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ACIDITY OF PROTON SATURATED AND AUTOTRANSFORMED SMECTITES CHARACTERIZED WITH PROTON AFFINITY DISTRIBUTION

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Abstract: Potentiometric titration of proton saturated fine fractions of three bentonites were used to characterize the acid centre at the smectite-water interface in dispersions. The H-forms were prepared by $H^+ \rightarrow OH^- \rightarrow H^+$ ion exchange with resins. The obtained titration data were used in a thermodynamic calculation of proton affinity distribution. Numerical solving of an integral adsorption equation revealed a continuous distribution of proton interaction sites. Proton affinity distributions clearly detected up to 5 different proton interaction sites in all the smectite-water systems, within accessible experimental range of pH's between 2 and 12. The amount of the strongest acid sites, i.e. those with the lowest p*K* values, decreased on aging, while the amounts of all weaker acid sites increased with the progress of autotransformation. The strongest acid sites are connected with free protons present in the dispersion, while the weaker acid sites are connected with the titration of released structural Al^{3+}, Fe^{3+}, Mg^{2+} cations and/or their hydrolyzed species, and deprotonation of SiOH groups. These results indicate the sources of acidity in acid activated bentonites.

Key words: acid sites, autotransformation, potentiometric titration, proton affinity distribution, smectite.

Introduction

Characterization of acidity of clay minerals is connected with fundamental questions of the existence of proton interaction sites, which may influence their colloid properties, rheology, reactivity, applicability, potential equilibrium reactions in natural systems and aquatic environments, and geochemical processes on solid oxide-water interfaces (Stumm et al. 1980; Hayes & Leckie 1987; Bleam 1993; Contescu et al. 1993a). This topic is also related to the characteristics of acid activated bentonites due to their advantageous properties and the wide scale of applications (Siddiqui 1968; Fahn & Fenderl 1983; Breen 1991; Breen & Watson 1998).

The main constituents of bentonite ores are clay minerals from the smectite group. During the activation with strong inorganic acid solutions, protons diffuse in the interlayer space of smectite, exchange the original exchangeable cations, and acid attack on the layers starts (Siddiqui 1968; Číčel 1991). Acid attack on smectite structure proceeds from the marginal interface of the particles and structural cations of octahedral sheets are leached out. However, a significant contribution to leaching of structural cations via interlayer space interface can occur (Číčel 1991; Komadel et al. 1996; Janek et al. 1997). Depending on the extent of acid activation, affected by temperature, time, acid concentration, solid to acid ratio, etc., the resulting solid product contains unaffected layers and amorphous three-dimensional cross-linked silica (Madejová et al. 1998; Tkáč et al. 1994), while the acid solution contains ions according to the chemical composition of smectite and the acid used.

Surface acidity of a solid can be assessed by investigation of its interaction with suitable probe molecules (Tanabe 1970; Breen 1991; Brown & Rhodes 1997) or by potentiometric titrations of its suspension (Janek & Komadel 1993; Wanner et al. 1994; Brady et al. 1996; Qing et al. 1997). However, a sufficient number of reliable potentiometric titration data is important for their meaningful numerical treatment, involving thermodynamic equilibrium calculations (Contescu et al. 1993a).

Potentiometric titrations were employed by Brady et al. (1996) to obtain pH dependent surface charge properties of kaolinite, acid-base chemistry of illite (Qing et al. 1997) and of montmorillonite (Wanner et al. 1994). A proton affinity distribution calculation was used by Bandosz et al. (1994) and Jagiełło et al. (1995) for characterization of pillared clays and by Bandosz et al. (1996, 1997) to study surface acidity of hydroxychromium taeniolites or bentonite. A stable numerical solution of the adsorption integral equation using splines (SAIEUS) was applied to obtain the proton affinity distribution by the latter authors. The details of this numerical approach were presented by Jagiełło (1994).

An important aspect of these potentiometric measurements is their simplicity and achievement of apparent and/or intrinsic equilibrium constant values. Jagiełło et al. (1995) showed by potentiometric titration of citric acid and by analysis of attained proton affinity distribution that this approach revealed the p*K* values which were in an excellent agreement with formerly reported p*K* values of citric acid deprotonation. In addition, the obtained values of molar ratios of detected carboxylic groups were in a very good agreement with the known structural composition of this acid and can be regarded as a suitable test of reliability of this approach.

In the presented study, potentiometric titrations of freshly proton-saturated forms of smectites of various chemical compositions were used to obtain their proton affinity distri-

bution. However, proton saturated smectites are known as unstable materials, spontaneously changing to (H, Al, Fe, Mg)-forms (Barshad & Foscolos 1970; Bednáriková et al. 1993; Janek & Komadel 1993) upon aging, that is with the progress of autotransformation. This process is closely related to proton attack on smectite structure in acids, which occurs during the preparation of acid-activated bentonites. Therefore, our interest was also focused on proton affinity distributions of equilibrium product autotransformation reaction. The main objective of this paper was to characterize the acid sites of three fresh proton saturated and autotransformed smectites of various chemical composition using proton affinity distribution analysis.

Materials and methods

Fine fractions of three bentonites were used in this study: JP montmorillonite (Jelšový Potok, Slovakia), ST iron rich beidelite (Stebno, Czech Republic), and SWa-1 ferruginous smectite (Grant County, Washington). The clays were Ca^{2+} saturated, fractionated to < 2 μm, washed free of excess ions, dried at 60 °C and ground to pass a 0.2 mm sieve. XRD and IR spectroscopy revealed dioctahedral smectite as the dominant mineral in all of these fine fractions of bentonites, however, minor admixtures of quartz and kaolinite were identified in ST sample. About 21 % of total iron present in ST was bound in goethite and 79 % in smectite (Čičel et al. 1992). The structural formulas of all samples used were published elsewhere (Janek et al. 1997).

Before preparation of H-forms, the samples were Na^+ saturated using 1 M NaCl solution, washed free of excess ions with water and ethanol, air dried at 60 °C, and ground to pass a 0.2 mm sieve. Subsequent treatments, employed to remove readily soluble oxo/hydroxo phases, such as iron and/or aluminum oxides/hydroxides, were performed with sodium oxalate solution. This procedure ensured maximal saturation of smectite with protons (Aldrich & Buchanan 1958; Barshad 1969). The dispersions of Na-smectites were passed through a train of three columns under applied suction. The first and the last column was filled with the resin Amberlit IR-120 in the H^+ form, the middle one with the resin Wofatit SBW in the OH^- form (Barshad 1969).

The autotransformation process was monitored by potentiometric titration at 25 °C using a Mettler DL-21 automatic titrator. About 170 data points were collected for each sample in a step-mode titration and pH values were recorded after 30 second reaction and electrode response stabilization times. A combined-glass microelectrode Schott-Geräte (N 6000 A) with a platin diaphragm was used as a pH reading sensor. Calibration was performed prior to measurements with Merck buffer solutions of pH_1 = 4.00 and pH_2 = 9.18 according to National Bureau of Standards (NBS). The slope of the electrode response was 58.9 mV/pH, which means a 99.6 % response of theoretical ideal value was achieved and changed by less than 0.1 % per month during the period of about two months needed to complete the titration experiments.

50 ml of freshly prepared H-smectite dispersion were immediately titrated with 0.1 M KOH (Titrisol Merck standard solution) and the rest of the dispersion was left to age in a tightly closed polyethylene flask at 90 °C. After four days and again after an additional 48 hours of aging 50 ml portions of dispersion were used for the next titrations. If the last two potentiometric curves obtained were identical, that is the part of the titration curves indicating consumption of free protons was not present any more, the autotransformation process was considered to be completed. To facilitate the calculation of the molar amount of protons interacting with the solid from potentiometric titration curves, parallel determination of dispersion density and mass fraction of the solid phase were performed gravimetrically.

Proton affinity distributions were calculated from potentiometric titration curves of freshly proton saturated and autotransformed smectite dispersions using the SAIEUS programme (Jagiełło 1994). Theoretical considerations of proton affinity distribution calculations on alumina and alumina modified surfaces, published by Contescu et al. (1993a, 1993b), can be briefly summarized as follows:

(*i*) It is assumed that the proton affinity of various oxygen/hydroxyl groups at the solid–solution interface is determined by the same factors as the number and type of the subadjacent coordinating structural atoms, which is a fundamental base for the differences of acid/base properties of surface oxygen atoms (Bleam 1993).

(*ii*) Proton transfer reaction may be described with the equilibrium reaction characterized by experimentally distinguished apparent equilibrium constant; one-pK model (Van Riemsdijk et al. 1987; De Wit et al. 1990).

(*iii*) A single population of proton transfer sites in a protonated state at a given pH is described by a Langmuir type adsorption isotherm:

$$q = [1 + 10^{(\mathrm{pH} + \mathrm{p}K)}]^{-1} \quad [1]$$

where q is the fraction of sites with characteristic apparent affinity constant pK, which are protonated at the given pH.

(*iv*) Investigation of apparent rather than intrinsic affinity constants ensures that coulombic interactions as long range interactions are neglected, but chemical binding forces as short range interactions are reflected by this model. The ionic strength of used solution was found to have a minor effect on deconvoluted distributions (Contescu et al. 1993a).

(*v*) The experimentally measured proton binding isotherm derived from potentiometric titration curve involves the theoretical proton balance equation:

$$Q = \frac{1}{\mathrm{m}}\{V.C_\mathrm{t} - (V_0 + V).([\mathrm{H}]_\mathrm{f} - [\mathrm{OH}]_\mathrm{f})\} \quad [2]$$

where m is the mass of the solid in dispersion, V_0 is the initial volume of the solution, V is the volume of added titrant, C_t is the concentration of the titrant and $[\mathrm{H}]_\mathrm{f}$ and $[\mathrm{OH}]_\mathrm{f}$ are the concentrations of actual pH determining species calculated from the values of dispersion pH after its correction for activity coefficients using Davie's equation (Contescu et al. 1993b).

(*vi*) Q represents the total amount of protonated sites within an experimental window varied within limits of experimentally accessible pH range and depends on pK of distinguished individual sites via the integral equation:

$$Q(\mathrm{pH}) = \int_{\alpha}^{\beta} q(\mathrm{pH}, \mathrm{p}K)\, f(\mathrm{p}K)\, d\mathrm{p}K + Q_0 \qquad [3]$$

which is a Fredholm integral equation of the first kind (Nederlof et al. 1990). Here $f(\mathrm{p}K)$ is distribution function of acid sites and is the differential quantity, which represents the number of sites with pK values in the interval (pK–dpK, pK+dpK). Q_0 is an arbitrary reference level constant referring to the amount of bonded sites outside the integration limits α, β (Bandosz et al. 1994; Jagiełło et al. 1995). Solution of the Fredholm integral equation is a formidable mathematical task and is complicated by problems with the ill-conditioned character of the matrix obtained from the system of linear equations during its numerical solution. Nederlof et al. (1990) discussed related problems with respect to determination of the adsorption affinity distributions and local isotherm approximations. Jagiełło (1994) proposed a numerical method for stable solution of the adsorption integral equation utilizing a non-negativity constrain of B-spline functions for $f(\mathrm{p}K)$ representation and regularization principle as stabilization procedures of the solution.

(*vii*) Release of structural cations in course of autotransformation should be reflected in the proton affinity distribution as proton interaction sites due to hydrolysis and/or their amphoteric character. These simultaneous equilibrium reactions are expected to be superimposed in the resulting proton affinity distribution. The released cations are supposed to be adsorbed on the surface of the particles as hydrated or partially hydrolyzed outer-sphere complexes (Sposito 1992).

Results and discussion

Typical proton desorption isotherms of freshly prepared and autotransformed H-smectites of characteristic shapes for these materials are presented in Figs. 1a–3a. The isotherms of freshly prepared H-forms show titration of both strong and weak acid sites. The addition of 0.1 M KOH solution resulted in an access of sites which were neutralized by the added basic solution without changing the pH of the titrated dispersion. This is indicated by the steep decrement of Q function. It is notable that the used clays differ in their ability of proton retention which depends on the different structural 'resistivity' of each sample against the attack of protons upon preparation (Janek & Komadel 1993; Janek et al. 1997). The sample preparation procedure ensured maximal saturation with protons for the very beginning of the experiment with their molar amount equal to the cation exchange capacity of smectite. Once the protons exchange the original exchangeable cations, they are consumed in the reaction of autotransformation. Therefore pH values of freshly proton saturated and autotransformed samples were found to be 2.48, 2.61, 2.62; and 3.40, 3.66, 3.11; for JP, ST and SWa-1, respectively. The rate of autotransformation is different for each smectite used and the structural cations are released in various ratios (Barshad & Foscolos 1970; Janek & Komadel 1993).

Proton desorption isotherms of autotransformed samples differ from those of the fresh samples. They revealed dependencies with missing parts of the strongest acid sites at the lowest pH's. An obvious decline of Q was found for all samples near pH = 6, which indicates the presence of weak acid sites in this pH region. Distinguishing of proton interaction sites by the evaluation of the slope of tangent to Q function only provides the same qualitative information as investigation of the original volumetric titration curves. However, in the case of reliable solution of the adsorption integral equation [3], the proton interaction sites can be detected on the pK scale.

The obtained proton affinity distributions in the studied smectite-water systems are shown in Figs. 1b–3b. Several resolved peaks representing different proton interaction sites of various pK values protonated at the intervals pK–dpK, pK+dpK were found within the accessible experimental pH window. In agreement with characterization of deprotonation equilibrium reactions, the strongest acid sites are of the lowest pK values and the weakest acid sites are those of the highest pK values. With increasing pH of the dispersion, the single sites are gradually deprotonated. Jagiełło et al. (1995) has proposed that the theoretical pK distribution of a pure chemical compound should be represented by a sum of delta Dirac functions. Nevertheless, we believe that representation of such a dependence using continuous spline functions are strongly realistic due to the existence of Boltzmann energy distribution of any investigated proton interaction site.

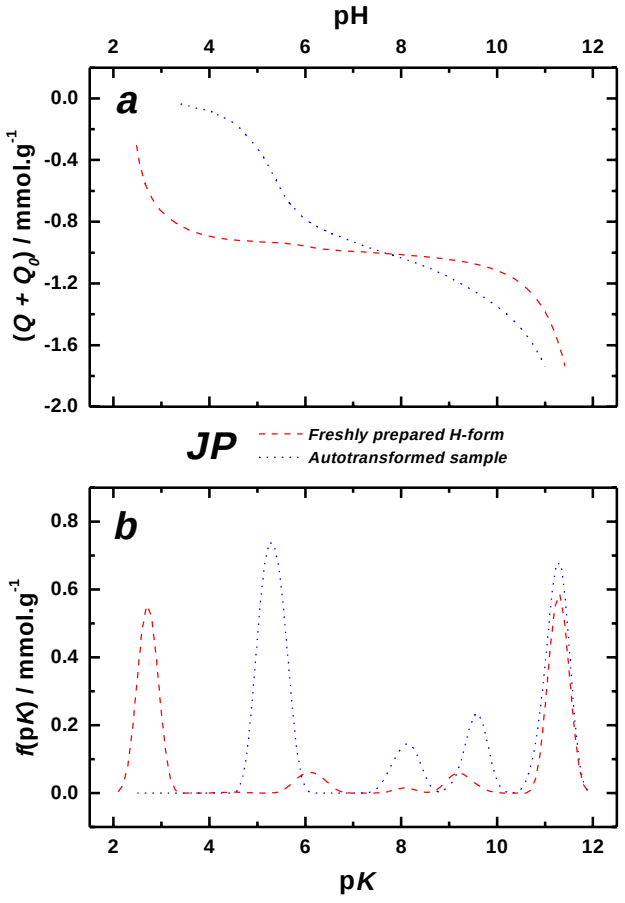

Fig. 1. Recalculated proton desorption isotherms of JP sample (a) and revealed proton affinity distribution (b).

The results of observed pK values are summarized in Table 1. Strong acid proton interaction sites with pK's between 2 and 3 and weak acid sites with pK's above 5 were found in all freshly proton saturated smectites. The existence of both sites is in agreement with the previously reported qualitative characteristics of proton saturated smectites (Janek & Komadel 1993; Janek et al. 1997; Komadel et al. 1997). Several weak proton interaction sites are detected in the affinity distribution. Upon autotransformation, the amounts of weak acid sites of pK's above 5 increased while the strongest acid sites disappeared or decreased in amount for all samples studied (Figs.1b–3b). This is connected with consumption of protons in the reaction of autotransformation. The strong acid sites are also consumed during the storage of acid-activated bentonites.

Assignment of single interaction sites from calculated proton affinity distributions is important for better understanding of acidity in acid treated clays. As mentioned above, the strongest acid sites with pK of about 2.7 are connected with protons in the diffuse doublelayers on the surface and in the interlayers, potentially interacting with the edges of the particles. Relatively strong acid sites in autotransformed ferruginous smectite SWa-1 with pK = 2.9 are noteworthy. Such strong acid sites are absent from the other two autotransformed clays (Figs. 1b–3b, Table 1). This is due to differences in the chemical composition of the smectites used. SWa-1 contains much more iron than JP and ST samples. The strong acid sites present after autotransformation result from titration of released $[Fe(H_2O)_6]^{3+}$ cations which have the highest tendency for hydrolysis in comparison to $[Al(H_2O)_6]^{3+}$ and $[Mg(H_2O)_6]^{2+}$ (Baes & Mesmer 1976). Absence of these sites on JP and ST samples, which also contain some structural iron, is either because concentrations of iron are below their possible detection by potentiometric titrations, or their aqueous chemistry is influenced by the common iron substitution by aluminum in their oxo/hydroxides originated by precipitation using a solution of alkali metal hydroxides (Schwertmann 1984), thus the presence of other cationic species hindered the detection of small amounts in JP and ST.

Weak acid sites detected in the range of pK's between 5 and 9 are due to the amphoteric character of the released

Table 1: pK values of five proton interaction sites obtained from proton affinity distributions for freshly proton saturated (pK_{Fps}) and autotransformed (pK_{Au}) samples.

Sample	pK_{Fps} / pK_{Au}				
	protonation	2 ←	pH	→ 12	deprotonation
JP	2.7 / –	6.1 / 5.3	8.1 / 8.1	9.2 / 9.6	11.3 / 11.2
ST	2.7 / –	5.1 / 5.6	8.5 / 8.5	9.7 / 9.8	11.3 / 11.3
SWa-1	2.7 / 2.9	5.6 / 5.4	8.1 / 7.0	9.4 / 9.6	11.3 / 11.3

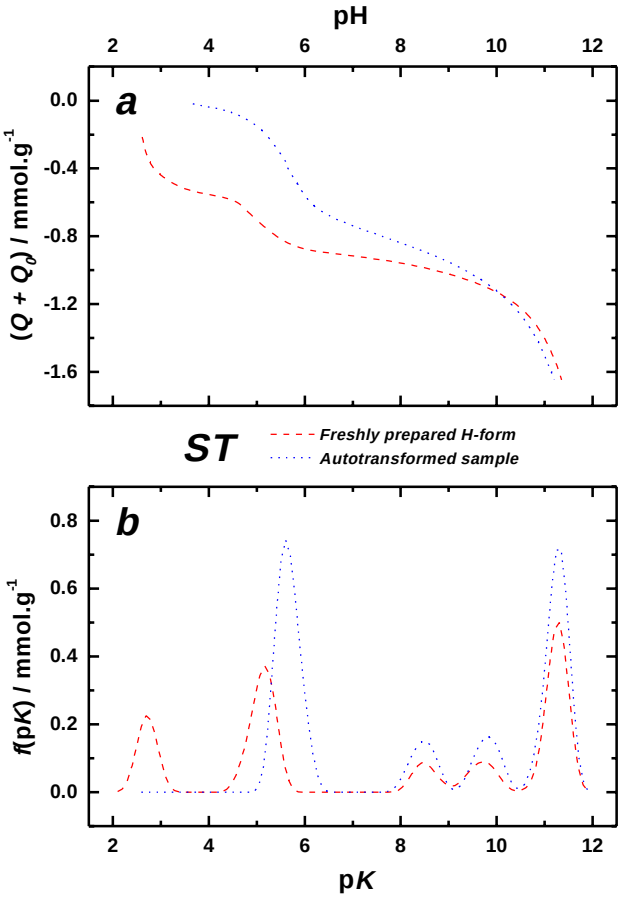

Fig. 2. Recalculated proton desorption isotherms of ST sample (a) and revealed proton affinity distribution (b).

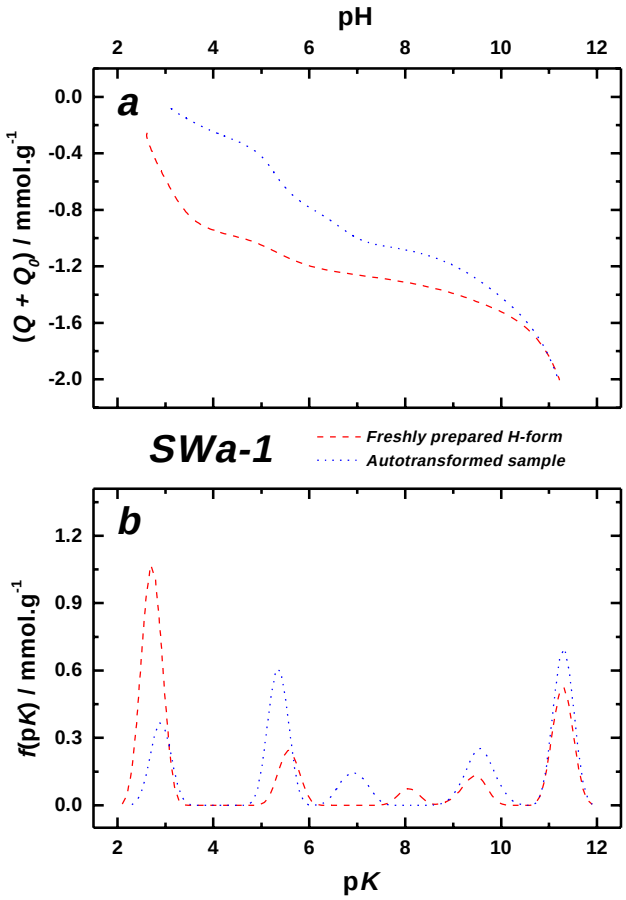

Fig. 3. Recalculated proton desorption isotherms of SWa-1 sample (a) and revealed proton affinity distribution (b).

structural cations and/or their hydrolysis. In the course of a potentiometric titration, firstly are neutralized $[Al(H_2O)_6]^{3+}$ cations with pK of about 5.5, forming a hydroxide (Low 1955). By following additions of the titrant, $Al(OH)_4^-$ anions are probably formed at a pK of about 8.3. The next proton interaction site with pK = 9.5 is supposed to be due to titration of $[Mg(H_2O)_6]^{2+}$ cations, however, some iron cations can possibly get titrated in this region. On the basis of these considerations, released structural cations can be involved in the following reactions taking place during titration, which could be considered for simulations of titration curves:

$$[M(H_2O)_6]^{z+} + zOH^- \Leftrightarrow M(OH)_z + 6H_2O \quad [4]$$

$$[M(H_2O)_6]^{z+} + nH_2O \Leftrightarrow [M(OH)_n(H_2O)_{6-n}]^{(z-n)} + nH_3O^+ \quad [5]$$

$$m[M(H_2O)_6]^{z+} + nH_2O \Leftrightarrow [M_m(OH)_n(H_2O)_{6m-n}]^{(zm-n)} + nH_3O^+ \quad [6]$$

$$M(OH)_3 + OH^- \Leftrightarrow M(OH)_4^- \quad [7]$$

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \quad [8]$$

M is one of the released structural cations with charge z (Al^{3+}, Fe^{3+}, Mg^{2+}). Possible reactions including different ion species are not shown.

Reactions [4] to [7] can accompany the interactions of present hydrolytic and/or hydroxo species with the surface of mineral particles (Thompson & Tahir 1991; Thompson & Mitchell 1993) as simultaneous equilibrium reactions. Titration of homosaturated and/or in defined cation ratios prepared (Al/Fe/Mg)-forms can possibly help to identify interaction sites on the proton affinity curves in future experiments. Furthermore, all these effects are clearly responsible for the detected shifts of the peak positions with pK's from 5 to 9 (Figs. 1b–3b, Table 1).

The weakest acid sites appearing within experimentally accessible pH window were identified at pK = 11.3. These sites are supposed to be due to deprotonation of structural SiOH groups present on the edges of smectite particles. These functional groups occur in some acid untreated clays as well as in amorphous silica, the reaction product of acid treatment of clays. The amount of these groups increased upon autotransformation (Figs. 1b–3b). A similar trend was found by Tkáč et al. (1994) and Komadel et al. (1996) who reported formation of SiOH groups with the extent of acid treatment of smectites detected by ^{29}Si MAS NMR.

Moreover, Rand et al. (1980) have concluded from their rheological investigations of montmorillonite dispersions, that isoelectic points of the edge-surface of montmorillonite particles should exist at pH's below 4 and above 10. Here, the lowest (2.7) and the highest (11.3) pK values reported in this work are in agreement with edge-surface proton interaction reaction, as was schematically presented by Lagaly (1989). Hence, proton affinity distribution offers detailed characterization of proton interaction reactions at clay mineral/water interface which are fundamental for rheological studies of clay mineral particles in dispersions (Brandenburg & Lagaly 1988; Güven & Pollastro 1992; Permien & Lagaly 1994).

Conclusions

Proton saturated smectites were prepared from the < 2 μm fractions of three bentonites. Potentiometric titration of proton saturated forms was used to characterize the acid centers at the smectite-water interface. The H-forms were prepared by $H^+ \rightarrow OH^- \rightarrow H^+$ ion exchange with resins. Autotransformation of smectite dispersions was performed at 90 °C. Titration data were further used in the thermodynamic calculation of proton affinity distribution. Numerical solution of an integral adsorption equation offered continuous distribution of proton interaction sites.

Proton affinity distributions clearly detected up to 5 different proton interaction sites in all proton saturated smectite/water systems, within the accessible experimental range of pH's between 2 and 12. The amount of the strongest acid sites, that is those with the lowest pK values, decreased on aging, while the amounts of all weaker acid sites increased with the progress of autotransformation. The strongest acid sites are connected with free protons present in the dispersion, while the weaker acid sites are connected with the titration of released structural Al^{3+}, Fe^{3+}, Mg^{2+} cations and/or their hydrolyzed species, and with deprotonation of functional SiOH groups. These results indicate the nature of acid sites in H-bentonites and can be helpful for interpretation of the rheological properties of acid/base conditioned smectites dispersions.

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References

Aldrich D.G. & Buchanan J.R., 1958: Anomalies in techniques for preparing H-bentonites. *Soil Sci. Soc. Amer. Proc*., 22, 281–285.

Baes C.F. & Mesmer R.E., 1976: The hydrolysis of cations. *John Wiley & Sons*, New York, 1–489.

Bandosz T.J., Jagiełło J., Putyera K. & Schwarz J.A., 1994: Characterisation of acidity of pillared clays by proton affinity distribution and DRIFT spectroscopy. *J. Chem. Soc., Faraday Trans*., 90, 3573–3578.

Bandosz T.J., Jagiełło J. & Schwarz J.A., 1996: Characterisation of the structure and surface acidity of hydroxychromium taeniolites. *J. Phys. Chem*., 100, 15569–15574.

Bandosz T.J., Jagiełło J. & Schwarz J.A., 1997: A study of acidity and structure of hydroxy-Cr intercalated bentonites. *J. Colloid Interface Sci*., 182, 570–577.

Barshad I., 1969: Preparation of H saturated montmorillonites. *Soil Sci*., 108, 38–42.

Barshad I. & Foscolos A.E., 1970: Factors affecting the rate of interchange reaction of adsorbed H^+ on the 2:1 clay minerals. *Soil Sci*., 110, 52–60.

Bednáriková E., Komadel P. & Čičel B., 1993: Preparation and autotransformation of H-saturated montmorillonites. In: *Proc. Eleventh Conference on Clay Mineralogy and Petrology. Č. Budějovice 1990,* 93–97.

Bleam W.F., 1993: On modeling proton affinity at the oxide/water

interface. *J. Colloid Interface Sci*., 159, 312–318.
Brady P.V., Cygan R.T. & Nagy K.L., 1996: Molecular controls of kaolinite surface charge. *J. Colloid Interface Sci*., 183, 356–364.
Brandenburg U. & Lagaly G., 1988: Rheological properties of sodium montmorillonite dispersions. *Appl. Clay Sci*., 3, 263–279.
Breen C., 1991: Thermogravimetric study of the desorption of cyclohexylamine and pyridine from acid-treated Wyoming bentonite. *Clay Miner*., 26, 473–486.
Breen C. & Watson R., 1998: Acid-activated organoclays: preparation, characterisation and catalytic activity of polycation-treated bentonites. *Appl. Clay Sci*., 12, 479–494.
Brown D.R. & Rhodes C.N., 1997: A new technique for measuring surface acidity by ammonia adsorption. *Thermochim. Acta*, 294, 33–37.
Contescu C., Jagiełło J. & Schwarz J.A., 1993a: Heterogeneity of proton binding sites at the oxide/solution interface. *Langmuir*, 9, 1754–1765.
Contescu C., Jiafen H. & Schwarz J.A., 1993b: 1-pK multisites decription of charge development at the aqueous alumina interface. Adsorption of Pd^{II}-amine complexes. *J. Chem. Soc., Faraday Trans*., 89, 4091–4099.
Čičel B., 1991: Mechanism and kinetics of proton attack of smectites. *DrSc. thesis, Institute of Inorganic Chemistry*, SAS, Bratislava, 1–203 (in Slovak).
Čičel B., Komadel P., Lego S., Madejová J. & Vlčková L., 1992: Iron-rich beidelite in the fine fraction of Stebno bentonite. *Geol. Carphatica, Ser. Clays*, 43, 121–124.
De Wit J.C.M., Van Riemsdijk W.H. & Nederlof M.M., 1990: Analyses of ion binding on humic substances and determination of intrinsic affinity distribution. *Analyt. Chim. Acta*, 232, 189–207.
Fahn R. & Fenderl K., 1983: Reaction products of organic dye molecules with acid treated montmorillonite. *Clay Miner*., 18, 447–458.
Güven N. & Pollastro R.M., 1992: Clay-water interface and its rheological implications. *Clay Miner. Soc. Workshop Lectures 4*, Boulder, CO, USA, 244.
Hayes K.F. & Leckie J.O., 1987: Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces. *J. Colloid Interface Sci*., 115, 564–572.
Janek M. & Komadel P., 1993: Autotransformation of H-smectites in aqueous solution. Effect of octahedral iron content. *Geol. Carpathica, Ser. Clays*, 44, 59–64.
Janek M., Komadel P. & Lagaly G., 1997: Effect of autotransformation on the layer charge of smectites determined by the alkylammonium method. *Clay Miner*., 32, 623–632.
Jagiełło J., 1994: Stable numerical solution of the adsorption integral equation using splines. *Langmuir*, 10, 2778–2785.
Jagiełło J., Bandosz T.J., Putyera K. & Schwarz J.A., 1995: Determination of proton affinity distribution for chemical systems in aqueous environments using a stable numerical solution of the adsorption integral equation. *J. Colloid Interface Sci*., 172, 341–346.
Komadel P., Bujdák J., Madejová J., Šucha V. & Elsass F., 1996: Effect of non-swelling layers on dissolution of reduced-charge montmorillonite in hydrochloric acid. *Clay Miner*., 31, 333–345.
Komadel P., Janek M., Madejová J., Weeks A. & Breen C., 1997: Acidity and catalytic activity of mildly acid-treated Mg-rich montmorillonite and hectorite. *J. Chem. Soc., Faraday Trans*., 93, 4207–4210.
Lagaly G., 1989: Principles of flow of kaolin and bentonite dispersions. *Appl. Clay Sci*., 4, 105–123.
Low P.F., 1955: The role of aluminium in the titration of bentonite. *Soil Sci. Soc. Amer. Proc*., 19, 135–139.
Madejová J., Bujdák J., Janek M. & Komadel P., 1998: Comparative FT-IR study of structural modifications during acid treatment of dioctahedral smectites and hectorite. *Spectrochim. Acta, Part A*, 54, 1397–1406.
Nederlof M.M., Van Riemsdijk W.H. & Koopal L.K., 1990: Determination of adsorption affinity distributions: A general framework for methods related to local isotherm approximations. *J. Colloid Interface Sci*., 135, 410–426.
Permien T. & Lagaly G., 1994: The rheological and colloidal properties of bentonite dispersions in the presence of organic compounds. IV. Sodium montmorillonite and acids. *Appl. Clay Sci*., 9, 251–263.
Qing D., Zhongxi S., Forsling W. & Hongxiao T., 1997: Acid-base properties of aqueous illite surfaces. *J. Colloid Interface Sci*., 187, 221–231.
Rand B., Pekenc E., Goodwin J. W. & Smith R.W., 1980: Investigations into the existence of edge-face coagulated structures in Na-montmorillonite suspensions. *J. Chem. Soc., Faraday Trans.*, 76, 225–235.
Schwertmann U., 1984: The influence of aluminium on iron oxides: IX. Dissolution of Al-goethites in 6 M HCl. *Clay Miner.,* 19, 9–19.
Siddiqui M.K.H., 1968: Bleaching earths. *Pergamon Press*, Oxford, 1–86.
Stumm W., Kummert R. & Sigg L., 1980: A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. *Croatica Chem. Acta,* 53, 291–312.
Sposito G., 1992: The diffuse-ion swarm near smectite particles suspended in 1:1 electrolyte solutions: Modified Gouy-Chapman theory and quasicrystal formation. In: Güven N. & Pollastro R.M. (Eds.): *Clay-water Interface and its rheological implications. Clay Miner. Soc. Workshop Lectures 4*, Boulder, CO, USA, 128–155.
Tanabe K., 1970: Solid acids and bases, their catalytic properties. *Academic Press*, London, 1–175.
Tkáč I., Komadel P. & Müller D., 1994: Acid-treated montmorillonites — a study by ^{29}Si and ^{27}Al MAS NMR. *Clay Miner*., 29, 11–19.
Thompson D.W. & Tahir N.M., 1991: The influence of a smectite clay on the hydrolysis of iron (III). *Coll. Surf*., 60, 369–398.
Thompson D.W. & Mitchell Ch.J., 1993: The hydrolytic precipitation of iron in aqueous dispersions of mineral particles. *Coll. Surf*., 73, 103–115.
Van Riemsdijk W.H., De Wit J.C.M., Koopal L.K. & Bolt G.H., 1987: Metal ion adsorption on heterogeneous surfaces: Adsorption models. *J. Colloid Interface Sci*., 116, 511–522.
Wanner H., Albinsson Y., Karnland O., Wieland E., Wersin P. & Charlet L., 1994: The acid/base chemistry of montmorillonite. *Radiochim. Acta*, 66/67, 157–162.