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EVOLUTION OF PZC WITH THERMAL TRANSFORMATION OF TUNISIAN KAOLINITE

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1. Introduction

Ceramic product depends on the nature and the properties of utilized raw material. The increase in temperature of ceramic clays produces a series of reactions and transformations that lead to the formation of new phases and the disappearance of others [1]. In this context, the kaolinite clay mineral forms metakaolinite by heating from 550°C and mullite mainly forms above 1200°C [2].

On the other hand, it is well known that the surface charge of clay minerals depends on activities of potentiel 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 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 most parameters or characteristics to describe variable-charge surfaces [3, 4]. According to Schroth and Sposito, 1997 [4], 3 parameters contributed to the surface charge of clay minerals. We can cite σ_0 which is the permanent structural charge density created by isomorphic substitution of Al^{3+} for Si^{4+} in the silica tetrahedral layer and Mg^{2+} for Al^{3+} in the aluminium (gibbsite) octahedral layer (for the kaolinite $\sigma_0 < 0$); σ_H, the net proton surface charge density created only by proton adsorption and desorption reactions at the interface clay-aqueous solution; Δq is 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).

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 (2003)	[3]
	3,0	Braggs et al (1994)	[8]
	< 4,0	Schindler et al (1987)	[9]
	4,5	Motta and Miranda (1989)	[10]
	4,5	Xie and Walther (1992)	[11]
	4,7	Sverjensky (1994)	[12]
	7,5	Wieland and Stumm, 1992	[13]
	5,0	Sposito G., 1997	[4]
	5,4		
	5,5	Huertas et al. 1998	[14]
	4,5	Brady et al. 1996	[15]
	3,0	Tschapek et al. 1974	[16]
Point of zero net charge (PZNC)	4,8	Ferris and Jepson (1975)	[17]
	4,0	Zhou and Gunter (1992)	[18]

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Many methods in the literature have been developed for determination point of zero charge in soils and clay-minerals [3–7]. The authors have generally used potentiometric titrations or ion adsorption measurements 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]. At the PZC the surface could be uncharged or charged with equal densities of positive and negative charges.

We must emphasis that many studies were carried out in the literature concerning surface charge behaviour of specimen kaolinite clay mineral. The main results, summarized in table 1, showed a significant variability in published experimental study of the points of zero charge. The data in this table illustrate the wide range of pH_{PZCs} values in the published literature. The values vary from 3,0 to above 7.0 Sposito G., [4] explained that the disagreement can be attributed to differences in sample preparation and to the use of different models to interpret data.

The composition of kaolinite indicates that the PZC may depend on the SiO_2 and Al_2O_3. It is known that the dehydroxylation of kaolinite takes place at T >500°C, therefore the PZC of kaolinte heated at temperature > 500°C must be different.

The aim of this work is to find the main PZC value of Tunisian kaolinite sample and its dependence on the heating treatment.

2. Material and Methods

2.1. Clay

Sample of specimen kaolinite used in this study was provided from Tabarka (Ka-Tab) situated in the north west of Tunisia. The particles with a diameter < 45 µm were obtained by sedimentation and saturated with Na+ by 7 washing cycles (successive centrifugal treatments) with 1M NaCl solution. After each centrifugation of the suspension, the supernatant was discarded and replaced with a fresh solution of NaCl. After that, the sample was dialysed through a specific membrane until free from Cl-, dried at 80°C and finally stored at room temperature.

2.2. 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. The diffractogram studied is that with disorientated powder where all the lines (h,k,l) appear. This makes it possible to follow the periodicity of the stratification of the layers, with the reflection (001) for which the identification is based.

2.3. 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.

2.4. Chemical analysis

The clay sample was 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).

2.5. Cationic exchange capacity (CEC) and specific surface area (SSA)

CEC was determined by the method of copper ethylendiamine $(EDA)_2$ $CuCl_2$ complex [19], specific surface areas BET was determined by nitrogen gas adsorption at 77K, using a “Quantachrom-Autosorb1” sorptiometer.

2.6. Thermo gravimetric analysis (TGA)

Differential Thermal Analysis (DTA) and Thermal Gravimetric (TG) were performed on a SETSYS Evolution-1750 instrument. Approximately 10-20 mg samples were placed in a platinum crucible on the pan of a microbalance and then heated from room temperature up to 1100°C at a heating rate of 10°C/mn while being purged with argon at a flow rate of 100 mL/mn and constantly weighted.

2.7. Experimental materials of potentiometrtic 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.

3. Charaharacterization of kaolinite clay

3.1. X ray Diffraction

Figure 1 shows diffractogram of saturated Na$^+$-Ka.Tab. One can observe the peaks reflectance of kaolinite {(d$_{001}$ and d$_{002}$-spacing)), reflections at 7,15Å and 3,56Å. The sharp peaks observed at 4.44; 4.34; 4.17; 3.83 and 3.37 are due to well crystallized kaolinite [20].

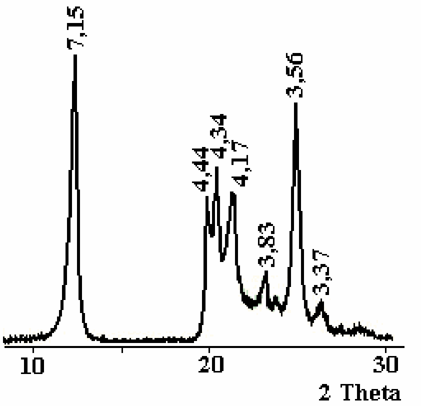

Fig.1. Diffractogram DRX of purified Na-Ka-Tab.

3.2. Analysis by Infrared spectra

Figure 2 shows infrared spectrum of saturated Na$^+$-Kaolinite-Tab. The main bonds are indicated on the spectrum. One can observe a typical structure of Kaolinite:

– OH stretching, hydroxyl sheet at (3695, 3620 cm^{-1})
– SiO stretching at (1062, and 1030 cm^{-1})
– OH deformation at 912 cm^{-1}
– Mixed SiO deformations and octahedral sheet vibrations at (790,753 and 694 cm^{-1})

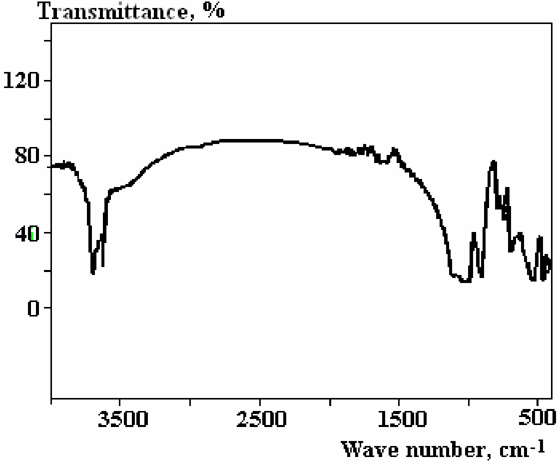

Fig. 2. Infrared spectra of purified Na- Ka-Tab

The chemical composition of modified of caolinite is presented in table 2; cation exchange capacity (CEC) and the specific surface area (SSA) are reported in table 3.

Table 2. Chemical analysis of the sample

%	Saturated Na-Kaolinite-Tab
SiO_2	46.03
MgO	0,08
Na_2O	0.04
Al_2O_3	37.20
Fe_2O_3	0.46
CaO	0,36
K_2O	0.05
Ignition loss	15.59

Table 3. C.E.C and S.S.A for the Na-Kaolinite-Tab

Specimen	CEC (meq /100g)	SSA (m^2/g)
Saturated Na-Kaolinite-Tab.	24,5	3.15

3.3. Thermogravimetric analysis

Figure 3 shows the DTA and TG curves of purified Kaolinite-Tab. The main transformations pointed out by TG and DTA analysis during heating of the samples are as follow:

a) *T*< 200°C: a first endothermic peak that can be attributed to a pre-dehydration process, which takes place as a result of the reorganization in the octahedral layer, first occurring at the OH of the surface [21].

b) 500-600°C: a second endothermic peak due to dehydroxylation of the kaolinite clay mineral. During this thermal transformation, kaolinite forms metakaolinite by dehydroxylation [22].

c) 976-1000°C: an exothermic peak indicates a phase transition at higher temperature leading to amorphous product, due to the decomposition of the kaolinite sample. This peak can be attributed to the formation of mullite that takes place at nearly 950°C and up to 1200°C.

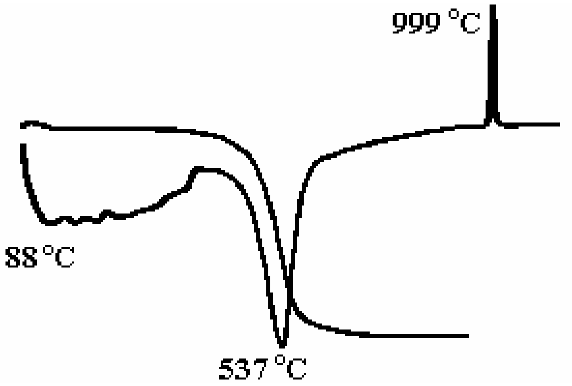

Fig. 3. DTA curve of purified Na-Ka-Tab

4. Result and discussion

The continuous 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 mn 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 ($\Delta pH < 0,03$ 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.

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]:

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

Where *V* is the volume of electrolyte solution equilibrated with kaolinite (40 mL)

[H+] is the solution proton concentration (mol/l) Kw 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 specfic surface area (m^2/g).

4.1. 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.

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 Schroth and Sposito [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 et al. [24], who reported 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, 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 и 6 show acid - base potentiometric titration curves of the purified Na^+-Kaolinite.Tab at 25°C and at different heating temperature, dispersed in different NaCl concentrations. 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 are 6.0, 7.0 and 7.3 respectively at 25°C, 500°C and 700°C and in agreement with the values reported by some authors and listed in table 1.

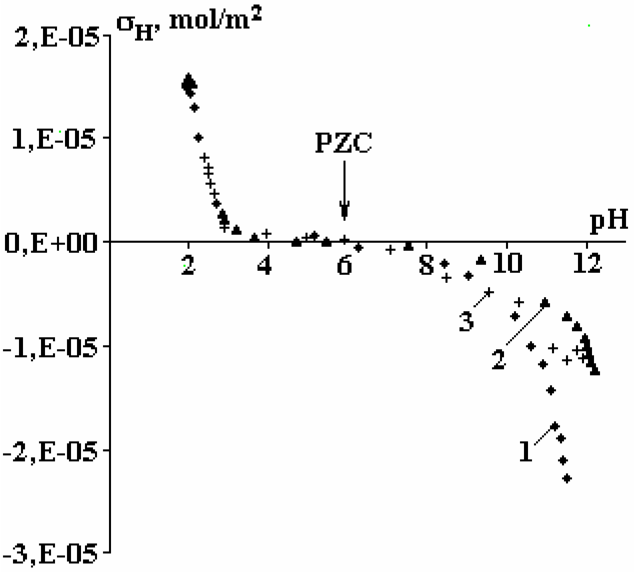

Fig. 4. Potentiometric titration curves of purifed Kaolinite-Tab as a function of pH at different ionic strengths, at T=25°C

Despite the low C.E.C value of the kaolinite sample, compared 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 σH vs pH.

This is could be due, since we know that kaolinite- solutions systems contain three kinds of surfaces (a gibbsite surface, a siloxane surface and an 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 hydroxylated sites at the edges with the consequent decreasing the protonation-deprotonation data between pH 5-8.

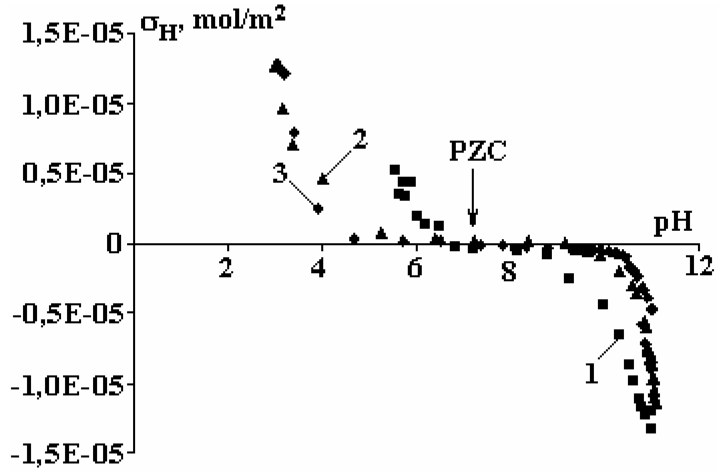

Fig. 5. Potentiometric titration curves of purified Kaolinite-Tab as a function of pH at different ionic strengths, at T=500°C

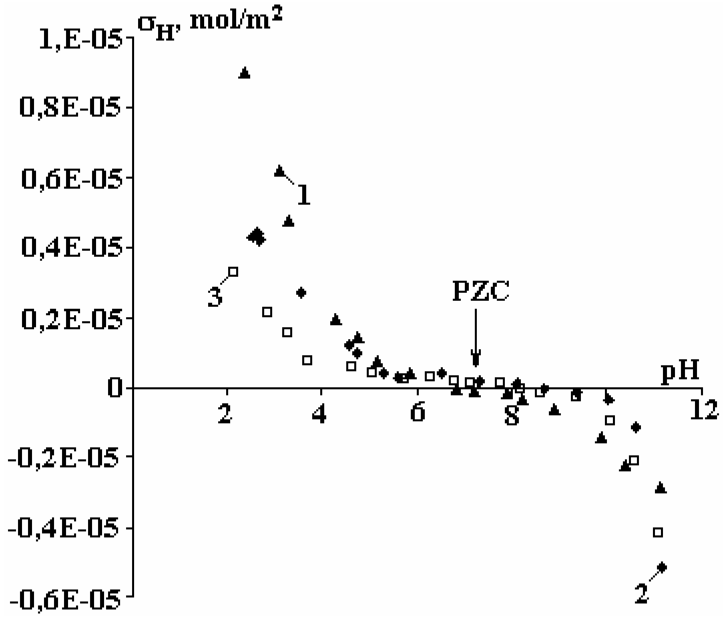

Fig. 6. Potentiometric titration curves of purified Kaolinite-Tab as a function of pH at different ionic strengths, at T=700°C

In a previous work, the thermal behaviour, structural changes and texture results of Tunisian Ka-Tab have been rigorously studied in our laboratory. Concerning the thermal analysis and as mentioned above, the second endothermic peak is the result of the dehydroxylation of Kaolinte. According to Tschapek et al., [16, see references therein] dehydroxylation of kaolinite begins at 400°C, but the principal part of OH is lost at 550-600°C. Between the endothermic peak and 800°C, the metakaolinite (the transition phase between dehydroxylation and formation of mullite) is formed. The metakaolinite decomposes at nearly 800°C and subsequently the γ-Al_2O_3 and free SiO_2 appear. The formation of mullite takes place at nearly 950°C and up to 1200°C.

The above transformations which occur during calcination of kaolinite should change pH_{PZC} . In general, the pH_{PZC} of kaolinite depends on its two principal components: SiO_2 and Al_2O_3. Some authors have found that the PZC of SiO_2 lies between pH =2.8 and 3.0 and of Al_2O_3 at pH =7.8 [16]. The PZC for SiO_2 coincides with values given by certain authors, whereas for Al_2O_3 the value listed is approximately 9. Tschapek et al., [16] have determined the PZC of different mixtures of SiO_2 + Al_2O_3. The results show that the PZCs values depend of the content of Al_2O_3. They conclude that the PZC is not additive but its dominant component in the mixture is γ-Al_2O_3.

It is interesting to present the study of dependence of the pH_{PZC} of kaolinite on the temperature of its calcinations. The calcined kaolinte samples were used without any further treatment. The pH_{PZC} vs. T°C curve is shown in Fig. 7.

Observing the curve of pH_{PZC} vs. T°C, we can conclude that it responds to the transformations occurring in kaolinite during its calcinations.

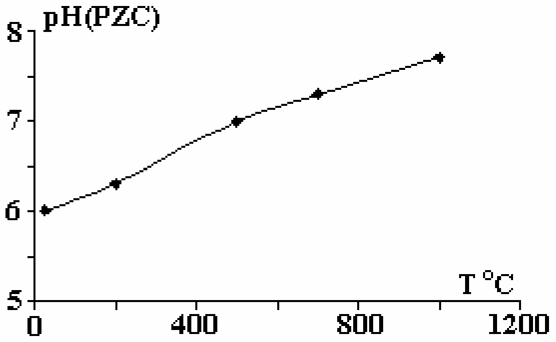

Fig. 7. Curve PZC vs. temperature for Kaolinite-Tab

Beginning at pH 6, the value slightly increases up to 200°C. The increase of pH_{PZC} between 200°C and 600°C is probably due to the onset of dehydroxylation of the octahedral layer. With a further increase of temperature, the pH_{PZC} increases up to 7.5 at 800°C, due to the formation of metakaolinite and afterwards of free γ-Al_2O_3. These results are consistent with works of Tschapek et al., [16] who found that the formation of mullite begins at 900°C accompanied by the appearance of free SiO_2. The pH_{PZC} of SiO_2 is near 3 [25], therefore the pH_{PZC} of the mixture (mullite + SiO_2) should be less than the pH_{PZC} of pure mullite. Acoording to Smolik et al., 1966 [26], the pH_{PZC} of mullite is 8, whereas that of aluminisilicates of composition $Al_2O_3.SiO_2$ is 6-7.

5. Conclusion

The pH_{PZC} of Kaolinite-Tab depends of the temperature treatment and responds to the transformations occurring in kaolinite during its calcinations. With increasing in temperature, the pH_{PZC} of Kaolinite- Tab shifts to the pH_{PZC} of γ-Al_2O_3 which is the dominant component in term of PZC in the clay mineral structure.

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Summary

The purpose of this paper is to study the thermal behaviour of Na^+-saturated Tunisian kaolinite (ka-Tab) with the evolution of its point of zero charge (PZC). The Fourier Transform Infrared spectroscopy (FTIR), X-Ray Diffraction (XRD), Differential Thermal Analysis (DTA), Cation Exchange Capacity (CEC) and specific surface area (SSA) were used to characterize the kaolinite sample. In the present investigation, the focus was on the surface charge characteristics of kaolinite at different temperature of heating. The results show that the formation of new phases in the kaolinite structure at temperature > 500-600°C, shifts the PZC value towards 8 which approximately PZC value of γ-Al_2O_3.
