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Determination Of Point Of Zero Charge Of Tunisian Kaolinites By Potentiometric And Mass Titration Methods

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ABSTRACT

This paper deals with determining points of zero charge of natural and Na^+- saturated mineral kaolinites using two methods: (1) acid-base potentiometric titration (2) mass titration. The two methods involved points of zero charge approximately similar for the two kaolinites between 6.5-7.8, comparable to those reported previously and were in the range expected for these clay minerals. The comparison of potentiometric surface titration curves obtained at 25°C and those published in the literature reveals significant discrepancies both in the shape and in the pH of PZNPCs values.

KEYWORDS

Kaolinite; Mass titration;
Potentiometric titration;
Point of zero net proton charge;
Proton surface charge

INTRODUCTION

Many physical and chemical properties of soils are directly or indirectly controlled by nature of surface charge as well as their variation with soil solution characteristics[1]. In addition, the dispersion/ flocculation behaviour of soils colloids is closely regulated by the charge characteristic of these colloids[2]. Therefore, knowledge of electrical and adsorptive properties of the clay-water interface are very important in soil chemistry and in several processes. The interaction of the clay surface with ions has great influence on soil fertility. In these systems, according to some authors[3], the surface charge depends on activities of potential determining ions (H^+ and OH^-) and electrolyte concentrations (ionic strength). Depending on mineral pH, these surfaces can bear net negative, or positive or no charge. Some authors[3-4] reported that the pH value where the net total particle charge is zero is called the point of zero charge (P.Z.C) which is one of the parameters or characteristics to describe variable-charge surfaces. It is evident when the pH of soils is above its P.Z.C, the soil surface will have a net negative charge and tends to exchange cations (CEC-exchange of one positive ion by another). In the other hands, when the pH of soils is below its P.Z.C, the soil surface have a positive charge and tends to exchange anions (AEC-exchange of one negative ion for another). We must emphasis that the determina tion of P.Z.C from experimental data has been the subject of many studies on clay mineral as well as on oxide minerals[1-5]. The knowledge of this important parameter on the basis of potentiometric titration analysis or by mass titration concept, leads to acid-base properties of clay/water suspensions. This can be realized since we refer to surface complexation models taking into account the total surface site concentration of the mineral. According to[4]; three parameters contributed on surface charge of clay minerals: σ_O, the permanent structural charge density created by isomorphic substitutions in a mineral structure (for the kaolinite $\sigma_O < 0$). σ_H, the net proton surface charge density created only by proton adsorption and desorption reactions at the interface clay-aqueous solution. This parameter has been determined by ion adsorption measurements and Δq, the net adsorbed ion surface charge density from background electrolyte, exclusive of that contributed by adsorbed protons and hydroxide ions. These components are relied by the law of surface charge balance: $\sigma_O + \sigma_H + \Delta q = 0$

As we can expected, the sign of σ_H varies with aqueous solution pH, taking on zero at the P.Z.N.P.C and becoming negative at higher pH values. In our study, we have only determined by potentiometric titration the net surface charge σ_H (mol/m^2).

Many methods in the literature have been carried out for determination point of zero charge in soils and clay-minerals[1-5]. The authors have generally used potentiometric titrations or ion adsorption measure ments which evaluates changes in surface potential with changes in the activities of H^+ and OH^- to determinate point of zero net proton charge P.Z.N.P.C or point of zero salt effect (P.Z.SE.)[3]. These authors [2-4,6-9] have also used the ion adsorption measurements to quantify point of zero net charge (P.Z.N.C). The comparison of P.Z.S.E or P.Z.N.P.C determined by potentiometric titration to ion adsorption techniques (PZNC) was studied by some authors[8-10] to establish the point of zero charge in soils and pure minerals. The results are not homogenous. Some authors[8] found not good correlation between the two measurements for the kaolinite. This has been attributed to the presence of permanent negative-charge colloids in the soil system. In the other hand, other authors[10] found good agreement between P.Z.S.E. and P.Z.N.P.C. explaining that in this condition, the amount of adsorbed H^+ or OH^- on exchange sites equals that of the index cation or anion, respectively, suggesting that hydration energies of competing ions are similar.

We must emphasis that many studies were carried out about surface charge behaviour of specimen kaolinite as already mentioned above. The main results, summarized in TABLE 1, showed a significant variability in published experimental study

TABLE 1: Published experimental studies of points of zero charge reported for kaolinite obtained by surface titration.

	Value	Reference
Point of zero net proton charge (PZNPC) or (PZSE)	2.8	C.Appel et al., (2003)[3]
	3	Braggs et al., (1994)[12]
	< 4	Schindler et al., (1987)[13]
	4.5	Motta and Miranda, (1989)[14]
	4.5	Xie and Walther, (1992)[15]
	4.66	Sverjensky, (1994)[16]
	7.5	Wieland and Stumm, (1992)[17]
	5	Schroth and Sposito, (1997)[4]
	5.5	Huertas et al., (1998)[18]
	4.5	Brady et al., (1996)[19]
Point of zero net charge (PZNC)	4.8	Ferris and Jepson, (1975)[20]
	4	Zhou and Gunter, (1992)[21]
Isoelectric point (i.e.p)	5	Ferris and Jepson, (1975)[20]
	3.8	C.Appel et al., (2003)[3]

of the points of zero charge. The values vary from 3 to above 7[4] explained that the disagreement can be attributed to differences in sample preparation and to the use of different models to interpret data. The data in this table illustrate the wide range of pH values in the published literature.

In this paper, in order to estimate PZNPC, we have used, in addition to traditional acid/base titration method, the mass titration method described by some authors[6-11] by measuring a limiting pH value with increasing mass fractions of clay mineral. The suspension pH value often reaches a steady value after addition of amount clay mineral in aqueous solution.

The present study aimed to evaluate charge characteristics with the purpose of determination PZNPCs values of two types of Tunisian kaolinite specimen: pure natural white Kaolinite from Kasserine (Ka-Kass) and brown kaolinite from Tabarka (ka-Tab). The latest has a small quantity of illite in mixture with kaolinite.

MATERIALS AND METHODS

Clays

Samples of two specimen kaolinites used in this study provided from Tabarka (Ka-Tab) and Kasserine (Ka-Kass) situated at the north west of Tunisia. It is important to notice that the later kaolinite is on natural pure state with no impurities. In the other hands, for Ka-Tab sample, The particles with diameter < 45 µm were obtained by sedimentation and saturated with Na^+ by 7 washing cycles (successive centrifugal treatments) with 1M NaCl. After each centrifugation of the suspension, the supernatant was discarded and replaced with fresh solution of NaCl. After that, the samples were dialysed through a specific membrane until free from Cl^-, dried at 80°C and finally stored at room temperature.

X-ray diffraction (XRD)

X-ray diffractograms were recorded using a "PANalytical X'Pert HighScore Plus" diffractometer with the radiation $K\alpha_1$ of copper. Two types of diffractograms are studied: diffractograms with disorientated powder where all the lines (h,k,l) appear, and diffractograms of oriented plate obtained by sedimentation. This makes it possible to follow the periodicity of the stratification of the layers, with the reflection (d_{001}) on which the identification is based.

Infrared spectroscopy (IRS)

The IR spectra were carried out using a Nicolet spectrophotometer, model 560 spectrophotometer. The samples are used in the pastille form containing 2mg clay mixed with 200 mg of KBr.

Chemical analysis

The clay samples were attacked by a mixture of three acids (HCl, H_2SO_4, HNO_3). All the elements pass in solution, except the silica (SiO_2) which is determined by gravimetry. The other elements, such as Al, Fe, Mg, Ca, Na and K are assayed by atomic absorption spectrophotometer (AAS).

Cation exchange capacities(CEC) and specific surface areas(SSA)

CEC was determined by the method of copper ethylendiamine $(EDA)_2 CuCl_2$ complex[22], specific surface areas BET was determined by nitrogen gas adsorption at 77K, using a 'Quantachrom-Autosorb1' sorptiometer.

Experimental materials of the potentiometric titration

All experimental curves used in this study, are performed with a micro burette 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.

CHARACTERIZATION OF CLAYS

X-ray diffraction

Figure 1 shows diffractograms of crude and saturated Na^+-Ka- Tab. One can observe the peak reflectance of kaolinite (d_{001} and d_{002}-spacing) reflections at 7.16 Å and 3.57Å. This peak disappear with heating at 500°C. Also, it can be seen that ethylene-

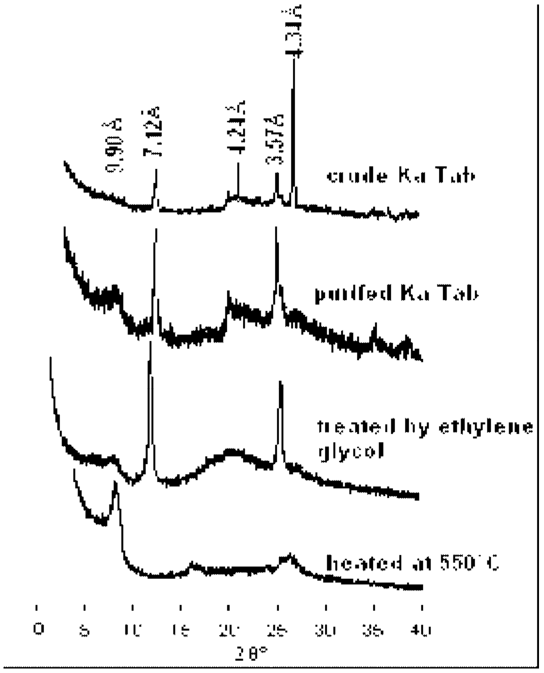

Figure 1: Diffractograms RX of crude and purified Ka-Tab.

glycol does not penetrate between the layers. We can observe clearly the presence of small quantity of illite in the kaolinite sample {d_{001}-spacing at 9.90 Å and d_{002} at 4.24 Å}. The peak at 4.34 Å can be attributed to quartz as impurity in the sample. Figure 2 shows a typical X-ray diffraction pattern of Kass kaolinite.

Analyse by Infra-red spectra

Figure 3 shows infrared spectrum of crude, saturated Na^+-Ka-tab, and pure Ka-Kass. The main bonds are indicated on the spectrum. One can observe a typical structure of Kaolinite:

- OH stretching, hydroxyl sheet at (3695, 3670, 3655 cm^{-1}).
- SiO stretching at (1110cm^{-1}, 1035 cm^{-1}, and 1030 cm^{-1}).
- OH deformation at 935 and 912 cm^{-1}.

Mixed SiO deformations and octahedral sheet vibrations at (650, 540, 470 and 430 cm^{-1})

TABLE 2: C.E.C and S.S.A for the two kaolinites

Samples	CEC (meq /100g)	SSA (m^2/g)
Crude ka-Tab.	19.6	35.54
Saturated Na-Ka-Tab.	24.83	73.13
Pure Ka-Kass	25.33	24.57

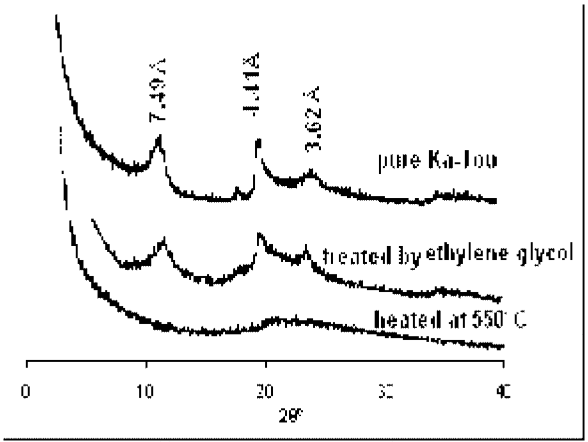

Figure 2: Diffractograms RX of pure Ka-Kass.

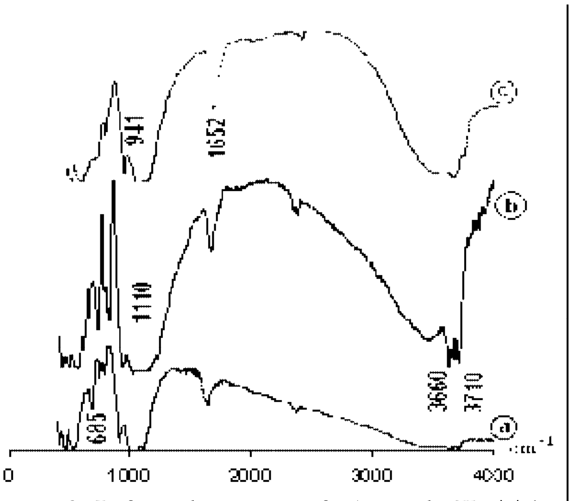

Figure 3: Infrared spectra of: a) crude Ka-Tab, b) purified Na- Ka-Tab, c) pure Ka-Kass.

The chemical composition Cation Exchange Capacity (CEC) and the Specific surface area (SSA) are reported in TABLE 2 and 3.

TABLE 3: Centesimal composition of the elements in the samples

%	Crude Ka-Tab	Saturated Na-Ka-Tab	Pure Ka-Kass
SiO_2	53.24	46.28	39.40
MgO	0.07	0.21	0.27
Na_2O	1.38	2.01	0,52
Al_2O_3	27.30	29.48	29.91
Fe_2O_3	1.90	2.23	0.19
CaO	0.30	0.79	0.65
K_2O	1.92	4.76	0.1
Ignition loss	13.89	14.24	28.96

RESULT AND DISCUSSION

The acid-base potentiometric titration curves at different salt concentrations, were used to measure the proton adsorption or proton charge. All experiments for charge determination were carried out under ambient laboratory conditions (25 ± 5°C). The experimental method employed was similar to that used with 'alumine, hematite and rutile'[23].

The NaCl electrolyte concentration was adjusted to a 0.1, 0.01 and 0.001 mol/l. For all experiments potentiometric titration curves, the aqueous suspension (40 ml) containing the immersed mineral (0.2g) was equilibrated for about 15 nm in order to reach an equilibrium pH value. At the beginning of the titration, when a small amount of HCl was added to protonate a significant part of the surface sites, the pH stabilized quickly (ΔpH < 0,03 unity pH) and was red within 30s. 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 2.5-3. All experiments were stirred magnetically in aerated medium under ambient laboratory conditions (the temperature = 25 ± 5 °C).

The proton adsorption or proton surface charge density σ_H(mol/m^2), 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[4]:

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

Where V is the volume of electrolyte solution equilibrated with kaolinite (40 x 10^{-3} l).

$[H^+]$ 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 (0.2g).

S is the specific surface area (m^2/g).

Potentiometric titration curves

It is important first to note that fast equilibration was observed for the successive increments of HCl. This is a useful observation because it allows one to perform adsorption experiments in a relatively short time making negligible the effect of other processes such as dissolution that could affect proton adsorption data especially at low pH[4]. The rapid pH stability indicating that the fast equilibration observed, can be interpreted as a result of reactions (adsorption or desorption) between proton ions and hydroxylated surface sites which are known to be very fast reactions. Avena et al.[6], therein/commented that data reported by others authors indicated that proton adsorption reactions on FeOOH and silica-alumina were in the order of milliseconds. Our potentiometric titration experiments are extended to acidic region (pH 2-3). Therefore, because of the short equilibration time (15 mn), the release of Si and Al caused by kaolinite dissolution (generally at pH 3-4) mentioned by[4] into the aqueous solution was not significant and assumed negligible during the titration experiments. This observation is supported by some authors[24], 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.

Otherwise, and as mentioned by the[4], we must include a correction factor for the value of σ_H taking into account the protons that would be consumed in Al release and generated by Al hydrolysis at pH = 6.

Figures 4, 5, 6 shows acid-base potentiometric titration curves of the purified, crude Ka-Tab and pure Ka-Kass dispersed in different NaCl concentrations. Equilibrium data were used to plot σ_H vs pH curves. We can notice first that the data obtained with HCl superimposed well with those obtained with NaOH indicating good reversibility of the H^+ adsorption process. The behaviour of our curves are almost the same in the considered pH range and resembled to those published in the literature with the difference that they had a weak slope at neutral pH. (curves almost super-imposed at pH between 5-8). As it can be seen the curves had a common intersection point, which is the PZNPC. Their values for the two Kaolinites are reported in TABLE 4. Therefore, our results show that purified saturated Na^+-ka-Tab has a PZNPC value lower (6.9) than

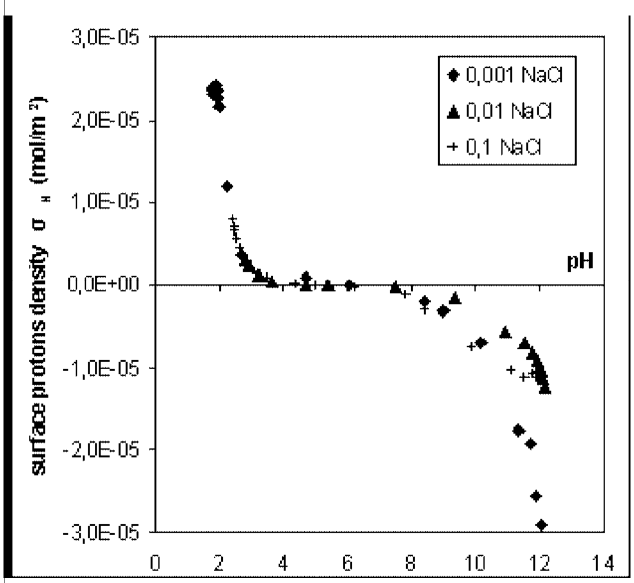

Figure 4: Potentiometric titration curves of purified Ka-Tab as a function of pH at different ionic strengths

TABLE 4: PZNPCs determined by potentiometric titration curves of two kaolinites

Samples	PZNPCs
Crude Ka-Tab	6.5
Purified Na^+-Ka-Tab	6.9-7.1
Pure Ka-Kass	7.5

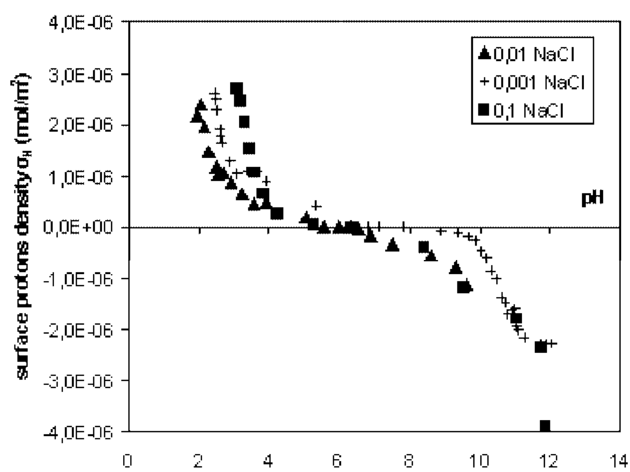

Figure 5: Potentiometric titration curves of crude Ka-Tab as a function of pH at different ionic strengths

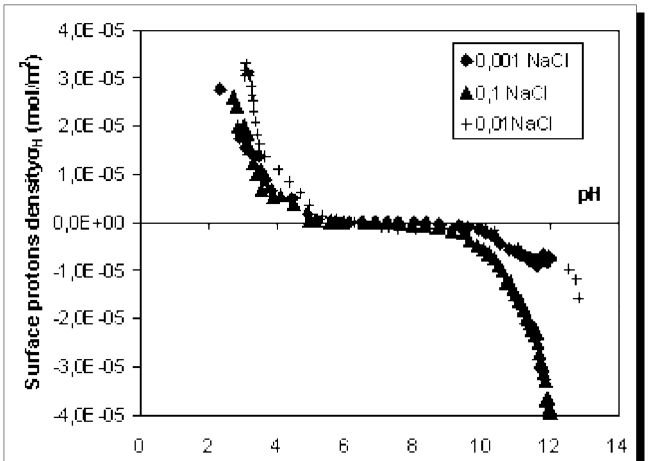

Figure 6: Potentiometric titration curves of pure Ka-Kass as a function of pH at different ionic strengths

pure ka-Kass (7.5). This is likely due to combined effect of cation exchangeable and to illite as associate to kaolinite that would decrease the PZNPC. Since some authors[1] found that the illite had a PZNPC lower than kaolinite (for kaolinite the PZC=3.7, whereas illite PZC= 2.5), we suggest that presence of amount illite mixed with kaolinite structure had a depressing effect on PZNPC of kaolinite samples as indicated in TABLE 4. Despite the low C.E.C values of the two kaolinites samples (TABLE 2), comparatively to other known swelling minerals (smectite), we suggest from our data that cation exchange (H^+-Na^+) reactions at the surface should be take into account especially at pH range 5-8 where a very weak slope had been observed in the data σ_H vs. pH. This is could be due, since we know that kaolinite-solutions systems contain three kinds of surfaces (gibbsite surface, siloxane surface and edge surface), either to edge-to face interactions between positively charged edges and negatively charged faces or H^+ adsorption exchanging some Na^+ ions in the faces that would slow the protonation of hydroxy lated sites at the edges with the consequent decreasing the protonation-deprotonation data between pH 5-8[9] commented that some authors, for the study of kaolinite, in addition to amphoteric surface hydroxyl group, ≡SOH, postulated a second functional group, ≡XH, which is weakly acidic and can undergo ion exchange with cations from the background electrolyte.

Mass titration curves

According to methods described in the literature[6-11], our experiments mass titration were per-

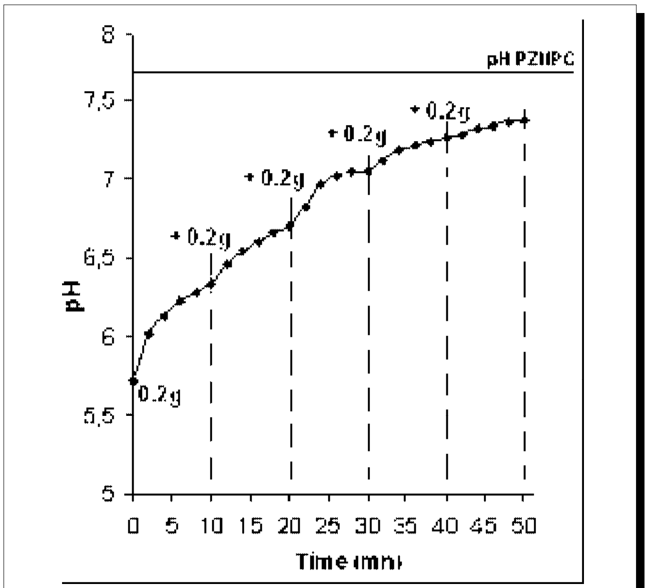

Figure 7: Evolution time after etch addition of 0.2g Ka-Kass.

formed at the same conditions of potentiometric titration by the following of the pH drift until a steady value. Each addition of approximately 0.2 g of dry kaolinite sample were added to 40 ml of NaCl solution at different ionic strength having a pH between 3 and 10. After each addition, the pH was recorded after an "equilibrium time" of about 10 mn. (We have verified that the pH reached a constant value during exactly 10 mn after each addition of the mineral) (Figure 7). Then, a new amount of sample is introduced to make change in pH. This procedure is repeated until a pH is found where no pH change occurs with the addition of the sample. This is the pH where proton adsorption is zero (PZNPC)[11]. Therefore, if the mineral is added to a solution at the pH of PZNPC, no change in pH should occur.

Mass titration data performed at three NaCl concentrations are presented in figure 8. The pH gradually changes with addition of solid mineral and asymptotically approaches a limiting value. The direction of pH variation depends on the pH of the starting NaCl solutions. Therefore, the pH were solid addition does not produce any change in the pH of the initial NaCl solution can be estimated by interpolation. The PZNPCs estimated this way are marked with arrows in the figure 8. Their values are reported in TABLE 5 for titrations performed at 0.001, 0.01 and 0.1 M NaCl. As shown in figure 8, all the results indicated the existence of a plateau in the pH vs mass curve. (S. Noh and A. Schwarz)[11] defined the pH at the plateau as "The acidity of infinite mass"(pH$_8$). For kaolinite samples, the pH$_\infty$ measured by mass titration is an agreement with the pH PZNPC values determined by acid/base titration method. However, it was not possible to obtain the precise pH PZNPCs by potentiometric titration because all titration curves were almost super-imposed between pH 5-8. Similar difficulties were noticed by some authors[11] concerning silica which found to have a very low slope in the σ-pH curve at low ionic strength near the PZC.

TABLE 5: PZNPCs determined from mass titration curves of the two kaolinites

[NaCl] mol/l	0.001	0.01	0.1
Crude Ka-Tab	6.8	7	7.1
Pure Ka-Kass	7.75	7.8	7.7

Our acid/base titration results demonstrated that PH PZNPC for crude ka-Tab is about 6.5 with somewhat experimental error Δ pH $\approx \pm$ 0.1. The value pH PZNPC $\approx$ 6.5 is lower than the pH$_\infty$ 7 (average value) measured by mass titration. This discrepancy is likely due to the to specific adsorption of background ions on the kaolinite surface leading to a shift in the pH PZNPC to a smaller value. Another possible cause for the discrepancy between pH$_\infty$ and pHPZNPC, in agreement with[11] is that there might be a slight contamination on the surface.

Comparing titration curves

Our potentiometric titration curves extended to acidic region are similar to those obtained at 25°C by[4-19-18] with the only difference that our curves showed a steep slope at pH range 5-8. It must be stressed that all the titration curves described above were performed in desaerated medium. Our titration curves were carried out in presence of CO_2 from air in the reactor. We suggest that the shape of our titration curves especially at neutral pH is probably influenced by the carbonates, in the neutral to alkaline pH domain. At acidic pH, the isotherm is unaffected because of volatilisation of CO_2, but in the basic pH, progressive solubility of carbonates occurs[24]. Some authors claim that carbonate

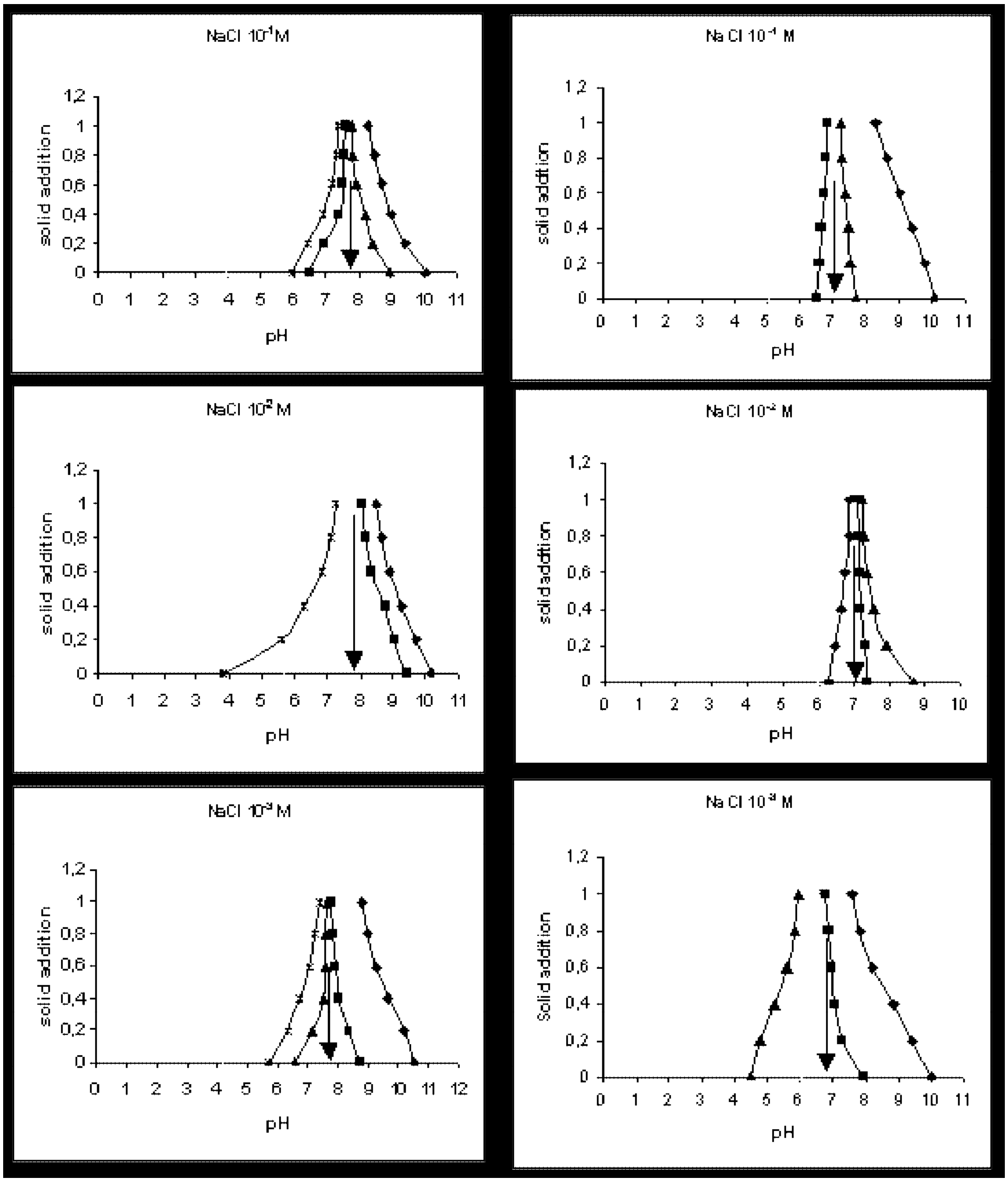

Figure 8: Mass titration curves of Ka-Kass (on the left) and Crude Ka-Tab (on the right) obtained at different electrolyte concentrations.
Each solid addition corresponds to 0.2g of dry kaolinite sample.

contamination is taken into account when the titration curves of electrolyte is subtracted from that of the suspension. In fact this correction is erroneous because the total contact time is much lower for the blank curve, inducing lower contamination. Therefore, we can conclude that our titration curves are not very altered by carbonate from the air but it is much better to perform titration curves under inert gas flow.

It must be stressed too that our experimental conditions are different of those described by these authors in background electrolyte, ionic strength and equilibration time of the aqueous suspension. The pH of zero net proton charge for kaolinite samples ranges in these titrations from 3.9-7.5. The comparing surface titration curves of kaolinite was studied by[5].

We suggest, in agreement with these authors that the differences in the shape of the isotherms may be explained by the differences in kaolinite samples, impurities and in composition of the background electrolyte[4-17-18].

We think also that the major reason for the differences in the observed surface protonation is the different ways in which the pH PZNPC was determined (technical experimental procedure, methodology). As defined by the proton consumption equation (1) the titration measures a relative change in surface concentration and not the absolute concentration[4]. Published experimental data in the literature, show that the pH PZNPCs of kaolinite vary significantly and range from 3 to 7.5[4-17] assume that pH PZNPC of the edge surfaces of kaolinite is 7.5 in agreement with our results using kaolinite sample (from Cornish China) with background electrolyte of $NaNO_3$ at 0.01 to 0.1M and different equilibration times (5mn, 10h, 24h and 48h). In contrast[19] used a starting suspension of 4g kaolinite (KGa-1 from Washington County) having a surface area of 10 m^2 /g in 50 ml background electrolyte of 0.1 M NaCl (equilibration time of 1 to 5 mn), whereas Huertas et al., used a suspension with a solid/solution ratio of 25g/l composed of kaolinite (from Twiggs County) having a surface area of about 8 m^2/g with background electrolyte solution of 0.001 to 0.1 M $KClO_4$ (equilibration time of 24h) . The measured surface protonation in each of these studies represents the change in surface protonation with respect to pH of the solution after its initial equilibra tion with the kaolinite; i.e. this pH was assumed to be pH PZNPC. The titration curves of[19] were composed of two independent titration curves one below pH 3.9 and the other above pH 4.3. After equilibration, the pH of one suspension was 3.9 and of the other 4.3. The first suspension was titrated with HCl and the other with NaOH. Accordingly, two different values of pH of the point of zero charge (3.9 and 4.3) were reported by[19].

Schroth and Sposito have measured by ionic adsorption, surface concentrations of both protons and ions of the background electrolyte solution LiCl (0.01M) for kaolinites (KGa-1 and KGa-2) having a surface area of 2.8 and 7 m^2 respectively. Using these measurements, they evaluated the absolute proton surface charge and the pH PZNPC based on surface charge balance. They obtained pH PZNPC values of 5 and 5.4 for kaolinite reference sample KGa-1 and KGa-2 respectively.

Jiwchar et al., emphasised that these different isotherms should be reviewed and if we want to compare them, we must define a common point of reference. The differences observed in pH PZNPCs values are mostly artefacts and that the titration curves of all kaolinite samples may be shifted so that they have similar pH PZNPC which is 5. At the end, an interesting question raised at this point is whether the PZNPCs of the two kaolinite specimen, determined by potentiometric titration are affected; i) by the nature of exchangeable cation, and thus by the surface acidity of kaolinite and. ii) by the presence of some other mineral (illite in our study) mixed with kaolinite. It is important to know the shifting direction of pH PZNPC with the two parameters cited above .The answer to these questions is not the aim of this paper but if we refer to published data,[25] for example have studied the surface acidity of montmorillonites (saturated with sodium, magnesium, aluminium and hydrogens ions), by titrating selected Hammett indicators adsorbed on the clay with n-butylamine. Accordingly, he found that the acidity was strongly affected by the exchangeable cations and the degree of hydration of the clay. On the other hand, the correlation between PZNPCs and kaolinite structure containing variable amount of illite has not yet discussed in the literature.

CONCLUSION

Within the framework of the above experimental conditions, a good agreement between pH PZNPCs values determined by potentiometric and mass titration curves of Ka-Tab and Ka-Kass. if we want to compare the two methods in evaluating PZNPC, we should take into account the specific adsorption of background ions such as Na^+, Cl^- that can affect the measurements of the pH PZNPC. We think that the major reason for the differences in the observed surface protonation is the different ways in which the pH PZNPC was determined i.e., it depends closely of the methodology applied. Also, from our experimental data, It should be important to know, in next paper, the role of exchangeable cation and the incidence of illite added with kaolinite structure on the shifting of PZNPC and therefore on the acid-base properties of kaolinite.

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