by dialysis against 0.01 M NaCl, to that used in the experiments. The progress of dialysis was controlled by measuring conductivities of inner and outer phases daily. Na-montmorillonite suspensions ($\sim 40 \text{ g/l}$) in dialysis tubes reach equilibrium state at 0.01 M within 2 weeks. This procedure provides a definite initial state with constant ionic strength at self-pH of suspensions for further work. The stock suspensions were

stored in refrigerator at 4–5 °C. The water was obtained directly from a Millipore apparatus. All the used chemicals were analytical reagent grade product (Reanal, Hungary).

2.2. Potentiometric acid–base titration

The pH-dependent surface charge was determined by potentiometric acid–base titration under a CO₂-free atmosphere using electrolyte NaCl to maintain a constant ionic strength 0.01, 0.1 and 1 M, respectively. Before titration, the suspensions containing ~ 0.5 g montmorillonite were stirred and bubbled with purified nitrogen for an hour. Equilibrium titration was performed by means of a self-developed titration system (GIMET1) with 665 Dosimat (Metrohm) burettes, nitrogen bubbling, magnetic stirrer, and high performance potentiometer at 25 ± 1 °C. The whole system (mV-measure, stirring, bubbling, amount and frequency of titrant) was controlled by IBM PS/1 computer using AUTOTITR software. A Radelkis OP-0808P (Hungary) combination pH electrode was calibrated for three buffer solutions to check the Nernstian response. The hydrogen ion activity vs. concentration relationship was determined from reference electrolyte solution titration, so that the electrode output could be converted directly to hydrogen ion concentration instead of activity. In the first cycle, suspensions were titrated with standard HCl solution down to pH 4 then with standard base solution (NaOH) up to pH 9, then again with acid solution in the second cycle. The titration was reversible within the reproducibility of this method except for the first down curve of montmorillonite suspensions at each ionic strength.

The net proton surface excess amount ($\Delta n_{\text{H/OH}}^{\sigma}$, mol/g) is defined as a difference of H⁺ ($n_{\text{H}^+}^{\sigma}$) and OH⁻ ($n_{\text{OH}^-}^{\sigma}$) surface excess amounts related to unit mass of solid, $\Delta n_{\text{H/OH}}^{\sigma} = n_{\text{H}^+}^{\sigma} - n_{\text{OH}^-}^{\sigma}$. The surface excess amount of any solute, like H⁺ and OH⁻ here, can be determined directly from the initial and equilibrium concentration of solute for adsorption from dilute solution (Everett, 1986). The values $n_{\text{H}^+}^{\sigma}$ and $n_{\text{OH}^-}^{\sigma}$ were calculated at each point of titration from the electrode output using the actual activity coefficient from the slope of H⁺/OH⁻ activity vs. concentration straight lines for background electrolyte titration.

2.3. Dynamic light scattering measurements

Dynamic light scattering (DLS) measurements were performed using a ZetaSizer 4 (MALVERN, UK) apparatus operating at $\lambda = 633$ nm produced by an He–Ne laser at scattering angle 90° at 25 ± 0.1 °C to determine average particle size in dilute suspensions. The stock suspensions were centrifuged at 13,000 RPM for an hour to obtain the finest montmorillonite particles, which were collected from the transparent top layer of sediments. The finest fractions were diluted by freshly prepared Millipore water solution to reach a constant solid content (0.5 g/l). Coagulation kinetics measurements were performed at pH ~ 4, ~ 6 and ~ 8.5 with the series of montmorillonite suspensions containing different (from 0.001 to 0.11 M) final concentrations of NaCl. The desired pH values in the suspensions and in the double concentrated NaCl solutions were preadjusted by HCl and NaOH solutions, respectively, and they were stored in a thermostat at 25 ± 0.1 °C. 1 ml of suspension was placed in the measuring cell and 1 ml of electrolyte solution with the same pH was mixed with it, then size measurement was started after 5 s and continued till 270 s (data collection time: 10 s, time between each sizing: 20 s). Size evolution of aggregates was followed in time. The correlation functions were evaluated by cumulant analysis (Brown, 1993). Supposing a monomodal distribution, a third-order cumulant fitting was used, and Z-average hydrodynamic radius was calculated.

2.4. X-ray diffraction measurements

X-ray diffraction pattern of oriented clay films on glass plates was determined over the scanning range 2° < 2 Θ < 15° at room temperature by using a Philips PW 1830 X-ray generator with CuK $_{\alpha}$ ($\lambda = 0.154$ nm) radiation and a Philips PW 1820 goniometer operating in the reflection mode. The clay films were prepared from dilute Na-montmorillonite suspensions with pH values adjusted to ~ 9, ~ 6.5 and ~ 4 with NaOH or HCl solutions, respectively. The spreading of suspensions was spontaneous on the surface of carefully cleaned glass plates forming thin layers, which were dried in a dewatering box at ~ 100 °C.

2.5. Rheological measurements

The rheological measurements were performed with a rate controlled HAAKE RV20, CV100 viscometer using Money-Ewart sensor system type ME15, and a stress controlled HAAKE RS 150 rheometer using cone-plate sensor (DC60/2° Ti) at temperature 25 ± 0.1 °C controlled by a HAAKE DC 30/K20 thermostat. The flow curve (upward) was measured with a shear rate ramp over either three minutes from 0 to 100 1/s (RV20) or one minute from 0 to 50 1/s (RS150), then the ramp was reversed to measure downward flow curve. The area between the upward and downward curves measured with RS150 was calculated as measure for thixotropy using data analysis option of RheoWin software.

Montmorillonite suspensions (4 g/100 g) containing 0.01 M NaCl were measured either pHs between 3.8 and 9.3, or at pH >8, ~ 6 and ~ 5, respectively. The pHs of dense suspensions were adjusted with adding estimated amounts of 1 M NaOH or HCl solutions. The pHs of well-homogenized suspensions were measured, then all were stored in sealed vials under nitrogen for a day. Suspensions were placed in the measuring cylinder of RV20 apparatus after ultrasonication for 10 s, and measured after 10-min-standstill. The portions of suspensions were carefully placed on the measuring plate of RS150 rheometer, and the measuring position was reached at low speed. The equilibrium pH values of suspensions were measured after rheological measurements. The pH shift during 1-day-standing was about 0.2–0.3 pH unit.

3. Results and discussion

3.1. Simultaneous pH-dependent charge development on edge sites and H^+/Na^+ ion exchange on permanent negative charge sites of faces

Potentiometric acid–base titration over the dissolution-free range of pH between 4 and 9 was used to characterize the pH-dependent charge development on the amphoteric surface sites of montmorillonite. Protolytic reactions at edges take place in parallel with the H^+/Na^+ ion exchange on permanent negative charge sites of faces, and the separation of the

individual contribution to the measurable H^+ and OH^- consumption is not possible experimentally. A prudent preparation of montmorillonite suspension provided a well-defined initial state of titration and allowed us to use an evaluation method developed before for oxides (Tombácz and Szekeres, 2001), which assumes only the mass conservation law for H^+/OH^- ions during titration. A constant NaCl concentration in liquid phase and a sufficient Na-saturation of ion exchange sites on faces was reached in an equilibrium dialysis of montmorillonite suspension against 0.01 M NaCl. The acid–base titration cycles at this ionic strength are shown in Fig. 3. The net proton consumption curves for Na-montmorillonite show a certain hysteresis, the first backward titration curve in the direction of decreasing pH never be repeated in a second backward titration after the forward titration up to pH ~ 9, while these two latter seem to be reversible for both samples within the reproducibility of the potentiometric titration.

To test the reversibility of acid–base processes, the same titration cycles were performed at higher salt concentrations titrating Na-montmorillonite suspensions after dilution them with salt solution to adjust the final NaCl concentration to 0.1 and 1 M, respectively. The net proton consumption curves at different salt concentrations can be seen in Fig. 4. Aforementioned hysteresis experienced to the highest degree at the lowest salt concentration decreases with increasing ionic strength, and almost disappears in the presence of 1 M NaCl in one of the two montmorillonite samples. Apart from the first downward curves, the acid–base processes in montmorillonite suspensions under the given experimental condition can be considered as reversible equilibria. It is remarkable how characteristic decrease in the initial pH of suspensions with increasing salt concentration was observed. While the extent of pH shift ($\Delta pH = pH_{i,0.01} - pH_{i,1}$) is almost the same, 0.76 and 0.79 for the Swy-2 and Swy-1 samples, respectively, the initial pHs of Swy-1 suspensions were significantly larger, than that in the Swy-2 suspensions. Comparing the initial pH values given in Fig. 4, it can be seen that the differences between the two samples are more than 1 pH unit at each salt concentration. The pH shift is indicative of the presence of permanent negative charges on solid in question according to the basic

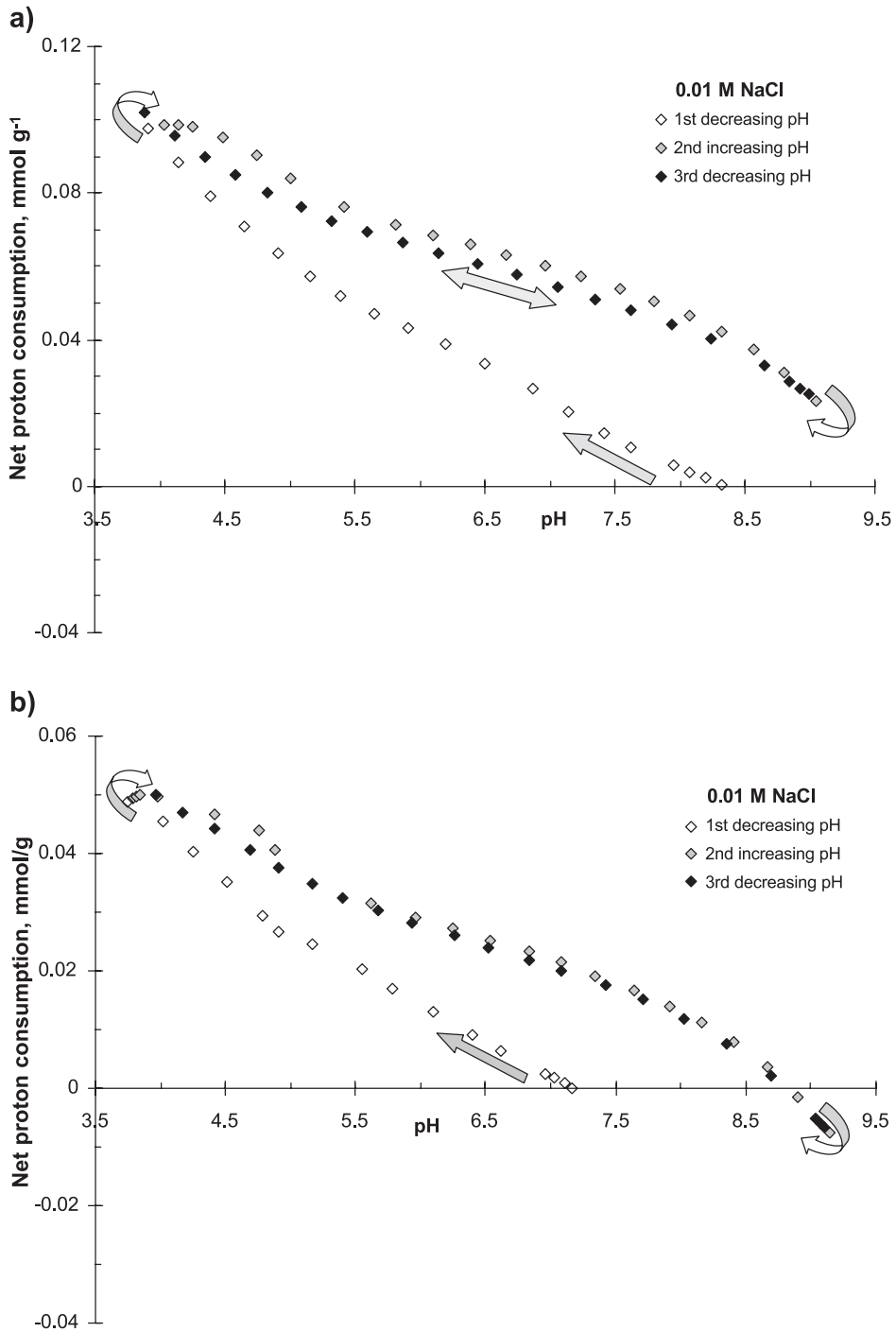


Fig. 3. Experimental net proton consumption curves for Na-montmorillonite dialyzed against and diluted with 0.01 M NaCl solutions at room temperature. The points were calculated from the data of an equilibrium titration cycle to test the reversibility of acid–base processes: first a backward (open symbols) with 0.1 M HCl solution, then a forward (gray symbols) with 0.1 M NaOH solution, finally a backward titration (black symbols) again. Wyoming montmorillonite samples: (a) Swy-1 and (b) Swy-2.

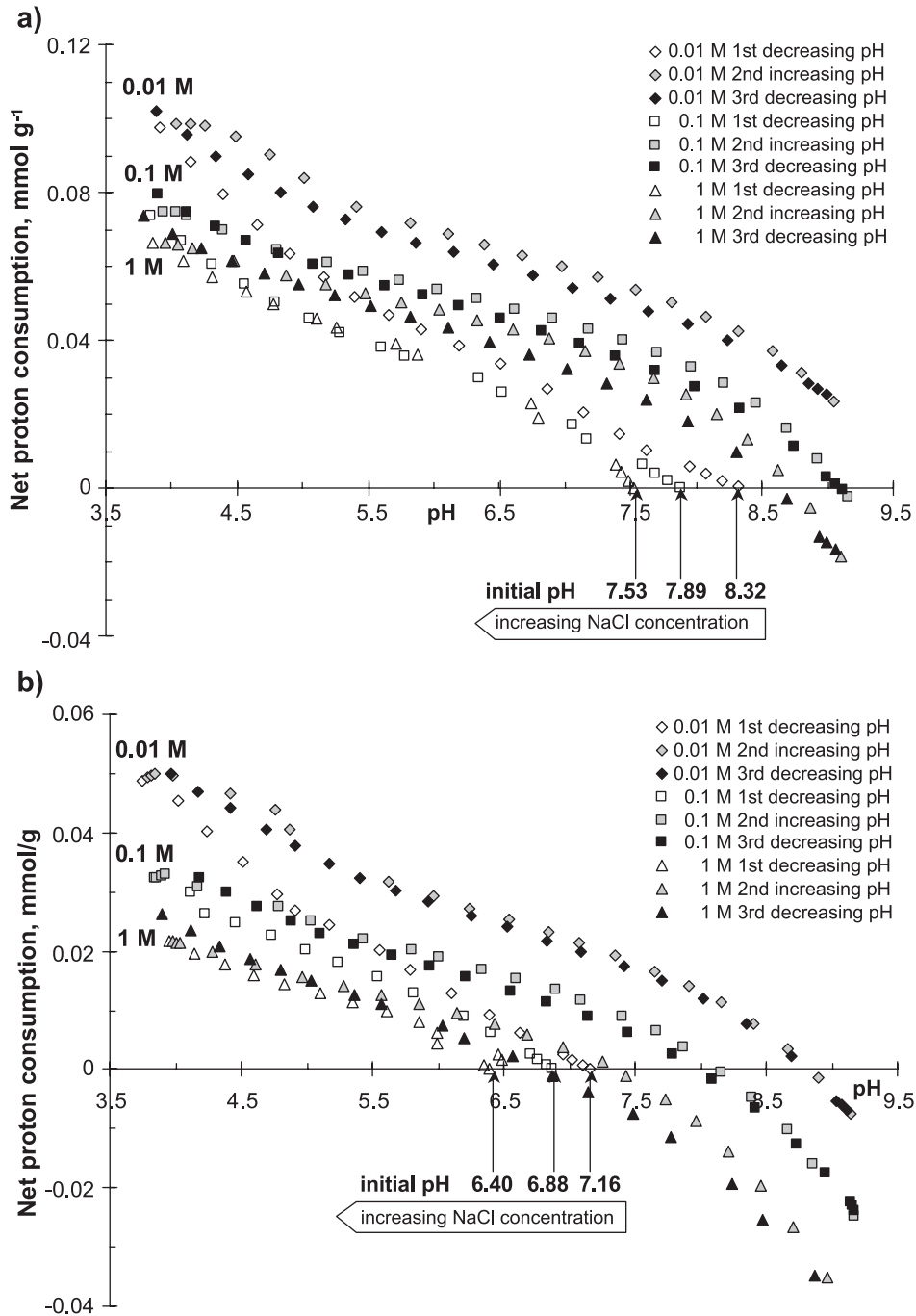


Fig. 4. Experimental net proton consumption curves for Na-montmorillonite dialyzed against 0.01 M NaCl solution then diluted with NaCl solutions to adjust salt concentrations 0.01, 0.1 and 1 M, respectively, at room temperature. The points were calculated from the data of an equilibrium titration cycles to test the reversibility of acid–base processes: first a backward (open symbols) with 0.1 M HCl solution, then a forward (gray symbols) with 0.1 M NaOH solution, finally a backward (black symbols) titration again. Wyoming montmorillonite samples: (a) Swy-1 and (b) Swy-2.

principles of acid–base surface chemistry of soils (Sposito, 1984). The lower pH values in the suspension of Swy-2 montmorillonite with higher cation exchange capacity (105 meq/100 g) indicate that more H^+ ions were exchanged during equilibrium dialysis against 0.01 M NaCl, than that in the case of Swy-1 montmorillonite (CEC = 76 meq/100 g).

The acid–base titration data exhibit unusual characteristics as compared to the “classic” curves usually obtained on oxides (e.g. Tombácz and Szekeres, 2001; James and Parks, 1982). To demonstrate the essential differences, we show two extreme examples for ionic strength-dependent surface charging of aluminum and silicon oxides in Fig. 5, which are relevant to the edge sites of montmorillonite in chemical point of view. Both oxides exhibit the common feature of net proton surface excess vs. pH curves at different ionic strengths. The main difference between the acid–base properties of these oxides is the pHs of their PZC, since it is above pH 8 for alumina and below pH 4 for silica (Tombácz et al., 1995). In the case of

montmorillonite, however, the reversible net proton surface excess curves at different ionic strengths (Fig. 4) never intersect, no any common intersection point such as PZC or PZSE (point of zero salt effect) can be identified. The extent of proton accumulation on the surface of montmorillonite particles is always greater at lower ionic strength similarly to those of the clays in literature (Kraepiel et al., 1998; 1999).

The evaluation of potentiometric data measured in the reversible cycles of acid–base titration at different ionic strengths allowed us to calculate the pH-dependent charging of amphoteric edge sites besides the Na^+/H^+ ion exchange process taking place on permanent charge sites of lamellae (Tombácz et al., in press) in accordance with the depicted processes in Fig. 1. A simple model approach using the principles of surface complexation modeling (SCM), and assuming the simultaneous ion exchange on the particle face and protonation/deprotonation processes at edges in the negative electrostatic field emanating from the particle face has been chosen. The exchange process for H^+

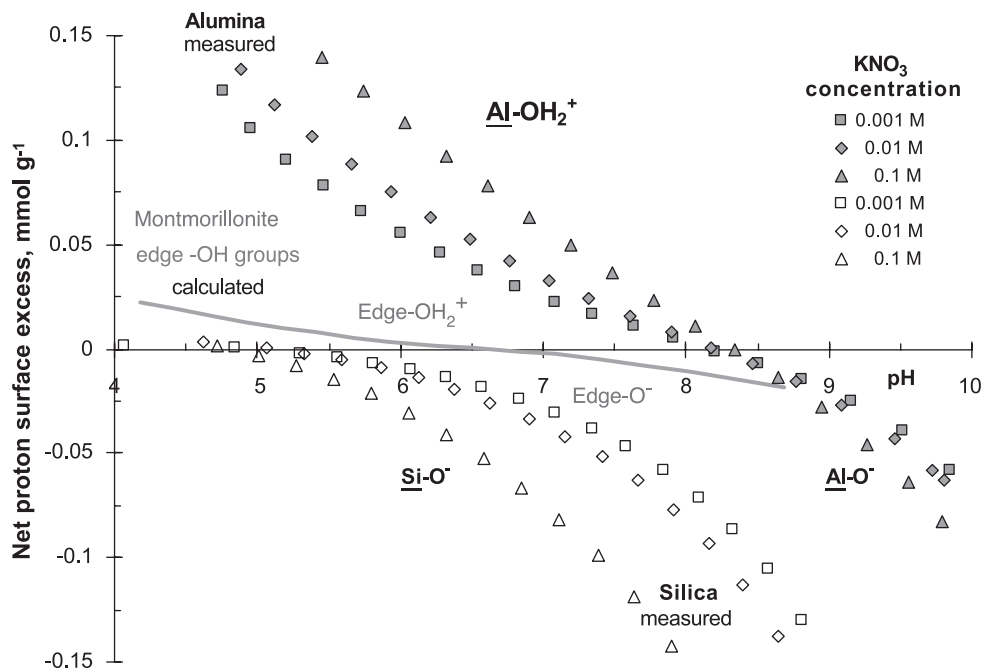
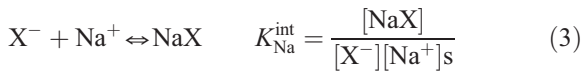
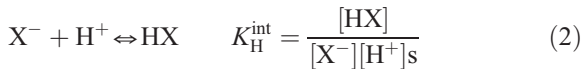


Fig. 5. The pH-dependence of net proton surface excess amounts for different solid materials. Experimental data measured at different ionic strengths for Al_2O_3 (Aluminum Oxide C, Degussa) and SiO_2 (Aerosil 200, Degussa), calculated curve for amphoteric edge sites of montmorillonite (Tombácz et al., in press).

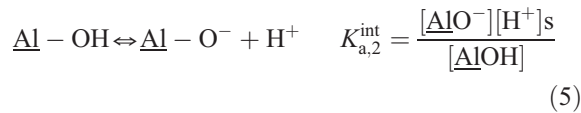
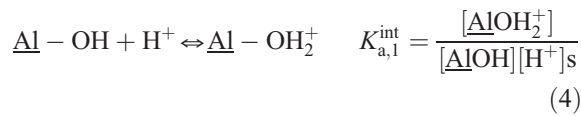
and Na^+ ions on a solid matrix (X) with permanent negative charges



was written as the reactions between H^+ and Na^+ ions, and a negatively charged surface site (X^-) with intrinsic equilibrium constants (K_i^{int}):



The protonation and deprotonation reactions were defined only on the amphoteric $\underline{\text{Al}}\text{-OH}$ sites of edges as following,



The effect of dominant electrostatic field with negative potential (Fig. 1) was considered by the Boltzmann equation. The fitting of reversible net proton surface excess vs. pH curves at different ionic strengths using FITEQL (Herbelin and Westall, 1996) resulted in an excellent fitting of experimental data at each ionic strength and the following intrinsic equilibrium constants for Swy-2 sample: $\log K_{\text{H}}^{\text{int}} = 8.77$, $\log K_{\text{Na}}^{\text{int}} = 0.78$ for the cation binding on permanent charged sites, and $\log K_{\text{a},1}^{\text{int}} = 5.1 \pm 0.1$, $\log K_{\text{a},2}^{\text{int}} = -7.9 \pm 0.1$ for the protonation and deprotonation of amphoteric edge sites (Tombácz et al., in press). The point of zero charge of edge sites ($\text{pH}_{\text{PZC, edge}}$) was given at $\text{pH} \sim 6.5$ in good harmony with the values $\text{pH} \sim 6.5\text{--}7$ in the literature (Kraepiel et al., 1998, 1999). Comparing the net proton surface excess vs. pH function calculated for the edge sites of montmorillonite with the measured data of the alumina and silica samples in Fig. 5, as well as the calculated equilibrium constant

and data with those for alumina $\log K_{\text{a},1}^{\text{int}} = 5.8 \pm 0.2$, $\log K_{\text{a},2}^{\text{int}} = -10.2 \pm 0.2$, $\text{pH}_{\text{PZC}} = 8.0 \pm 0.1$, and for silica $\log K_{\text{a},2}^{\text{int}} = -8.02 \pm 0.1$, $\text{pH}_{\text{PZC}} < 4.0$ (Tombácz et al., 1995), we can conclude that the acid–base properties of amphoteric edge sites of montmorillonite are just between the surface OH bound to the pure Al_2O_3 and SiO_2 solid matrix.

This conclusion based on the SCM modeling of surface processes of montmorillonite is in good agreement with an empirical approach of the edge site characterization, which assumes a weighted sum of the properties of pure $\underline{\text{Al}}\text{-OH}$ and $\underline{\text{Si}}\text{-OH}$ groups (Durán et al., 2000; Ramos-Tejeda et al., 2001, 2003). The calculated intrinsic equilibrium constants show much more details, since we can characterize the OH groups at edges having PZC at $\text{pH} \sim 6.5$ as less basic than the $\underline{\text{Al}}\text{-OH}$ and less acidic than the $\underline{\text{Si}}\text{-OH}$ groups. Positive charges can develop only on the $\underline{\text{Al}}\text{-OH}$ sites of edges at pHs below ~ 6.5 , however, these are hidden at low electrolyte concentration when the negative electrostatic field emanating from the face of particles covers them (Secor and Radke, 1985) as shown in Fig. 2. The unique surface charge heterogeneity of montmorillonite lamellae disappears, if the pH of suspensions is above the $\text{pH}_{\text{PZC, edge}} \sim 6.5$, since the deprotonation of $\underline{\text{Si}}\text{-OH}$ then that of the $\underline{\text{Al}}\text{-OH}$ sites takes place with increasing pH of solution resulting in negative charges at edges similarly to that on faces.

3.2. Edge-to-face and face-to-face aggregation in dilute suspensions

Coagulation kinetics measurements were performed to obtain exact data for the pH-dependent colloidal stability of fine montmorillonite particles dispersed in the aqueous solution of an indifferent electrolyte. Size evolution of aggregates in time was followed by dynamic light scattering. The initial slopes of hydrodynamic radius vs. time curves were calculated at different electrolyte concentrations. The electrolyte concentration in each series was increased above the limit of fast coagulation (diffusion limited aggregation), where the initial slope of kinetic curves becomes independent of the electrolyte concentration. The kinetic curves for Swy-1 sample at $\text{pH} \sim 8.5$ are shown as examples in Fig. 6. It can be seen that the extent of size increase in time becomes larger gradually with

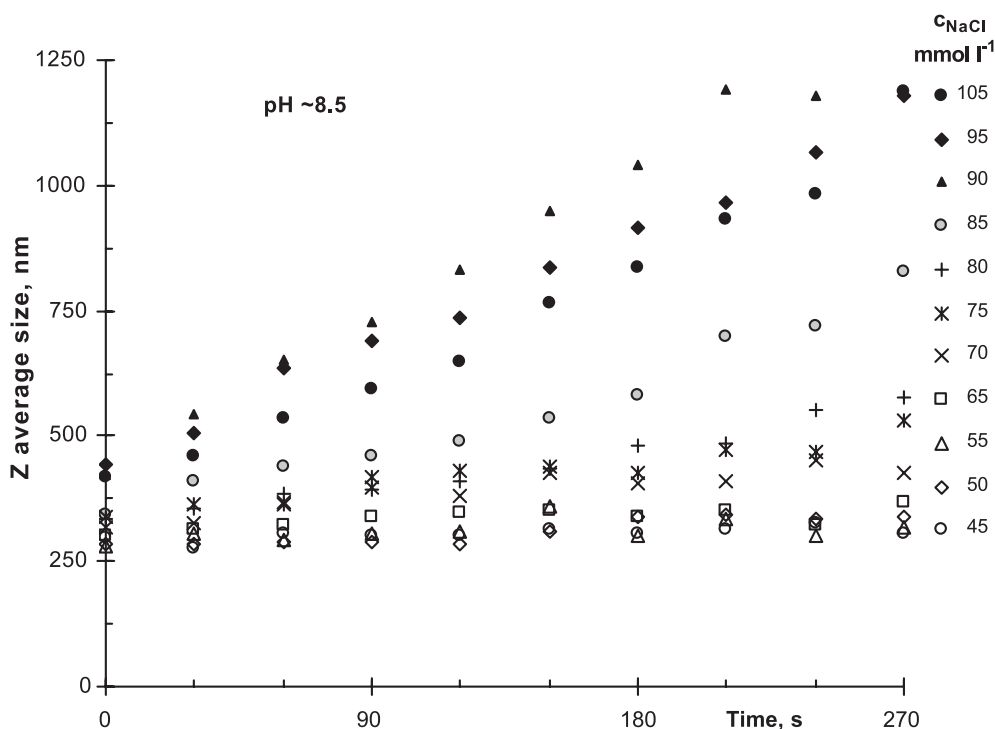


Fig. 6. Coagulation kinetics measured by dynamic light scattering: the size evolution of aggregates in Na-montmorillonite (Swy-1) suspensions at pH \sim 8.5 and different NaCl concentrations.

increasing salt content reaching a maximum above $\sim 90 \text{ mmol l}^{-1}$ salt concentrations. The stability ratio (w) was calculated from the initial slopes of kinetic curves belonging to the slow and fast coagulation as suggested in the literature (Holthoff et al., 1996).

The stability ratio values determined for montmorillonite sols at different pHs are plotted as a function of salt concentration in Fig. 7. The series of points for both montmorillonite samples at each pH do not differ from each other on the one hand, and on the other hand, they show the typical curves with a plateau of the fast coagulation regime ($w \sim 1$) and a slope of the slow coagulation regime in the function of electrolyte concentration. The critical coagulation concentration (c.c.c.) separates the fast from the slow coagulation regime. The calculated c.c.c. values are summarized in Table 1. This colloidal stability results provide an indisputable proof for the pH-dependent stability of montmorillonite, since the resistance of sols to electrolyte increases significantly with increasing pH of aqueous medium.

The enhanced stability is obvious especially at high pH ~ 8.5 , where the amphoteric edge sites of montmorillonite lamellae have become negatively charged similarly to the sign of the permanent charges on faces. Although the probability of edge-to-face collisions is larger from hydrodynamic point of view, even in the dispersion of the uniform negatively charged lamellae above the pH of PZC of edge sites ($\text{pH}_{\text{PZC, edge}} \sim 6.5$), the overlapping of the compressed dominant edl on faces probably results in face-to-face oriented aggregates. The difference between the c.c.c. values determined for the Swy-1 and Swy-2 montmorillonite samples only at pH ~ 8.5 supports this assumption, since the higher c.c.c. value was obtained for the Swy-2 sample with larger surface charge density than that of Swy-1 sample considering that the experimentally available CEC values (76 and 105 meq/100 g for Swy-1 and Swy-2 samples, respectively) are proportional to the amount of permanent charges and so to the surface charge density of plates on which the dominant edl exists.

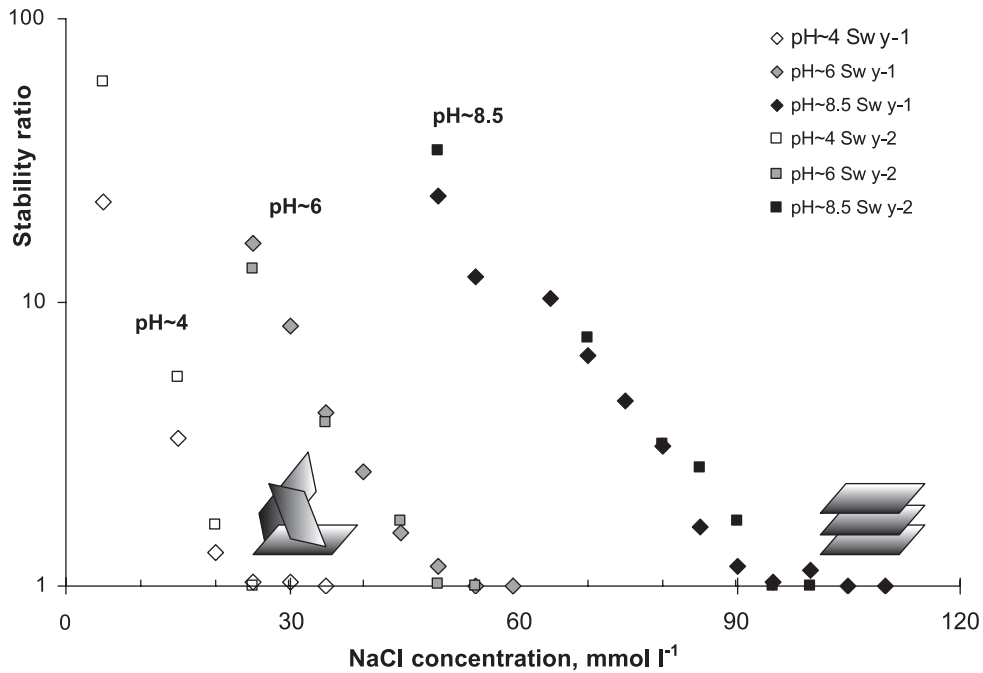


Fig. 7. pH-dependent sensitivity of montmorillonite sols to indifferent electrolyte. Wyoming montmorillonite samples: Swy-1 and Swy-2.

The onset of edge-to-face coagulation at pH ~ 4 starts only above a threshold (~ 0.01 M NaCl) of electrolyte concentration, where the positively charged edge region of lamellae has emerged. The highly charged particles form stable suspension at lower ionic strengths, the average particle sizes are constant (250–270 and 200–220 nm for Swy-1 and Swy-2 samples, respectively) in time independently of the existence of oppositely charged parts on lamellae. In principle, the positively charged edges can interact with the negative basal plates below pH ~ 6.5 , however, edge-to-face heterocoagulation does not take place at lower ionic strength because of the

spillover of the negative electrostatic field emanating from the face of montmorillonite plates (Secor and Radke, 1985) as shown in Fig. 2. These coagulation kinetics studies showed that diffusion limited aggregation is induced by 1:1 electrolyte (NaCl) concentration larger than 25–26 mmol l^{-1} at pH ~ 4 . This value is in good agreement with the critical coagulation concentration, 15–30 mmol l^{-1} NaCl, for sodium-rich Wyoming montmorillonite dispersions (Penner and Lagaly, 2000). It correlates well with the theoretical prediction of Secor and Radke (1985) for spillover of the diffuse double layer on montmorillonite particles. The exact solution of Poisson–Boltzmann equation for a thin disk with positive edge and negative face charges revealed that for salt content below about 10 mmol l^{-1} , the negative electrostatic field emanating from the particle face spills over into the edge region; therefore, the positively charged edge exhibits a negative electrostatic field (see the schematic representation in Fig. 2). This results in a repulsive electrostatic potential for interparticle edge-to-face interaction. At 100 mmol l^{-1} , where the diffuse layer is highly compressed and so the edge exhibits positive electrostatic

Table 1

The critical coagulation concentration (c.c.c.) values determined from coagulation kinetics measurements of dilute sols of Wyoming montmorillonite samples at different pHs using NaCl as indifferent electrolyte

Sample pH	Swy-1 c.c.c., mmol l^{-1}	Swy-2 c.c.c., mmol l^{-1}
~ 4	25	26
~ 6	52	52
~ 8.5	97	102

field already, an edge-to-face electrostatic attraction is expected. Therefore, the theoretically predicted region of edge-to-face aggregation falls into 10 to 100 mmol l⁻¹ of 1:1 salt concentration.

The pH region near to $\text{pH}_{\text{PZC, edge}} \sim 6.5$, where edges are uncharged, is interesting in colloidal stability point of view. The montmorillonite sols are highly sensitive to even a small change in pH in this region. The results of coagulation kinetics measurements at $\text{pH} \sim 6$ are shown in Fig. 7. The calculated c.c.c. value was 52 mmol l⁻¹ NaCl for both samples (Table 1). However, a small increase in the pH of sols resulted in considerable increase in the resistance against salt, e.g. the limit of fast coagulation was reached at ~ 60 and ~ 80 mmol l⁻¹ NaCl in sols, if the pH was increased by some tenths, to ~ 6.2 and ~ 6.5 , respectively. The probability of edge-to-face random collisions is larger in this pH region, too, than that of the face-to-face collisions of lamellae. However, the existence of different structure of aggregates, i.e. either edge-to-face or face-to-face arrangement of lamellae, in equilibrium state may be questionable.

It seems no any driving force exists under these solution conditions to rearrange the in situ formed edge-to-face aggregates.

3.3. Self-ordering of lamellae in montmorillonite film formed from dilute suspensions

Although the fact that dewatering of montmorillonite suspensions results in smooth layered solid phase, i.e. montmorillonite lamellae can spontaneously organize themselves into oriented clay film, is well-known and certainly used in some applications, a systematic study on the why and how questions has not published yet. We suppose that surface charge heterogeneity of highly anisometric montmorillonite plates influences the ordering of lamellae in the self-oriented films.

XRD patterns of oriented montmorillonite films (Fig. 8) prepared from suspensions with different pHs (4, 6.5 and 9) obviously support this assumption. The formation of packets of lamellae ordered in parallel to each other is hindered with decreasing pH, since the

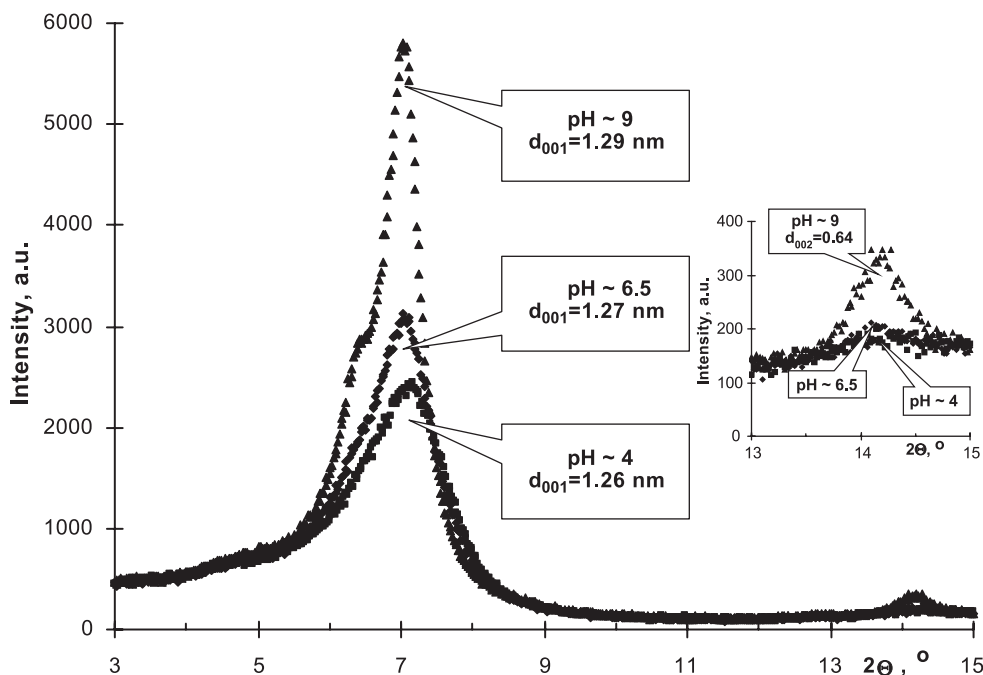


Fig. 8. XRD patterns of oriented montmorillonite films on glass plate prepared from dilute montmorillonite (Swy-1 sample) suspensions with different pHs at (~ 6.5), above (~ 9) and below (~ 4) the pH of PZC of edges, where the edges of lamellae are uncharged, and either similarly or oppositely charged as the faces of particles, respectively.

intensity of basal plane reflection (d_{001} at $\sim 7^\circ 2\theta$) decreases considerably with decreasing pH. We suppose the formation of random edge-to-face fractal aggregates below pH ~ 7 , and of oriented face-to-face structure above pH ~ 8 . As explained before, the amount of the amphoteric edge sites is not significant related to the total charge of particles, however, pH-dependent charge development (either edge-OH₂⁺ or edge-O⁻) on the -OH sites of broken edges governs the particle interactions. Edge-to-face heterocoagulated assembly of lamellae can form only below pH ~ 6.5 , where edges are positively charged and the parallel orientation of thin lamellae is hindered.

3.4. pH-dependent sol–gel state in aqueous montmorillonite suspensions at low salt concentration

The formation of jelly-like materials and the mechanical properties of particle network in suspensions can be investigated by means of rheology. Here we investigated the formation of pH-dependent structure in montmorillonite suspensions at 0.01 M NaCl by means of steady-state flow curve determination,

which is the most frequently used rheological measurement of aqueous clay suspensions. The results obtained for 4 g/100 g suspensions of Swy-1 and Swy-2 montmorillonite samples at different pHs of are shown in Figs. 9–11.

The rheological character of flow curves changed from Newtonian to pseudoplastic or to somewhat thixotropic with decreasing pH of Swy-1 sample suspensions (Fig. 9). The flow curves were evaluated according to the Bingham model (Barnes et al., 1989). The extrapolated Bingham yield values increase sharply below pH ~ 7 with decreasing pH of suspensions (Fig. 10) showing the formation of the stronger gel structure. This increase in yield value with decreasing pH is the same as measured before (Durán et al., 2000), and similar to the effect of increasing salt concentration (Abend and Lagaly, 2000). The yield value is proportional to the mechanical strength of physical network of particle formed in suspensions. It depends on the number and the strength of bondages between particles in unit volume of suspensions (Firth and Hunter, 1976). The formation of edge-to-face heterocoagulated network of montmorillonite plates

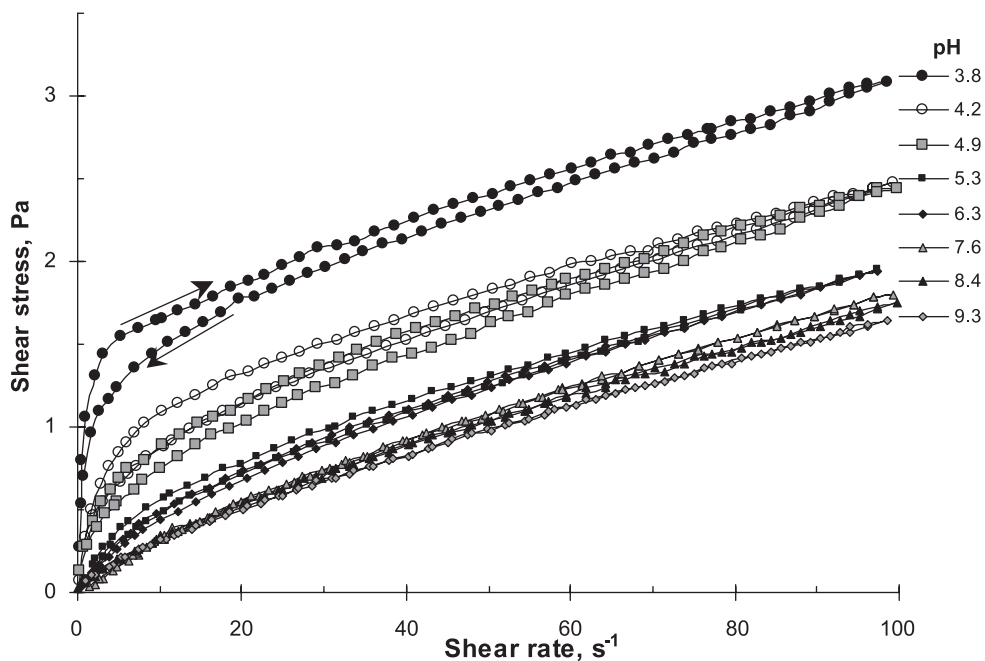


Fig. 9. pH-dependent flow properties of 4 g/100g montmorillonite (Swy-1 sample) suspensions in the presence of 0.01 M NaCl at 25 ± 0.1 °C.

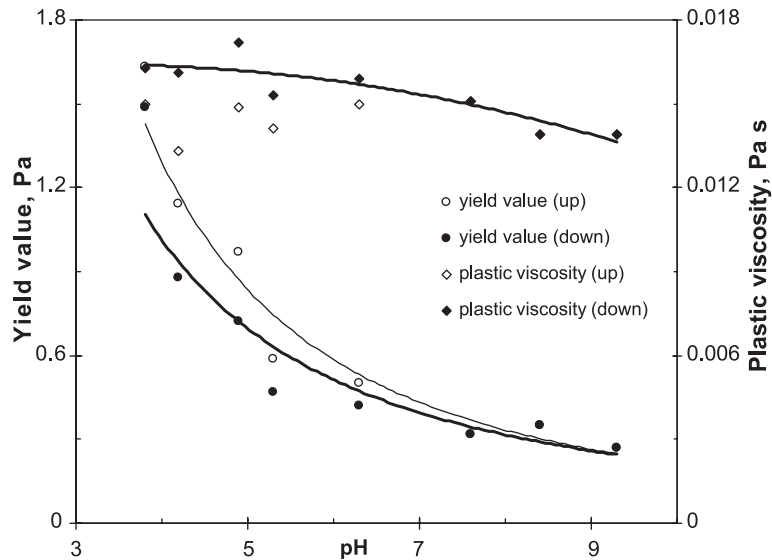


Fig. 10. pH-dependence of rheological parameters for montmorillonite (Swy-1 sample).

is assumed below the pH of $\text{pH}_{\text{PZC, edge}} \sim 6.5$ in the presence of 0.01 M NaCl. The lower the pH, the larger the amount of positive charges on the edges of montmorillonite lamellae (Fig. 5), therefore, the attraction between the positively charged edges and negative basal plates becomes stronger with decreasing pH.

The suspensions of sample Swy-2 were measured only at three characteristic pH values under otherwise same conditions. The significant change in flow character of suspensions with different pHs is obvious in Fig. 11. It can be seen that the upward and downward curves are not identical, especially at pHs below the PZC of amphoteric edges ($\text{pH}_{\text{PZC, edge}} \sim 6.5$). The edges of lamellae are negatively charged in alkaline suspension ($\text{pH} \sim 8.3$), therefore, the whole surface of lamellae bears similar charges. The uniformly charged particles repel each other, gel structure cannot form, and so the stable montmorillonite sol shows shear thinning flow character with a small thixotropy (bottom curve in Fig. 11). A decrease in pH slightly below the PZC of amphoteric edges causes an obvious change in flow behavior. A definite plastic character appears and the large thixotropic loop (middle curve measured at $\text{pH} \sim 6$ in Fig. 11) relates to a time dependent gel structure formation in the suspension. In acidic suspension (the uppermost curve at $\text{pH} \sim 5.2$ in Fig. 11) a strong attractive gel (Abend

and Lagaly, 2000), here the edge-to-face heterocoagulated network, can form because of the attraction of oppositely charged edges and faces of montmorillonite platelets. The area of thixotropic loops increases with decreasing pH showing an increasing ability of montmorillonite suspensions for gelation.

The pH-dependent viscoelastic properties of montmorillonite suspensions have been studied (Tombácz et al., in press). The elastic response of thixotropic montmorillonite gels below the pH of edge PZC could be measured if only the applied stress was below the yield values. The creep tests proved that attractive gel forms below the pH of edge PZC due to the electrostatic attraction between positively charged edges and negatively charged plates of montmorillonite lamellae, which has considerable elasticity besides viscous properties, while almost ideal Newtonian (liquid-like) behavior was detected for suspension containing uniformly charged particles in sol state under alkaline condition. The results of forced oscillation studies on pH-dependence were comparable with that of recent works on montmorillonite suspensions, in which the effect of pH (Durán et al., 2000) and coagulating electrolytes (Abend and Lagaly, 2000), and liquefying humic acid (Ramos-Tejeda et al., 2001) was investigated. Aggregation by NaCl was accompanied by an increase in yield value and storage moduli (Abend and

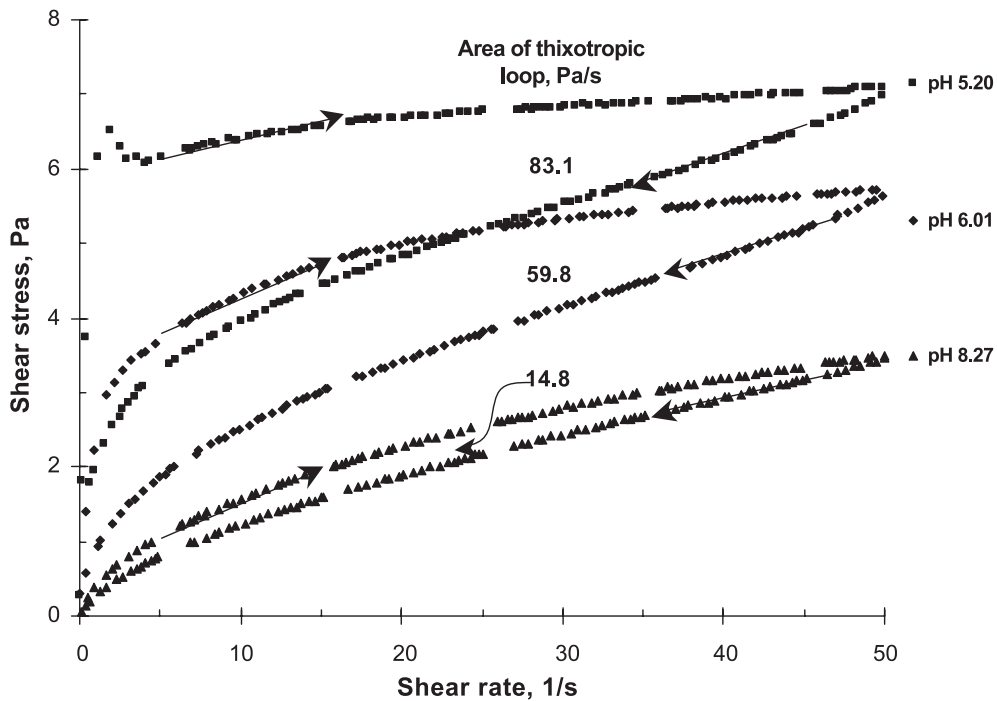


Fig. 11. Flow curves measured with an increasing (upward) then decreasing (downward) shear rate ramp for 4 g/100 g Na-montmorillonite suspensions (Swy-2 sample) containing 0.01 M NaCl at different pHs above (\blacktriangle : 8.27) and below (\blacklozenge : 6.01 and \blacksquare : 5.20) the pH of PZC of edges (~ 6.5) at 25 ± 0.1 °C.

Lagaly, 2000) similarly to the effect of decreasing pH in papers (Durán et al., 2000; Tombácz et al., in press).

4. Conclusions

The colloidal behavior of montmorillonite suspensions is influenced simultaneously by the pH and indifferent electrolyte content of aqueous medium. The specific effect of pH on surface charging of montmorillonite dispersed in indifferent electrolyte solutions, and on the interactions between the highly asymmetric clay mineral platelets (in respect of both the aspect ratio and surface charging of edges and faces) in dilute and concentrated suspensions under simultaneous pH and ionic strength controlled conditions were shown in the present work. The consequences of charge heterogeneity of montmorillonite platelets holding both permanent negative charges on faces and pH-dependent charges on OH sites at the broken edges have become interpretable.

The acid–base surface chemistry of montmorillonite lamellae involves the pH-dependent charging of amphoteric edge sites besides the H^+ ion exchange process taking place on permanent charge sites of faces. Therefore, the pH of aqueous medium has two kinds of specific role, one is the high affinity of H^+ ions to neutralize the permanent negative charges of dominant electric double layer on faces, and the other is providing chemical species (H^+ and OH^-) to the surface protolytic reactions on edge sites in which the pH-dependent hidden electric double layer forms (Fig. 1.). The fact that ion exchange reaction with H^+ ions always takes place with changing pH, but its extent is significantly influenced by the electrolyte concentration, results in a characteristic shift in the pH-dependent net proton surface excess curves measured with increasing ionic strength. Comparing the essential differences between the ionic strength-dependent surface charging of simple oxides and montmorillonite, it can be concluded that no any common intersection point such as PZC or PZSE (point of zero

salt effect) can be identified for montmorillonite, the extent of proton accumulation on the surface of montmorillonite particles is always greater at lower ionic strength, and that the acid–base properties of amphoteric edge sites of montmorillonite are just between the surface OH bound to the pure Al_2O_3 and SiO_2 solid matrix. It can be stated that the edge-OH groups are less basic than the $\text{Al}-\text{OH}$ and less acidic than the $\text{Si}-\text{OH}$ groups on the basis of the calculated equilibrium constants of protonation and deprotonation reactions on the different OH groups, i.e. at the edges of montmorillonite with $\text{pH}_{\text{PZC, edge}} \sim 6.5$, and on the surface of Al_2O_3 with $\text{pH}_{\text{PZC}} \sim 8$ and of SiO_2 with $\text{pH}_{\text{PZC}} < 4$.

The montmorillonite lamellae have patch-wise charge heterogeneity below the pH of PZC of edges ($\text{pH}_{\text{PZC, edge}} \sim 6.5$), where positively charged, protonated $\text{Al}-\text{OH}_2^+$ sites exist in small amount (~ 0.03 mmol/g) related to the abundance of permanent charges (0.7–1 mmol/g) on faces. This large amount of negative lattice charge is compensated by the exchangeable cations in the diffuse part of the dominant electric double layer (edl) on faces, while the hidden electric double layer of variable charges at the broken edges can develop by direct H^+ or OH^- transfer from aqueous phase depending on the pH as shown in Fig. 1. The dominant edl extending from the particle faces probable spills over at low concentration of indifferent electrolytes (top in Fig. 2), when the thickness of edl (Debye length, e.g. ~ 3 nm at 10 mmol l^{-1}) is larger than that of the thin lamella (~ 1 nm). The hidden edl at the edge region can emerge above a threshold of electrolyte concentration estimated between 10 and 100 mmol l^{-1} (bottom in Fig. 2). Coagulation kinetics measurements resulted in exact data for the pH-dependent colloidal stability of fine montmorillonite sols: edge-to-face coagulation occurs above NaCl concentration 25–26 mmol l^{-1} at pH ~ 4 , where the positively charged edge region of lamellae has emerged. Edge-to-face attraction between the poorly or non-charged edges and negatively charged faces of platelets is induced by a relatively low salt concentration (around 50 mmol l^{-1} NaCl) at the pH of PZC of edge sites. While well-ordered lamellae packets cannot form in montmorillonite films under these conditions, the gelation of montmorillonite sols is advanced, an easy formation of semi-solid attractive gels with significant thixotropy and viscoelasticity is obvious below pH

~ 6.5 at 0.01 M NaCl concentration. At higher pHs, however, the repulsion is the overall interaction between the uniformly charged lamellae, and so rather liquid-like, colloiddally stable sol of montmorillonite exists in dilute solutions of indifferent electrolytes (e.g. NaCl). The homocoagulation of uniformly charged lamellae under slightly alkaline conditions (e.g. at pH 8–8.5), formation of face-to-face aggregates requires much higher salt concentration (around 100 mmol l^{-1} NaCl) to compress the dominant edl on the faces of lamellae. It would be worth paying larger attention to the specific role of pH in the behavior of clay suspensions not only in laboratory studies but also in practical applications. Finally, it should be mentioned that the application of extended DLVO theory by Durán et al. (2000) for montmorillonite has to be reconsidered keeping in mind not only the “anisotropic nature of clay particles” (Durán et al., 2000), but also the double specific role of H^+ -ions to explain the pH-dependent aggregation of montmorillonite particles. Beyond that the description of edge site properties as weighted average of SiO_2 and Al_2O_3 is questionable, the surface free energy components (van der Waals and polar acid–base) is determined from contact angle measurement for montmorillonite film using different liquids. If the film is prepared from Na-montmorillonite as made in the work of Durán’s paper (2000) how to use the data over the pH range from 3 to 10 with knowledge of the specific affinity of H^+ -ions to ion exchange sites resulting in an inherent change in the acid–base properties of face surfaces. The electrostatic term calculation using HHF approach for heterocoagulation (Hogg et al., 1966), which assumes constant potentials during overlapping of electric double layers of interacting particles, is also worth reconsidering, since the edge-to-face interaction of montmorillonite lamellae seems to be a fairly unusual case in colloid stability point of view (Gregory, 1975), and assuming a constant charge for face and a constant potential (at constant pH) for edge as depicted in Fig. 1 would be more realistic in theoretical point of view.

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