

SURFACE PROPERTIES AND MODELLING POTENTIOMETRIC TITRATION OF AQUEOUS ILLITE SUSPENSIONS

^{*}*Département de Chimie, Ecole Supérieure des Sciences et Techniques de Tunis.*

Rue Taha Hussein- Montfleury Tunis, Tunisia

^{**}*Unité matériaux, Technopole Borj Cedria, BP 95-2050 Hammam lif, Tunisia*

kriaa1993@yahoo.fr

Introduction

Over the past several decades, significant advances have been achieved in the understanding of the chemistry of mineral surfaces and the mineral-water interface. One of the major developments is the successful application of surface complexation models (SCMs) to enhance understanding of surface interactions involving simple minerals as well as synthesized single metal oxide and hydroxide minerals [1–5]. Among SCMs commonly used in the literature, the diffuse layer, constant capacitance model and the triple layer model, based on their ability to simulate the acid-base titration behaviour of oxide surfaces. These three models are similar in their descriptions of surface reactions, each treating the surface as if it were composed of amphoteric hydroxide functional groups which are capable of reacting with sorbing cationic or anionic species to form surface complexes. However, these models differ in complexity and descriptions of the electrical double layer and the manners in which changes in the background electrolyte concentration are incorporated in model computations. Some authors have given a schematic representation of the electrical properties of the interfacial region [1] where the three SCMs in terms of adjustable parameters, including surface chemical reactions and the charge-potential relationships, are summarized in Table 1.

Table 1. Surface complexation reactions and model parameters

	DLM	CCM	TLM
Surface chemical reactions	$\equiv \text{SOH} + \text{H}^+ \rightleftharpoons \equiv \text{SOH}_2^+ \quad K_{a1}$ $\equiv \text{SOH} \rightleftharpoons \equiv \text{SO}^- + \text{H}^+ \quad K_{a2}$ $K_{a1}^{\text{int}} = K_{a1} \exp(F\Psi_0/RT)$ $K_{a2}^{\text{int}} = K_{a2} \exp(-F\Psi_0/RT)$	Same as DLM	Same as DLM Ion pair complexes $\equiv \text{SOH} + \text{Cat}^+ \rightleftharpoons \equiv \text{SO}^- - \text{Cat}^+ + \text{H}^+ \quad K_{\text{Cat}}$ $\equiv \text{SOH} + \text{An}^- + \text{H}^+ \rightleftharpoons \equiv \text{SOH}_2^+ - \text{An}^- \quad K_{\text{An}}$
Charge-potential relationships	$-\sigma_0 = \sigma_d = -0,1174\sqrt{I} \text{Sinh}(ZF\Psi_d/2RT)$	$\sigma_0 = C_1\Psi_0$	$\sigma_d = -0,1174\sqrt{I} \text{Sinh}(ZF\Psi_d/2RT)$ $\sigma_0 = (\Psi_0 - \Psi_\beta) C_1$ $\sigma_0 + \sigma_\beta = (\Psi_\beta - \Psi_d)C_2$
Adjustable parameters	$K_{a1}^{\text{int}}, K_{a2}^{\text{int}}, D_s$ (total surface site density)	$K_{a1}^{\text{int}}, K_{a2}^{\text{int}}, C_1$ and D_s	$K_{a1}^{\text{int}}, K_{a2}^{\text{int}}, K_{\text{Cat}}, K_{\text{An}}, D_s, C_1, C_2$

In the other side, because of their complex chemical composition, application of SCMs to complex natural clay minerals as well to purified phyllosilicate clay minerals is relatively rare. We can cite some studies on kaolinite [6,7], on montmorillonite [8,9], on bentonites [10], on natural illite and glauconite [11–14]. We must notice that some experimental studies based on surface complexation modelling on natural and complex clay minerals, taking into account considerable aqueous dissolution, has been carried out by some authors [7, 11, 14]. But as mentioned by these authors, the correction for dissolution effects yielded a modest improvement in model simulation. The complexity of the model calculations were found to be increased greatly when the numerous additional chemical reactions are considered. Also, the inclusion of ion exchange interactions produced no substantive improvement in the model fit, by using the NEM and CCM. In general, the involvement of the CEC sites in proton adsorption has been most frequently neglected. Some authors emphasised that the exchange reactions between alkali or alkaline earth cations and protons is important only at low pH [15]. Other studies have corrected for the contribution of the CEC, because the reached pH was low enough [16, 17].

In this study, potentiometric titration experiments were used to investigate the acid-base chemistry of different illitic complex clay minerals. A new simple model approach based on derived parameters of Gran method titration was proposed in order to determine the surface ionisations constants. And the well-known SCMs with different formulations and assumptions were applied neither to model the experimental data nor to compare with pKas values obtained from Gran parameters analysis.

It is well known that illite occupy half or more of the clay minerals in the earth's crust. Some works on different aspects of its behaviour have been studied [11, 12], e.g., electrochemical properties and adsorption of contaminants.

Structurally, illite is a 2:1 layer-type clay mineral composed of one gibbsite sheet (γ -Al(OH)₃) sandwiched between two silica sheets (SiO₄) and the illite solution systems have only two kinds of surfaces: a siloxane surface and an edge surface [12]. Moreover, Katari and Tauhe [18], reported that certain clays like illite could acquire a permanent negative charge on the face due to isomorphous substitution of Al³⁺ for Si⁴⁺ in the layer with tetrahedral coordination. A cloud of oppositely charged counter ions forming a diffuse double layer surrounds this negative surface. In addition, the flat basal surface of clay minerals is negatively charged due to cation exchange, but the edge surface behaves like an oxide. On their edges (\approx 10 % of total surface area), charges arise from the breaking of Al-O and Si-O bonds resulting in amphoteric Al-OH and Si-OH surface function groups. These surface hydroxyls can be protonated or deprotonated depending on the pH of the suspension and the PZC of the edge of the clay particles. At a pH below PZC, there will be an excess of Al(OH)₂⁺ relative to Al-O, resulting in a net positive charge for the edges. Some crystallographic considerations, done by Keren and Sparks [19], concerning the structure of pyrophyllite show that the most reactive surface functional group on the edge surfaces is the hydroxyl exposed on the periphery of the clay mineral. This functional group is associated with the structural cations Al(III) and Si(IV) which are located in the octahedral and tetrahedral sheets, respectively. At the edge of the octahedral sheet, the Al(III) OH is a Bronsted acid site. The hydroxyl group associated with this site can interact with a proton at low pH values. At the edge of the tetrahedral sheet, hydroxyl groups are singly coordinated to Si⁴⁺ cations.

The major purposes of the study are (i) to investigate the surface charge characteristics of three illitic clay minerals provided from different locations by potentiometric titration, using Gran method and fast titration technique (ii) to implement a new simple model in order to determine pKas values using derived parameters of Gran plot method and (iii) to confirm these pKas values by implementing the SCMs to characterize the acid-base chemistry of the complex illite samples. These aspects have not been widely studied in the literature in relation to the few studies concerning illite clay mineral [11–14]. We think in agreement with [13]; that in order to acquire more details on acid-base properties at illite surface binding sites, a comparative study, concerning illite samples collected from different locations, would be conducive to obtain a comprehensive understanding of adsorption. Furthermore, a unified thermodynamic model can be set up to describe the general behaviour of surface acid-base properties over a group of illitic minerals.

Materials and Methods

Clays

The solid samples were gathered from three sources: (1): an American illite sample from Montana (USA), (light green colour specimen), (2) an illite sample (glauconite) from Gafsa, in southern Tunisia, (dark green colour specimen) and (3) an illite-chlorite mixed-layer sample from El Hamma, in southern Tunisia too (red colour specimen) (hereafter abbreviated to It (Mo), It (Ga) and It (Ha), respectively). The clay fraction (particle size < 2 micrometers) was purified by classical methods [20], transformed into the sodium

form with 1M NaCl solution. After washing, sedimentation and dialysis, the fine clean sediment was freeze dried.

Chemical analysis

The chemical analysis of purified samples is summarized in table2. It follows from this analysis that:

Table 2. Chemical composition of the samples

%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	CaO	Ignition loss
It (Mo)	50,24	24,38	5,58	2,13	1,21	9,39	0,05	7,53
It (Ga)	53,34	3,41	24,98	4,04	0,5	7,58	0,19	7
It (Ha)	53,42	15,82	9,44	3,49	2,08	7,04	0,89	8,05

Comparatively to American illite, the Tunisian glauconite, It (Ga), contains a higher content of Fe₂O₃ and a low ratio of Al₂O₃. One can notice that our samples contain a high amount of K indicating that all samples are illitic clay minerals.

The peak surfaces of the d₀₀₁ reflections of illite and chlorite respectively were determined using 'PANalytical X'Pert High Score plus' software. The amount of chlorite in illite was estimated as 20%.

The average structural formulas of the purified It (Mo) and It (Ga) samples are:



The structural formula of It (Ha) has not been determined; the presence of chlorite makes the formula more complicated.

It follows from these formulas, that illite samples used in this study, presented two types of substitutions (octahedral and tetrahedral substitutions). The charge per unit cell is 1,61 for It (Ga) and 1,98 for It (Mo). As can be noticed, the It (Ga) sample contains essentially Fe in the octahedral sheet, but in the It (Mo) sample, Al (III) occupies the octahedral sheet. Moreover, the tetrahedral substitution rate is more important for It (Mo) than for It (Ga).

The cationic exchange capacities (CEC) and the specific surface areas (SSA) for the three purified samples are summarized in table 3. It appears that all CEC values are relatively lower than other clay minerals (smectite) confirming that these solid samples belong to illitic minerals. The S_{BET} values of these samples are close.

Table3. CEC cationic exchange capacity and SSA specific surface area values of the three illitic samples

Specimen	CEC(meq/100g)	S _{BET} (m ² /g)
It (Mo)	27	45
It (Ga)	24	60
It (Ha)	34	51

PZC determination by fast titration

Potentiometric titrations of the illite samples are conducted in a reactor pyrex cell, a microburette of very fine tip containing the titrant (HCl) and a HI 9321 Microprocessor pH meter (Hanna Instruments) combination electrode, calibrated with two commercial pH buffers at ambient temperature and aerated medium.

The acid base potentiometric titration curves at different salt concentrations were used to measure the proton adsorption or proton charge. The experimental method employed was similar to that used by Boisset [21], for "alumine, hematite and rutile" and Kriaa [22] for Kaolinite. 30 ml of background electrolyte (NaCl) solution of concentration (0.1, 0.01, 0.001) containing 0.05 g sample was equilibrated for 15 mn with continuous stirring in order to reach an equilibrium pH value. When a small amount of HCl was added to protonate a significant part of the surface sites, the pH stabilized quickly ($\Delta\text{pH} < 0.03$ unity pH) and was red within 30 s. During the titration and after addition of HCl, the pH rapidly reached a constant value and

remained invariable with time. The titration was stopped when the pH was around 4 in order to avoid possible occurring chemical phenomena such as dissolution of illite clay mineral. All the experiments were repeated at least in duplicate to confirm the results. The blank titrations were also performed with similar solutions in the absence of the clay suspensions.

Potentiometric titration curves using Gran plot method

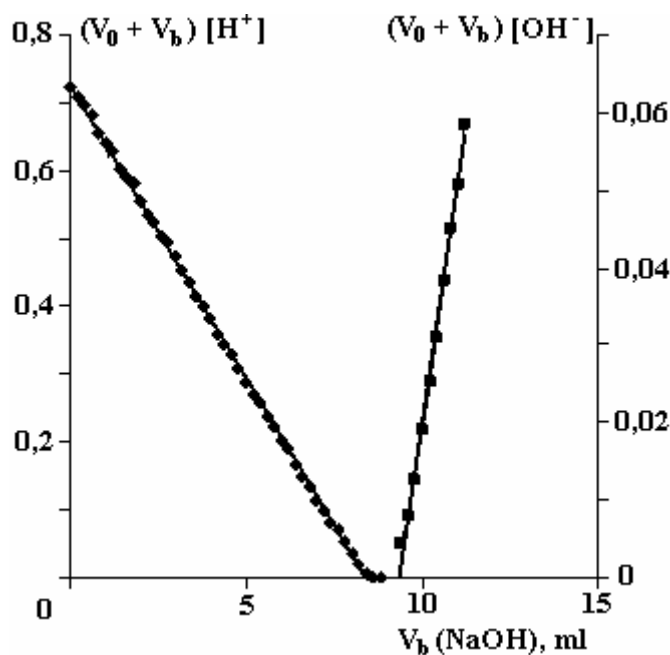
The experimental method was similar to that used by Du [11] for illite suspensions. For all the acid-base titrations, illite suspensions were firstly acidified by HCl 10^{-2} M at pH approximately 2 and then titrated immediately with hydroxide solution ($5 \cdot 10^{-2}$ M) to an alkaline pH range. For each titration, a certain amount of 0.1 g illite stock suspension was added to a 15 ml water flask and stirred during 24 hours in order to attain equilibrium criteria. NaCl solution was used to stabilize the system at a given ionic strength. Distilled water was added to bring the total initial volume of the suspension to 50 ml. The temperature is being held constant at $25 \pm 0,5^{\circ}\text{C}$. Afterwards, $5 \cdot 10^{-2}$ M NaOH in 0,2 ml increments was used to titrate the suspension up to a pH approximately 11. The equilibrium criterion for each addition of the titrant was the stability of pH value measured.

Concerning the blank system for each sample, we have used the supernatant of the corresponding sample system as the titration blank. The procedure for obtaining the supernatant was as follows: an illite sample suspension with the same composition as the one used in the corresponding sample titration was prepared. The suspension was centrifugated at 3 000 rpm during 10 mn. The supernatant thus obtained was titrated according to the procedure described above. The controlling condition during the titration was the same as that for the sample titration.

The NaCl electrolyte concentration was adjusted to a 0.1, 0.01 and 0.001 mol/l. For all experiments potentiometric titration curves and before each titration, the aqueous suspensions and their corresponding supernatant blank systems were equilibrated for about 10mn in order to reach an equilibrium pH value.

Data treatment

For the titration of solid / water systems and their corresponding supernatant, we have choose the Gran titration method, as used by some researchers [11,12,23,24], to determine accurately the equivalence points of potentiometric titrations in aqueous solutions and the net number of protons reacted per surface site (Z_{net}). Then, the point of zero charge is evaluated by determining the common intersection points of illite suspensions. For each studied system, Gran plot was made, from experimental data, for the hydroxide titration. The V_{e1} and V_{e2} values determined by linear regression in the corresponding Gran plot are shown in the Fig. 1.



a

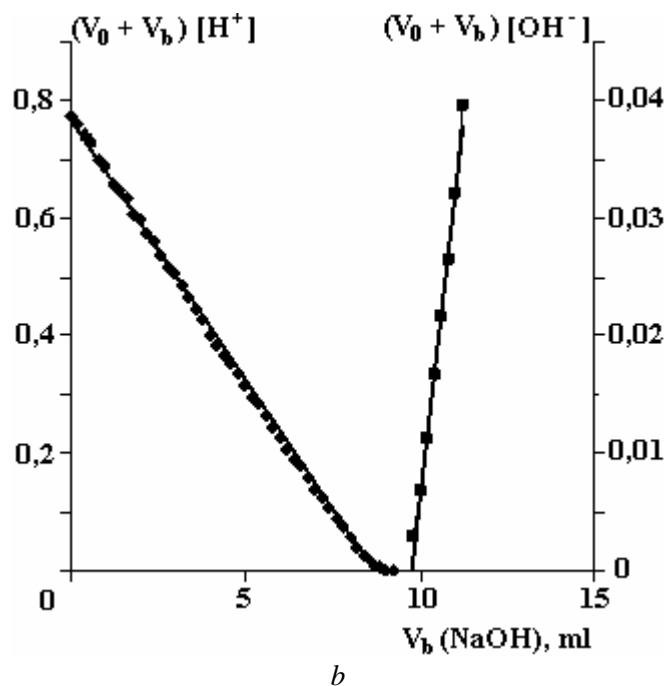


Fig.1. Gran plot of It (Mo) suspension in 0,1M NaCl solutions. a – blank system, $Ve_1 = 8,416$, $Ve_2 = 9,348$; b – aqueous suspension, $Ve_1 = 8,687$, $Ve_2 = 9,748$

Parameters of Gran method

Therefore, for each titration point, the concentration of the total protons added to the system was calculated by:

$$\text{TOT H} = - (V_b - Ve_1)C_b / (V_0 + V_b), \text{ mol / l} \quad (1)$$

Where: V_b is the volume of NaOH added in the hydroxide titration, V_0 is the initial volume of the suspension and C_b is the concentration of NaOH.

The determination of the total surface site concentration (H_s) was calculated from the two equivalence points in the Gran plot of the hydroxide titration (see figure 1, Ve_1 and Ve_2) after subtracting the hydroxide consumed by the blank solution, as shown in the equation below:

$$H_s = [Ve_2 - Ve_1]C_b]_{\text{sample}} - [(Ve_2 - Ve_1)C_b]_{\text{blank}} / V_0, \text{ mol/l} \quad (2)$$

The calculation of average number of protons reacted per surface site (Z) was determined at each titration point by:

$$Z = [\text{TOT H} - 10^{-\text{pH}} + 10^{-(\text{pK}_w - \text{pH})}](V_0 + V_b) / H_s V_0. \quad (3)$$

TOT H and H_s were calculated by equations (1) and (2) respectively. For each illite system, the net number of surface reacted protons per surface site, $Z_{\text{net}}(\text{pH}, I)$ was obtained from the difference between the Z values of the sample titration and the corresponding blank titration at the same pH:

$$Z_{\text{net}}(\text{pH}, I) = Z_{\text{sample}} - Z_{\text{blank}}$$

The surface site density (D_s) was calculated at a given ionic strength, from H_s value, using equation:

$$D_s = (H_s \cdot N_A) / (S \cdot C_s \cdot 10^{18}) \text{ sites / nm}^2 \quad (4)$$

Where: N_A the Avogadro's number ($6,02 \cdot 10^{23} \text{ mol}^{-1}$), S the N_2 / BET surface area and C_s is the illite solid concentration (g/l).

Determination of surface acidic constants

The two most common methods for determining surface equilibrium constants from titration data are by using objective curve fitting routines or by graphical extrapolation methods, on pure mineral oxides [15,25,26], on synthetic mixed oxides of iron and silicon [4], on kaolinite [7], by computing the proton adsorption according to surface complexation models (nonelectrostatic model and constant capacitance model), on glauconite [14] and on illite [11–13], by using non linear least-square optimisation program FITEQL. In this study, graphical methods were mainly selected. From the derived parameters of Gran plot data, the surface constants ionisation were computed using the method based on Hasselbach equation [24] on colloidal aqueous solution of soils. In order to confirm these pKas values, the surface complexation models (SCMs) were used to describe titration data and thus to calculate these equilibrium constants. The nonelectrostatic model (NEM), The constant capacitance model (CCM) and the triple layer model (TLM) were implemented without dissolution correction approach.

Analysis and Discussion

Titration curves

The proton adsorption or proton surface charge density σ_H (mol/m²), determined from potentiometric titration was calculated as the difference between total amounts of H⁺ or (OH⁻) added to the dispersion and that required to bring a blank solution of the same NaCl concentration to the same pH [27]

$$\sigma_H \text{ (mol/m}^2\text{)} = \frac{V}{m} S \left\{ \left([\text{H}^+]_b - [\text{H}^+]_s \right) - \left(\frac{K_w}{[\text{H}^+]_b} - \frac{K_w}{[\text{H}^+]_s} \right) \right\}, \quad (1)$$

Where V is the volume of electrolyte solution equilibrated with illite sample (30 ml), [H⁺] is the solution proton concentration (mol/l), K_w is the dissociation product of water (10⁻¹⁴) and the subscripts s and b refer to sample and blank solutions respectively. M is the mass of sample used (0,05g), S is the specific surface area (m²/g)

Sensitivity estimations: Based on the calibration titration and on the readings of the electrode potentials, the uncertainty in the measured pH is estimated to be ± 10%.

Furthermore, in our titration experiments, because of short equilibration time (15 mn), the release of Si and Al caused by illite dissolution (generally at pH 3-4) into the aqueous solution was not significant and assumed negligible during the titration experiments. This observation is supported by some authors cited by Duc [28] who found that two major processes occur simultaneously during titration: surface site dissociation / complexation and dissolution. At ambient temperature, dissolution is kinetically slower than acid-base surface site reactions.

For all the illite samples, equilibrium data were used to plot σ_H vs pH curves. We have verified that the data obtained with HCl superimposed well with those obtained with NaOH indicating good reversibility of the H⁺ adsorption process, in agreement with some authors for montmorillonites [29, 30].

Our experimental titration curves demonstrate that the studied illite samples does not present a net crossing point in the proton adsorption curves (see for example fig. 2 for It (Mo)) comparatively to classical curves of pure simple oxides at different ionic strengths [25,31]. The absence of intersection point for montmorillonite was attributed to the combined effect of both variable charges and permanent negative charges [29].

In the absence of any specific adsorption, the PZNPC is equivalent to the pH of zero point of charge [27]. Their values for illites samples are situated at pH ~7.5-8.4; ~8.2- 8.7 and ~9.1-9.3 for It (Mo), It (Ha) and It (Ga) respectively. It reveals that the presence of chlorite has an effect on the shifting PZC value of It (Ha) toward higher pH value. In this case, no experimental studies dealing with H⁺ adsorption of chlorite were found in the literature. Hendershot and lavkulich [32] found PZC value in the range ~7.5-8 for Na⁺ illite in different NaCl solutions; I varying from 0.002M to 0.1M. Comparatively to others published experimental data for illite, these values are higher; this is probably due to the basic character of our illite samples (the stability pH of the equilibrium suspensions in distilled water is in the range 7.9-9.5)

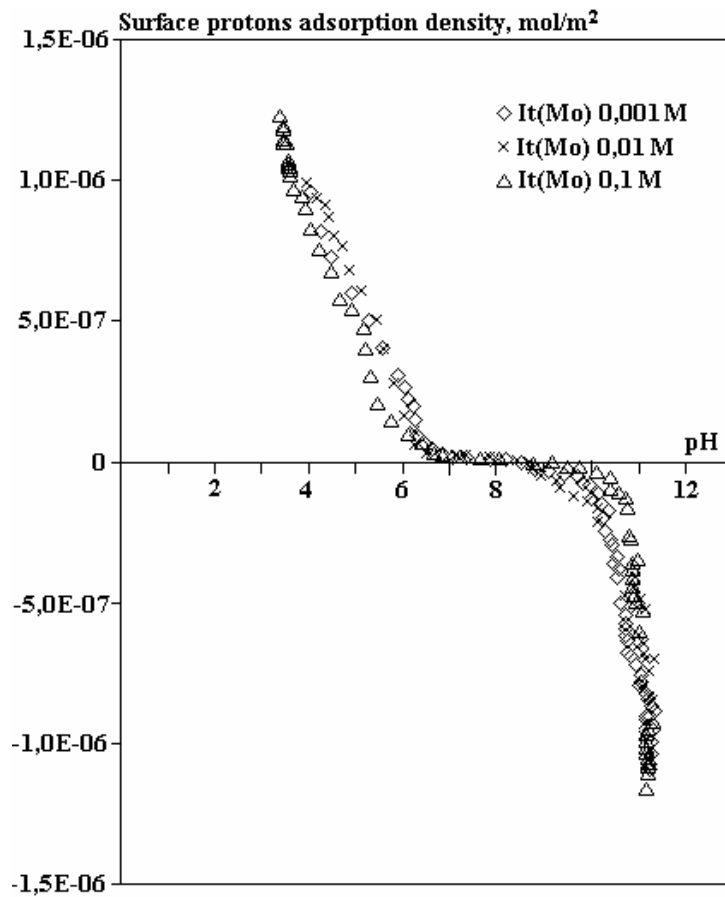
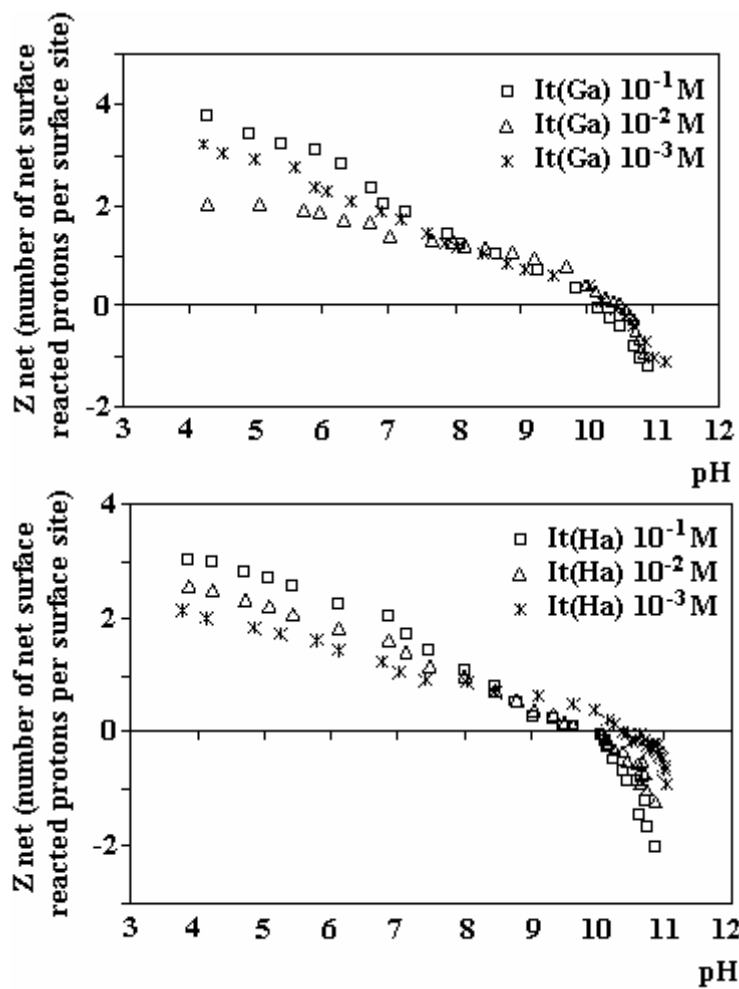


Fig. 2. Experimental acid-base of pure It (Mo) obtained at various ionic strengths, in aerated medium, at 25°C



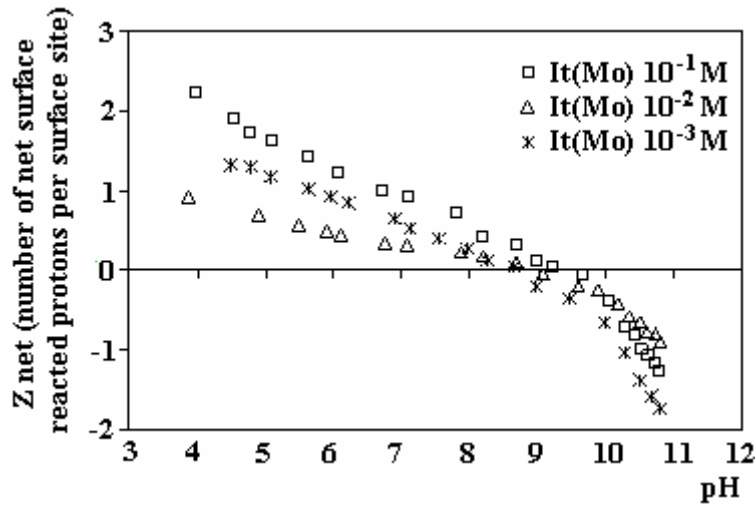


Fig. 3. pH-dependent net number of surface- reacted protons per surface site. (a) It(Ga), (b) It(Ha), (c) It(Mo)

On the other hand, our acid–base titration results, determined from Gran plot method (Znet vs pH), are presented in fig. 3, for It (Mo), It (Ga) and It (Ha) respectively. The curves do not show also a crossing point corresponding to pH PZC. They demonstrate clearly that pH PZCs for illitic samples are nearly similar to those determined by fast titration technique (table 4). One may deduce that there is a very good agreement between acid-base potentiometric curves and fast titration technique.

Table 4. Point of zero charge determined by Gran method and fast titration technique

Sample	PZC		pH in distilled water
	Gran Method	Fast titration technique	
It(Mo)	~ 8,2	~ 8,5	7,9
It(Ga)	~ 8,8	~ 9,2	9,5
It(Ha)	~ 8,3	~ 8,6	8,2

Simple model approach

From experimental data and the derived parameters of Gran plot, we suggest that the determination of the surface acidic constants can be determined, using the two sites two pKas model. One can notice that the one-site two pKas model can be chosen for the following reasons (see below).

In the two sites two pKas model, we assume the existence of two kinds of sites as shown in the following equations: The weak acidic sites which dissociates at pH between 4–8, having a concentrate of sites [Wa] and weak basic sites which dissociates at pH ~ 8.5 and having a concentration of sites [Wb] [24].



Where $\equiv\text{SOH}$ is amphoteric surface hydroxyl group for the surface protonation model.

Moreover, when the interface clay mineral / water has many different acidic sites, the successive dissociation can be defined by their dissociation coefficients α_1 and α_2 corresponding to pKa_1 and pKa_2 respectively:

$$\alpha_1 = [\equiv\text{S}_I\text{OH}_2^+] / [\text{Wa}] \quad \text{and} \quad \alpha_2 = [\equiv\text{S}_{II}\text{O}^-] - [\text{Wa}] / [\text{Wb}] + [\text{Wa}].$$

Where $[\text{Wa}] = (\text{V}_{\text{eq}} - \text{V}_{\text{e}_1}) \times \text{Cb} / (\text{V}_0 + \text{V}_{\text{e}_1})$ and $[\text{Wb}] = (\text{V}_{\text{e}_2} - \text{V}_{\text{eq}}) \times \text{Cb} / (\text{V}_0 + \text{V}_{\text{e}_2})$.

With V_{eq} is the equivalence point determined by the maximum of the differential curve dpH / dV . From (1), $1 / \text{Ka}_1 = [\equiv\text{S}_I\text{OH}_2^+] / [\equiv\text{S}_I\text{OH}] \times [\text{H}^+]$ or $\text{pH} = \text{pKa}_1 - \log [\equiv\text{S}_I\text{OH}_2^+] / [\equiv\text{S}_I\text{OH}]$. If $\alpha_1 = [\equiv\text{S}_I\text{OH}_2^+] / [\equiv\text{S}_I\text{OH}_2^+] + [\equiv\text{S}_I\text{OH}]$, then $\text{pH} = \text{pKa}_1 - \log \alpha_1 / 1 - \alpha_1$: Hasselbach equation By extrapolating the linear regression curve pH vs. $\log \alpha_1 / 1 - \alpha_1$ to zero, we can access to pKa_1 value. For determining $[\equiv\text{S}_I\text{OH}_2^+]$ concentration, we have used the charge balance equation and the Gran plot data:



With $[Na^+] = C_b \times V_b / V_0 + V_b$ and $[Cl^-] = C_b \times V_{e1} / V_0 + V_b$

$$[≡S_I OH_2^+] = [OH^-] - [H^+] + C_b (V_{e1} - V_b) / V_0 + V_b$$

$$[≡S_I OH_2^+] = TOT H + 10^{(pH - pK_w)} - 10^{-pH}$$

From (2); $\alpha_2 = [≡S_{II} O^-] - [Wa] / [Wb] + [Wa]$. Also, we have determined the $[≡S_{II} O^-]$ concentration from charge balance equation:

$$[≡S_{II} O^-] + [OH^-] + [Cl^-] = [H^+] + [Na^+] + [≡S_I OH_2^+]$$

After $pH > 8.5$, we can neglect the concentration of $[≡S_I OH_2^+]$

$$\text{Then, } [≡S_{II} O^-] = [H^+] - [OH^-] + C_b (V_b - V_{e1}) / V_0 + V_b$$

$$[≡S_{II} O^-] = 10^{-pH} - 10^{(pH - pK_w)} + C_b (V_b - V_{e1}) / V_0 + V_b$$

$$[≡S_{II} O^-] = -TOT H + 10^{-pH} - 10^{(pH - pK_w)}$$

For each illite sample and at a given ionic strength, the pK_{a1} and pK_{a2} values are determined by extrapolation pH vs. $\log \alpha / (1 - \alpha)$ to zero (fig.4) and are reported in Table 5.

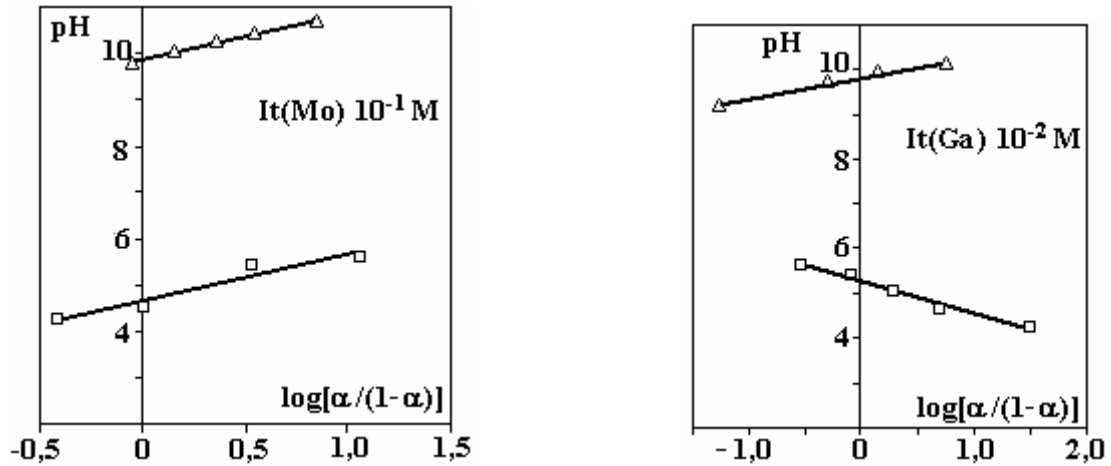


Fig.4. Plots of pH vs. $\log \alpha / (1 - \alpha)$ for It (Mo) and It (Ga) at $10^{-1}M$ and $10^{-2}M$ NaCl solutions at ambient temperature

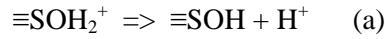
Table 5. pK_{a1} and pK_{a2} values determined from parameters of Gran plot method

Sample	It (Mo)			It (Ga)			It (Ha)		
	10^{-1}	10^{-2}	10^{-3}	10^{-1}	10^{-2}	10^{-3}	10^{-1}	10^{-2}	10^{-3}
I (M)	10^{-1}	10^{-2}	10^{-3}	10^{-1}	10^{-2}	10^{-3}	10^{-1}	10^{-2}	10^{-3}
pK_{a1}	4.72	4.87	4.5	4.78	5.27	4.56	5.15	5.52	5.44
pK_{a2}	9.78	9.95	10.17	10.29	9.82	10.03	10.42	10.34	10.24
Ds(sites/nm ²)	0.864	0.98	2.46	0.984	1.39	1.22	0.242	1.39	1.22

The overall surface ionization constants for protonation (AlOH groups) and deprotonation (SiOH groups) reactions of our illite edge sites are in the range ($4.5 < pK_{a1} < 5.52$ and $9.78 < pK_{a2} < 10.42$). It may be interesting to compare these values with those reported in the literature for other complex clay minerals. For example, Lu and Smith [14] listed $pK_{a1}^{int} = 4.77-5.115$ and $pK_{a2}^{int} = 7.63-7.56$ for glauconite without dissolution correct; Du [12], by using two sites-two pK_a model for illite from China found $pK_{a1}^{int} = 4.17-4.44$ and $pK_{a2}^{int} = 6.35-7.74$; Avena and De Pauli [29] listed for illite $pK_{a1}^{int} = -3.90$ and $pK_{a2}^{int} = -7.60$. Our pK_{a1} values are not significantly different from that reported in [10] but our pK_{a2} values seem to be much higher. The basic character of our complex clay minerals is likely the origin of the shifting of pK_{a2} values to

more basic region (see stability pH values in distilled water, table 4). This discrepancy might be due to the differences in the sources of the sample and /or in the experimental method, in agreement with [12].

On the other side, the one site two pKas model can also be used to describe our titration data since we assume that the illite surface is homogeneous and that two acidic reactions, one protonation and one deprotonation, analogous to that used in CCM model (see below), occur at the illite surface (as shown in equation a and b). It should be pointed out that [13], by using this surface protonation model on illite complex mineral listed two acid-base constants in the neutral and alkaline regions ($pK_{a1}^{int}=7.5$ and $pK_{a2}^{int}=11.7$).



Implementation of surface complexation models (SCMs)

The surface complexation models (SCM) were used to describe and interpret the titration behaviour of illite samples.

NEM model

The simplest SCM is the nonelectrostatic model (NEM), whose formulation is similar to the classical adsorption isotherms. It assumes an ideal behaviour of the surface species. Thus the electrical double layer is ignored and the electrostatic terms in the mass law expressions of surface reactions are excluded [33]. We must emphasize that the NEM has been applied in some studies of surface speciation of kaolinite [7], montmorillonitic clays [34] and on glauconite [14], respectively. It assumes that adsorption is a reversible process that can be described by a simple mass action law, where the activity coefficients of the surface species remain constant during the experiments. Our approach to describe the behavior of illitic aqueous suspension is similar to that used by Huertas et al. [7] on kaolinitic sample. We have assumed that one protonation / deprotonation reaction occurs at the illite surface and then the surface site density was estimated by fitting the sections of the potentiometric titration curves using least-square non-linear regression analysis.

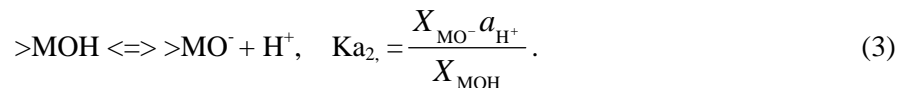
The protonation reaction of a surface site $>\text{MOH}$ is represented by the following reaction:



And the equilibrium constant, considered as the first equilibrium constant of the acid.

$$>\text{MOH}_2^+, \text{ is: } K_{a1} = \frac{X_{\text{MOH}} a_{\text{H}^+}}{X_{\text{MOH}_2^+}} \quad (2)$$

Where X_i denotes the molar fraction of the surface species and a_{H^+} is the aqueous proton activity. In the case of deprotonation of the $>\text{MOH}$ sites, the reaction is given by the following equation:



Where K_{a2app} is the second apparent equilibrium constant of $>\text{MOH}_2^+$.

The surface density of any complex, θ_i is defined as the number of complexes per unit of surface area ($\mu\text{mol}/\text{m}^2$ or sites/nm^2). If θ_M is the total surface density of $>M$ site, the surface density of any species can be obtained by:

$$\theta_i = \theta_M X_i \quad (\mu\text{mol}/\text{m}^2 \text{ or } \text{sites}/\text{nm}^2) \quad (4)$$

Where, θ_i is the surface density of any site. The mass balance for each kind of surface sites will be given by the sum of the positive, neutral and negative species.

$$\theta_M = \theta_{\text{MOH}_2^+} + \theta_{\text{MOH}} + \theta_{\text{MO}^-} = \theta_M (X_{\text{MOH}_2^+} + X_{\text{MOH}} + X_{\text{MO}^-}) \quad (5)$$

On the other hand, one may, as a first approximation assumes that the positive and negative complexes are the only charged species respectively below and above pH_{PZC} . Equation (5) may be simplified as follows:

$$\theta_M \approx \theta_{\text{MOH}_2^+} + \theta_{\text{MOH}} = \theta_M (X_{\text{MOH}_2^+} + X_{\text{MOH}}), \text{ pH} < \text{pH}_{\text{PZC}}, \quad (6)$$

$$\theta_M \approx \theta_{MOH} + \theta_{MO^-} = \theta_M (X_{MOH} + X_{MO^-}), \text{pH} > \text{pH}_{PZC}. \quad (7)$$

Rearranging the expression (2) and (3), the molar fractions of the charged sites can be obtained:

$$X_{MOH_2^+} = \frac{a_{H^+}}{(K_{a1} + a_{H^+})} \quad (8) \quad \text{and} \quad X_{MO^-} = \frac{K_{a2}}{(K_{a2} + a_{H^+})}. \quad (8)$$

We have analyzed distinctively each potentiometric titration curve at a given ionic strength in order to determine surface site density. Then, the apparent equilibrium constants ionization (K_{a1app} and K_{a2app}) for each reaction described above, were calculated. From these curves, one can assume that going from acidic to basic conditions, i.e, from positive to negative surface charges; the clay mineral samples of our study undergo two successive reactions. The weak acidic sites (θ_1) release the adsorbed proton at approximately 4–8. At pH PZNPC, the sites (θ_2) start to deprotonate forming negative complexes up to pH ~ 8.5. The main results concerning surface site densities and calculated apparent equilibrium constants for the three-illitic clay minerals are given in Table 6.

Table 6. Surface site densities, θ ($\mu\text{mol}/\text{m}^2$) and calculated equilibrium constants for protonation and deprotonation surface reactions for It (Mo), It (Ga) and It (Ha), respectively. (Subscripts 1 corresponds to protonation and subscript 2 to deprotonation reaction, equilibrium constants are expressed as the surface dissociation constant of the acid $>MOH_2^+$, using pK scale.

It(Mo)							
I(M)	θ_1 ($\mu\text{mol}/\text{m}^2$)	pKa ₁	θ_2 ($\mu\text{mol}/\text{m}^2$)	pKa ₂	θ total ($\mu\text{mol}/\text{m}^2$)	PZC=1/2 (pKa ₁ +pKa ₂)	PZC observed
It (Mo)							
0.1	0.89	6.73	0.64	10.32	1.53	8.5	8.5
0.01	0.93	6.82	0.75	9.99	1.67	8.4	
0.001	1.02	6.32	0.68	10.62	1.7	8.46	
It (Ga)							
0.1	6.6	6.43	5.7	10.01	12.3	8.22	9.3
0.01	4.3	5.88	7.08	9.98	11.35	7.93	
0.001	7.2	6.91	3.05	10.67	10.25	8.8	
It (Ha)							
0.1	2.34	6.20	3.46	9.66	5.8	7.93	8.6
0.01	2.81	6.24	2.65	9.71	5.46	7.97	
0.001	3.98	6.59	4.78	9.84	8.76	8.21	

Constant capacitance model

The constant capacitance model was also used by some authors on complex clay minerals like illite [12], kaolinite [7] and glauconite to model titration data and to compare NEM calculations with CCM simulations [14]. The model assumes that the EDL at the mineral / water interface behaves as a flat capacitor, whose capacitance C is the proportionality constant (F/m^2) between the charge σ_H (Coulombs / m^2) and the surface potential ψ (volt):

$$\sigma_H = C \psi$$

$$K_{a1}^{int} = K_{a1} e^{(-F \psi)/RT}$$

$$K_{a2}^{int} = K_{a2} e^{(-F \psi)/RT}$$

Where F is the Faraday constant (coulombs/ mol), R and T are the gas constant (cal / K° mol) and temperature (K°) respectively.

The intrinsic constants for the surface groups were calculated by extrapolating the linear regression curve pKa vs. σ_H to zero surface charge (fig.5). The total site density was estimated by extrapolating the

sections of the titration curves to low or high pH values. The intrinsic equilibrium constants of illite samples were computed from potentiometric titration data by employing polynomial of the fourth degree equation (table 7).

Concerning determination of capacity values, no methods exist for independently measuring electrical double layer capacitance parameters for complex clay water systems. Some researchers have suggested that values for C can be obtained from titration data [1, 5]. Since no methods are currently available for measuring interfacial capacitance, we have also used extrapolation method to determinate capacity values.

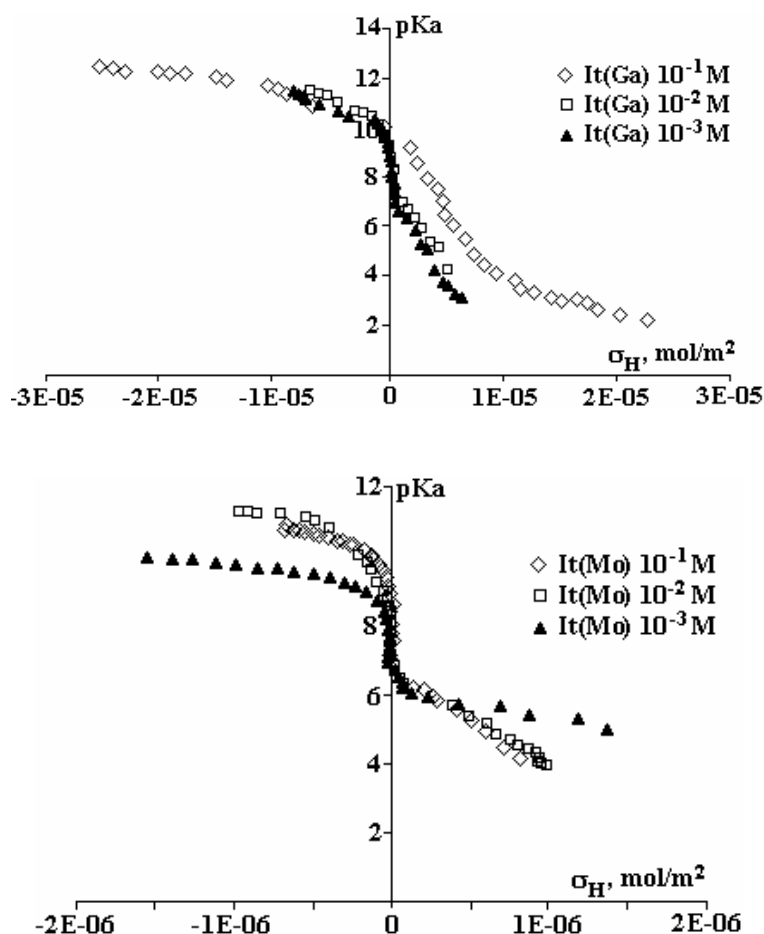


Fig.5. plots of pK_a vs. σ_H for It (Ga) and It (Ha), respectively, at different ionic strength and ambient temperature

Table 7. Surface site densities θ ($\mu\text{mol}/\text{m}^2$) and intrinsic equilibrium constants for protonation and deprotonation surface reactions calculated according to the CCM, for It (Mo), It (Ga) and It (Ha), respectively. The capacitance (C) is in F/m^2

It (Mo)

I(M)	$\theta_1(\mu\text{mol}/\text{m}^2)$	pK_{a1}^{int}	$C(\text{F}/\text{m}^2)$	$\theta_2(\mu\text{mol}/\text{m}^2)$	pK_{a2}^{int}	$C(\text{F}/\text{m}^2)$	$\theta_{\text{total}}(\mu\text{mol}/\text{m}^2)$
0,1	1.23	6,69	0,54	1.21	9.96	1,3	2.44
0,01	1.2	6.56	0.53	1.14	9.71	2.71	2.34
0,001	1.56	6	2.086	1.63	9.25	3.76	3.19

It (Ga)

I(M)	$\theta_1(\mu\text{mol}/\text{m}^2)$	pK_{a1}^{int}	$C(\text{F}/\text{m}^2)$	$\theta_2(\mu\text{mol}/\text{m}^2)$	pK_{a2}^{int}	$C(\text{F}/\text{m}^2)$	$\theta_{\text{total}}(\mu\text{mol}/\text{m}^2)$
0,1	10.6	5.78	8.35	8.09	10.37	11.76	18.69
0,01	9.74	6.7	5.32	2.66	10.43	14.98	12.4
0,001	9.32	6.46	4.9	4.09	10.26	13.32	13.41

It(Ha)

I(M)	$\theta_1(\mu\text{mol}/\text{m}^2)$	$\text{pK}_{a1}^{\text{int}}$	$C(\text{F}/\text{m}^2)$	$\theta_2(\mu\text{mol}/\text{m}^2)$	$\text{pK}_{a2}^{\text{int}}$	$C(\text{F}/\text{m}^2)$	$\theta_{\text{total}}(\mu\text{mol}/\text{m}^2)$
0,1	3.67	6.11	3.15	4.53	9.33	3.59	8.2
0,01	3.31	7.6	2.53	3.45	10.04	7.32	6.76
0,001	5.08	7.06	2.33	7.2	9.95	8.97	12.28

The $\text{pK}_{a1}^{\text{int}}$ intrinsic values are in the range 5.78-7.6 and $\text{pK}_{a2}^{\text{int}}$ are in the range 9.25-10.43, respectively. Comparatively to surface equilibrium constants determined by NEM, we conclude that the inclusion of electrostatic term, does not improve much the description of the adsorption reactions, in agreement with [7, 14, 17].

Triple Layer Model (TLM)

The intrinsic acidity constants $\text{pK}_{a1}^{\text{int}}$ and $\text{pK}_{a2}^{\text{int}}$ of the illite samples were also computed from the potentiometric titration data by employing polynomial of the fourth degree equation by using the triple layer model (TLM) described in the literature [1, 35] in the forms:

$$\text{pK}_{a1}^{\text{int}} = \text{pH} + \log [\alpha^+ / 1 - \alpha^+] + [F\psi_0 / 2.3RT]$$

$$\text{pK}_{a2}^{\text{int}} = \text{pH} - \log [\alpha^- / 1 - \alpha^-] + [F\psi_0 / 2.3RT],$$

where $\alpha^+(\sigma_{\text{H}^+}/\text{Ds})$ and $\alpha^-(\sigma_{\text{H}^-}/\text{Ds})$, σ_{H^+} and σ_{H^-} represent the surface charge densities ($\mu\text{mol}/\text{m}^2$) below and above the PZC of the sample, respectively, Ds is the total density of sites determined by extrapolation method, F is the Faraday constant (Cmol^{-1}), ψ_0 is the potential mean in the plane of the surface and T is the absolute temperature (K).

The plots of $\text{pH} + \log [\alpha^+ / 1 - \alpha^+]$ versus α^+ and $\text{pH} - \log [\alpha^- / 1 - \alpha^-]$ versus α^- were extrapolated to $\alpha^\pm = 0$ using MS EXCEL 5 (fig.6). The values of intrinsic acidity constants, thus obtained are listed in table 8, which are comparable to the values reported for other complex clay minerals [14].

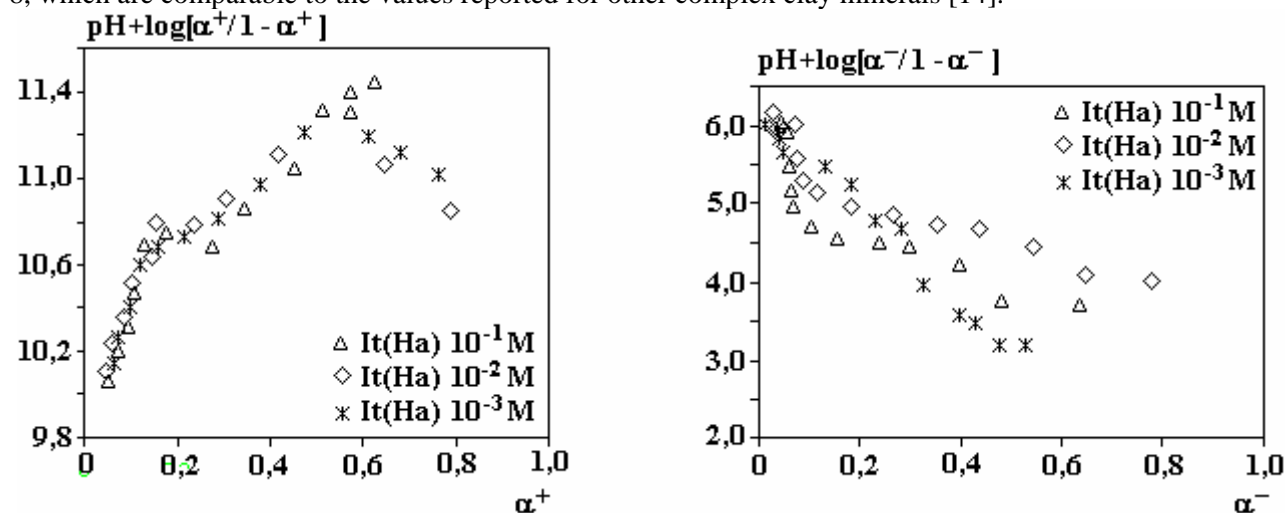


Fig.6. plots of $\text{pH} + \log [\alpha^+ / 1 - \alpha^+]$ versus α^+ and $\text{pH} - \log [\alpha^- / 1 - \alpha^-]$ versus α^- , for It (Ha) in different NaCl solutions, at ambient temperature

Table 8. Surface ionization constants for the illite samples at different NaCl solutions

I	It (Mo)			It (Ga)			It (Ha)		
	10^{-1}M	10^{-2}M	10^{-3}M	10^{-1}M	10^{-2}M	10^{-3}M	10^{-1}M	10^{-2}M	10^{-3}M
$\text{pK}_{a1}^{\text{int}}$	4.56	4.74	4.63	5.8	6	5.82	6.15	5.57	6.67
$\text{pK}_{a2}^{\text{int}}$	10.31	10.59	10.46	10.82	10.84	10.80	10.68	10.64	10.01

The TLM model gives $\text{pK}_{a1}^{\text{int}}$ values in the range 4.56-6.67 whereas for $\text{pK}_{a2}^{\text{int}}$ in the range 10.01-10.84. In general, as is seen the NEM, CCM and the TLM models have given approximately the same surface ionization constants. Comparatively to pKas values determined from our model approach, we can observe that the SCMs described above give differences in pKas values, i.e, depending on the methodology chosen, small differences in values of model parameters, for a given SCM and titration data, are obtained. We think that the major reason for the differences in the observed surface constants ionization, is mainly due to the manner of which extrapolation method was made, involving in some cases to large pKas values. This remark is supported by Hayes et al. [1], who reported that the extrapolation procedures cannot be used conveniently to produce a unique set of surface constants since there are no objective methods to determine

which range of titration data should be used in the extrapolations. Furthermore, some authors reported that the accuracy of determination of surface ionisation constants using potentiometric titration data is rather poor because extrapolated smooth curves tend asymptotically to the vertical lines (curves σH vs. pH) [5]. Thus, any inexactitude in tracing of the curves, can give large differences in surface ionization constant values. We think also that using proton binding affinity distribution method [36] in order to detect new acidic centers that have not been identified by regression method, should complete this study. Although difficulties of extrapolation technique exist, it remains one of the most practical methods that can access to pKas values.

Conclusion

Our systematic study of the acid-base reactions at the illite water interface indicates that the surface charge of illite in inert electrolyte solutions involves two kind of sites: weak acidic sites at pH 4–8 groups and weak basic sites at pH ~ 8.5 of the crystal edges. The protonation (AlOH groups) and deprotonation (SiOH groups) at these sites occur at different pH ranges and thus each site is responsible for the surface charge under a given pH condition. The overall pH_{ZPC} (~8.5–9.2) determined by Gran method or fast titration technique, is the result of the balance between positive and negative charges irrespective of the nature of the sites. From parameters derived of Gran plot method, surface ionisation constants were determined according an algorithm of the two sites two pKas model. For illite samples, the pK_{a1} values are in the range 4.5–5.52 and pK_{a2} values are 9.78–10.42. SCMs (CCM, TLM) were implemented to our titration data in order to confirm these surface constants ionisation. It reveals that according the methodology chosen some differences in pKas values appear, due very likely to errors made in extrapolation procedure. However, the inconvenience of this regression method, we can take it into consideration as a solution in determining acid-base characteristics of complex illitic samples.

REFERENCES

- [1]. Hayes K.F., Redden G., Ela W. and Leckie J.O. Surface complexation models: An evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *J. Colloid Interface Sci.*, 1991, 142.
- [2]. Davis, J.A. and Leckie, J.O. Surface ionization and complexation at the oxide/water interface. *Journal of Colloid and Interface Science*, 1978, 67, No1, 15.
- [3]. Sverjensky D. Prediction of surface charge on oxides in salt solutions: Revisions for 1:1 (M+L-) electrolytes. *Geochim. Cosmochim. Acta*, 2005, 69, 225.
- [4]. Mustapha S., Dilara B., Nargis K., Naeem A., Shahida P. Surface properties of the mixed oxides of iron and silica. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2002, 205 273–282.
- [5]. Sprycha R.. Electrical double layer at alumina/Electrolyte interface. *J. Colloid Interface Sci.*, 1989, 127, 1.
- [6]. Schindler, P.W., Stumm, W. *Aquatic surface chemistry*; Stumm, W., Ed. Wiley: New York 1987.
- [7]. Huertas. Javier F, Lei. Chou and Roland wollast. mechanism of kaolinite dissolution at room temperature and pressure: Part 1. Surface speciation. *Geochim. Cosmochim. Acta*. 1998, 62, 417–434.
- [8]. Stadler M. and Schindler P.W. Modeling of H^+ and Cu^{++} adsorption on calcium-montmorillonite. *Clays Clay Miner.* 1993, 41, 288–296.
- [9]. Stadler M. and schindler P.W. The effect of dissolved ligands on the sorption of Cu(II) by Ca-montmorillonite. *Clays Clay Miner.* 1994, 42, 148–160.
- [10]. Nagy N.M., Konya J. Acid-base properties of bentonite rocks with different origins. *Journal of Colloid and Interface Science*, 2006, 295 173–180.
- [11]. Du Q., Sun Z., W. Forsling and H. Tang. Adsorption of copper at aqueous illite surfaces. *Journal of Colloid and Interface Science*, 1997a, 187, 232–242.
- [12]. Du Q., Sun Z., Willis Forsling, And Hongxiao Tang. Acid-base properties of aqueous illite surface. *Journal of Colloid and Interface Science*. 1997b, 187, 221–231.
- [13]. Liu W., Sun Z., Forsling W., Du Q. and Tang H., A comparative study of surface acid-base characteristics of natural illites from different origins. *Journal of Colloid and Interface Science*, 1999, 219, 48–61.
- [14]. Lu W. and Smith E.H., Modeling potentiometric behaviour of glauconite. *Geochim. Cosmochim. Acta*. 1996, 60, 3363–3373.
- [15]. Motta MM, Miranda CF. Molybdate adsorption on kaolinite, montmorillonite, and illite: constant capacitance modelling. *Soil Sci Soc Am J*. 1989, 53, 380–385.
- [16]. Wieland E. and Stumm W., Dissolution kinetics of kaolinite in acidic aqueous solution at 25°C. *Geochim. Cosmochim. Acta*. 1992, 56, 3339–3355.

- [17]. *Majone M., Papini M. P., and Rolle E.*, Modeling lead adsorption on clays by models with and without electrostatic term. *J. Colloid Interface Sci.*, 1996, 183, 412–425.
- [18]. *Katari K., Tauxe L.* Effect of pH and salinity on the intensity of magnetisation in redeposited sediments. *Earth and Planetary Science Letters*, 2000, 181 489–496.
- [19]. *Keren and Sparks D.L.* The role of edge surfaces in flocculation of 2:1 clay minerals *R. Soil.Sci.Soc.Am.J.*, 1995, 59 pp. 430–435.
- [20]. Van Olphen an Introduction to clay Colloid Chemistry, 1963, interscience publishers, New York.
- [21]. *Sylvie Boissay.* Comparaison des méthodes de détermination des points de charge nulle. Thesis. Département Minéralurgie du Bureau de Recherche Géologique et Minières à Orléans, France 1984.
- [22]. *Kriaa, A., Hamdi, N. and Srasra, E.* Determination of point of zero charge of Tunisian kaolinite by potentiometric titration and mass titration. *J. Chin. Chem. Soc.*, 2008, Vol.55, No 1, 35–62.
- [23]. *Chorover, J. Sposito G.* Surface charge characteristics of kaolinitic tropical soils. *Geochim. Cosmochim. Acta*, 1995, 59, 875–884.
- [24]. *Latitia Citeau,* " Etude des colloïdes naturels présents dans les eaux gravitaires de sol contaminés: relation entre nature des colloïdes et réactivés vis à vis des métaux (Zn, Cd, Pb, Cu)" Thesis 18 may 2004, Institut National d' Agronomie Paris-Grignon.
- [25]. *James, R.O. and Parks, G.A.* in "surface and colloids science" (E. Matijevic, Ed.), 1982, Vol 12, pp.119. Plenum Press, New York.
- [26]. *James R.O. Davis J.A. and Leckie J.O.*, Computer simulation of the conductometric and potentiometric titrations of the surface groups on ionizable latexes, *J. Colloid Interface Sci.*, 1978, 65. 331.
- [27]. *Schroth B.L. and Sposito G.* Surface charge properties of kaolinite. *Clays Clay Miner.*, 1997, 45, 85.
- [28]. *Myriam Duc, Fabien Gaboriaud, Fabien Thomas.* Sensitivity of the acid–base properties of clays to the methods of preparation and measurement 2: Evidence from continuous potentiometric titrations. *Journal of Colloid and Interface Science*. 2005, 289, 148–156.
- [29]. *Avena M.J., de Pauli C.P.* Proton adsorption and electrokinetics of an Argentinean montmorillonite. *J. Colloid Interface Sci.* 1998, 202, pp.195.
- [30]. *Tombacz E. and Szekeres M.* Colloidal behaviour of aqueous montmorillonite suspensions: the specific role of pH in the presence of indifferent electrolytes. *Applied Clay Science*, 2004, 27, 75–94.
- [31]. *Tombacz E., Szekeres M. and Klumpp E.* Interfacial acid-base reactions of aluminum oxides dispersed in aqueous electrolyte solutions.2 Calorimetric study on ionization of surface sites. *Langmuir*, 2001,17, 1420–1425.
- [32]. *Hendershot, W.H., and Lavkulich, L.M.* Effect of sesquioxide coatings on surface charge of standard mineral and soil samples. *Soil Science Society of America Journal*, 1983, 47, 1252.
- [33]. *Davis J.A. and Kent D.B.* Surface complexation modelling in aqueous geochemistry. In *Mineral–water interface geochemistry* (ed.M.F. Hochella Jr. and A.F. White). Mineral .Soc. America (1990) pp.177–260.
- [34]. *Kriaa, A., Hamdi, N. and Srasra* Acid base characteristics of montmorillonite and montmorillonitic clays. *Russian journal of electrochemistry*, 2007, Vol. 43, No. 2, pp. 167–177.
- [35]. *Davis J.A., James R.O. and Leckie J.O.* Surface ionization and complexation at the oxide/water interface: I. Computation of electrical double layer properties in simple electrolytes *J. Colloid Interface Sci.* 1977, 63. 480
- [36]. *Janek M. and Lagaly G.* Proton saturation and rheological properties of smectite dispersions. *Applied Clay Science*, 2001, 19, 121–130.

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Summary

Potentiometric titration behaviour of complex illitic clay minerals, provided from different origins (two Tunisian illite samples and an American illite sample), were investigated and interpreted according to surface complexation theory. In the present investigation, the focus was on the surface charge characteristics. Proton surface charge can be calculated by subtracting supernatant titration curves from those of illite suspension at ambient temperature and aerated medium. The points of zero charge (PZC), determined by Gran plot method and fast titration technique, were in the range ~8.5-9.2. Our potentiometric titration curves were modelled using derived parameters of Gran method. The surface ionization constants were determined by implementing the theory of surface complexation models (SCMs): the NEM, the constant capacitance model (CCM) and the triple layer model (TLM). The pK_as values determined from derived parameters of Gran plot data were in the range (pK_{a1}= 4.5-5.52 and pK_{a2} =9.78-10.4) and are compared to those obtained by SCMs.