SURFACE CHARGE DENSITY FOR KAOLINITE IN AQUEOUS SUSPENSION

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Abstract

In the field of environmental science, the surface charge density (σ_o) determines how easily a solid substrate is able to adsorb potential ions from their solutions; also, this property has applications in colloids science, e.g., flotation of minerals. The point of zero charge (pH_{PZC}) for a given mineral surface is the pH value at which its surface has a net neutral charge. The significance of the pH_{PZC} value is that a given mineral surface will have a positive charge in the acid domain (less than the point of zero charge) and a negative charge in the alkaline domain of pH scale (more than the point of zero charge).

The aim of the paper is to evaluate the surface charge density of kaolinite (Aghireş, Romania) suspended in $NaNO_3$ electrolyte, using acid-base titration method. It was observed that the value of the point of zero charge for this mineral is pH = 4.9. Results obtained for three different electrolyte solutions show that the pH_{PZC} value for the mineral is in a good correlation with the data from the literature. Below this value the surface charge density (σ_o) increases with the electrolyte concentration, while above this value, σ_o decreases with the increase of the electrolyte concentration.

Key words: kaolinite, surface charge density, point of zero charge, acid-base titration method

Introduction

Water-mineral interactions affect geologic processes ranging from chemical weathering to the mobility of hazardous chemical specials, to nutrient availability in soils, to the

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formation of ores deposits. These interactions between aqueous solutions and mineral surfaces depend on characteristics of both the chemical species in solution and the complex and highly varied structure and composition of minerals surfaces.

It is well known that the surface of mineral silicates is insoluble in water and, consequently appears a positively or negatively charge at the interface. The H^+ or HO^- ions are commonly considered as the potential-determining ions, although it is impossible to show the sorption process of one ion and desorption of the other. The appearance of the charge at the interface of silicates with the solution is explained by adsorption, hydration, complexation and solubilising reactions. In solution, the surfaces of insoluble silicates behave as protons acceptor in interaction with an acid and as protons donor in interaction with an alkali.

$$R-OH_2{}^+Cl^- \xleftarrow{\quad HCl \quad} R-OH^{\mp} \xrightarrow{\quad MOH \quad} R-O^-M^+ + H_2O \qquad (1)$$
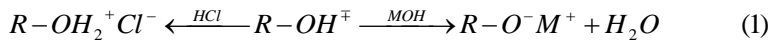
The *point of zero charge* (*pH_{PZC} or PZC*) is an important property of a mineral in aquatic systems, being the most important parameter that describes the electric double layer of a mineral-water solution. By definition, point of zero charge for a given mineral surface is the pH value at which the surface has a net neutral charge, $\sigma_0 = 0$ (or the number of positive ions, H^+ is equal with the number of negative ions, HO^-) (Isac et al., 1995; Preocanin and Kallay, 1998; White, 2004). This means that a given mineral has a specific pH_{PZC} value in static chemical conditions; the surface will have a positive charge at low pH (less the pH_{PZC}) and the anions may adsorb on it. On the other hand, the mineral surface will have a negative charge at solution pH values greater than the pH_{PZC} and the cations may adsorb on it. This point represents the main condition for aqueous solution at which the value of electric potential, σ_0 is zero and this is determined by a particular value of the activity of the potential-determining ion. In the literature of the field appears some names for this property; the *isoelectric point* (isoelectric pH, denoted **pH_{IEP}**) is the pH at which the average charge of the acid is zero or the pH at which the electrophoretic mobility is zero (Harris, 1998; Mândru and Ceacăreanu, 1976). The *isoionic point* (isoionic pH) is compared by the isoelectric point and it is used for organic compounds such as proteins, amino-acids (Harris, 1998).

The negative surface charge for kaolinite is born mainly by isomorphic substitution of Al^{3+} for Si^{4+} in the silica tetrahedra layer. The counter-ions of these charges are localized on the OH^- free face of the silica tetrahedral layer, function by the pH value. At low pH value a positively charge (H^+-rich) surface appears at interface, while at high pH value a negatively charge (HO^--rich) appears at mineral-solution interface. The potential determining ion does not originate by isomorphic substitution. Thus, the ionic layer on the kaolinite surface originated by isomorphic substitution is different from those originated by adsorption from solution (Tschapek et al., 1974). It is well know that the laws for the electric double layer are also applicable for „incomplete" electric double layer. Due to a great distance between surface charges (i.e., for aluminosilicates 7-10 Å) and in order to maintain the electroneutrality of the system, the counter ions (three or four valence cations) reverse the

potential (Tschapek et al., 1974). Because the Al^{3+} ion appears on the surface of kaolinite especially in acid medium, like $Al(OH)_2^+$ or $Al(OH)^{2+}$, the Al-compound is capable to reverse a negative potential into a positive one.

$$\langle RO^- \rangle H^+ + AlCl_3 \rightarrow \langle RO^- Al(OH)^{2+} \rangle Cl^- + H_2O \qquad (2)$$
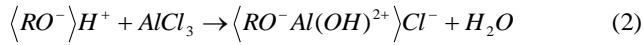
In addition, there is also the possibility for the appearance of charges: hydroxyl groups of Si and Al on the edges and on Al octahedral layer might react with acid or alkali resulting in the positive and negative charges (fig. 1). In conclusion, the change of the negative charge of kaolinite can be caused by Al complex ions and by the substitution of a polyvalent ion with protons, H^+.
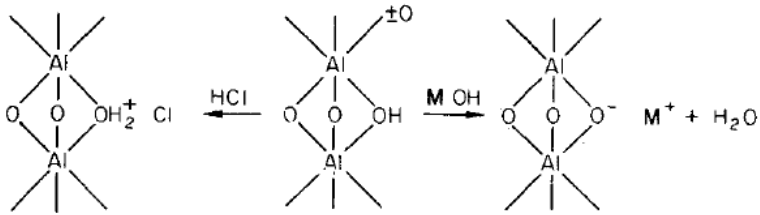

Fig. 1 Charge density on surface mineral in acid or alkaline solution

Material and method

Some chemical contents of kaolinite sample (Aghireş, Romania) used in experiment are given in tabel 1. The value of exchange capacity was taken from the literature and it was 21.6 m^2g^{-1} (Schroth and Sposito, 1997).

Tab. 1 Content of the main oxides (%) of kaolinite used in the experiment

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	H_2O_t
57.10	32.18	1.29	0.65	0.37	0.45	0.10	0.22	5.53

There are many methods used for the determination of pH_{PZC}. Among these, the most important are *mass titration* method and *acid-basic titration* method (Preocanin and Kallay, 1998; Isac et al., 1995; Hurduc, 1979; Mândru and Ceacăreanu, 1974). In this paper, a kaolinite sample and the acid-base titration method were used for the determination of pH_{PZC}. The electrolytic solution of $NaNO_3$ was obtained from commercial source.

The surface change density of kaolinite in an aqueous solution was determined by acid-base titration, which involves two series of measurements. First series is in the presence of

mineral (1.0g of kaolinite in 200 cm^3 aqueous electrolyte solution NaNO$_3$ of 10^{-1}, 10^{-2} and 10^{-3} mol·dm^{-3} concentration, respectively) and the second one with the same solution of electrolyte, but in the absence al mineral powder (blank). A solution of either HCl or NaOH (both 10^{-1} mol·dm^{-3}) was used as titrant in the pH range from 2 to 9. A small volume of titrant, 0.1 ml, depending on the solution pH and the electrolyte concentration, was added from time to time and, after 3 min of shaken on a magnetic stirrer, the pH value was recorded (using a Corning Pinnacle 555 pH-meter device). The temperature was kept almost constant at 28 ± 1^0C. For the contaminated samples it is better to use *the acid-base titration* method. The inflexion point of the graph $\sigma_0 = f$ (pH) (obtained at different ionic strengths of NaNO$_3$ electrolyte) gives information about the pH$_{PZC}$. The method involves a comparison with blank titration in the absence of the solid phase and different ionic strengths for the location of the values for pH$_{PZC}$.

The value of pH$_{PZC}$ can be calculated in two ways: one was linear regression of σ_H against pH to find the intercept with *x* axis where $\sigma_H = 0$. The second one is represented by the plot of the sum $(\Delta q + \sigma_0)$ against pH and determining, by linear regression, of its value when the sum equals zero (x-axis intercept). The pH$_{PZC}$ can be calculated by fitting Δq to a linear function of pH with regression analysis, then solving the resultant function for the condition $\Delta q = 0$ (x – axis intercept) (Schroth and Sposito, 1997). The *mass titration method* was also found to be suitable in the determination of pH$_{PZC}$ for mineral oxides. It was initially developed for pure metal oxides and later was extended for contaminated samples (Preocanin and Kallay, 1998).

The surface charge density (σ_0 in µC·cm^{-2}) was calculated from the following equation (Todorovic and Milonjic, 2004):

$$\sigma_0 = \frac{\Delta v \cdot M \cdot F}{S \cdot A \cdot V} \cdot 100 \qquad (3)$$

where Δv (cm^3) = the difference between the titrant volumes used for suspension and blank solutions at a given pH value, M = the molarity of the titrant, F = the Faraday constant (96.487 C), S (m^2·g^{-1}) = the specific surface area of mineral, A (g·dm^{-3}) = the amount of mineral used for the titration and V (cm^3) = the volume of the electrolyte used for the titration.

Results

In literature, based on electrophoretic measurements, the point of zero charge (pH$_{PZC}$) it was supposed at pH = 3.3 and this value is due to the fact that pure kaolinite is difficult to obtain, as long as kaolinite is present in kaolins beside many other minerals called „impurities" (Buchanan and Oppenheim, 1958, after Tschapek et al., 1974). The influence of the impurities on the pH$_{PZC}$ is not so large because the main minerals of kaolins is kaolinite (sometimes up to 99%). On the contrary, when the impurities are absent, the

values of pH_{PZC} (for kaolinite and for impurities, respectively) must be the same. It was shown that for kaolinite, the pH_{PZc} value may depend on the SiO_2 and Al_2O_3 contents.

The surface charge densities as a function of $NaNO_3$ electrolyte concentration and pH, calculated from the equation above are presented in figure 2. The curves obtained with this ionic strength intersect the pH axis at pH = 4.9 (fig. 3) which represents the point of zero charge of kaolinite (pH_{PZC} = 4.9). The obtained pH_{PZC} value is in good agreement with the other values, determined by both methods (acid-base titration or mass titration).
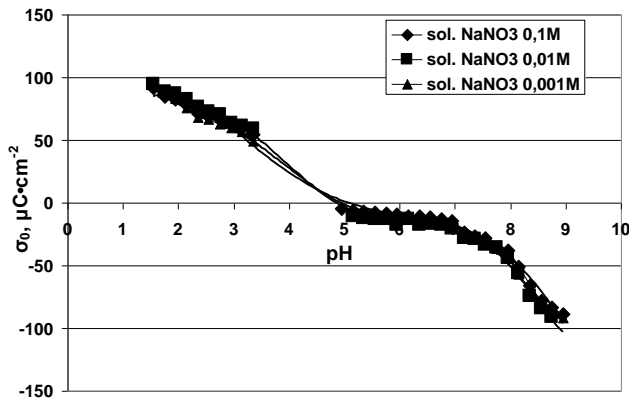

Fig. 2 Surface charge densities of kaolinite as a function of pH, for different ionic strengths of $NaNO_3$ solution, at constant temperature
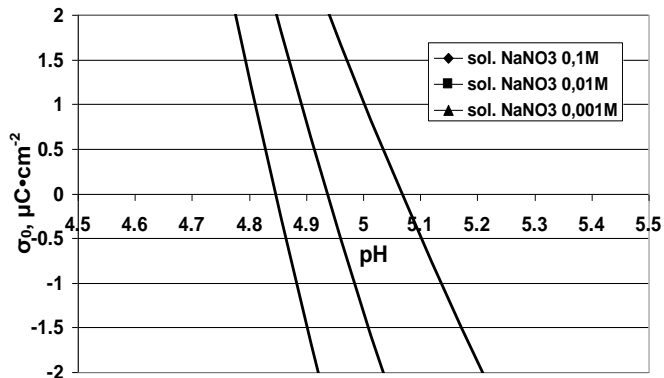

Fig. 3 Surface charge density for kaolinite obtained for pH 4.8 to pH 5.1 domain

Due to the fact that the pH_{PZC} for kaolinite is in acidic domain, the titration presents some difficulties, but it is no doubt on the intercept with the axis. Some authors (Tschapek et al., 1974) considered that the value of pH_{PZC} for kaolinite is higher than pH = 3, because

of the presence of Fe_2O_3 in large amount (for our sample 1.29%) is greater than usual (< 1%). Generally, the pH_{PZC} for kaolinite depends mainly on two components, SiO_2 and Al_2O_3, meaning that the adsorption capacity of the mineral plays an important role in the determination of its pH_{PZC}.

The authors have studied the relation between pH_{PZC} and the temperature and they concluded: beginning with pH = 3 the value does not change until 200^0C (fig. 4). The pH_{PZC} value for kaolinite increases between $200-500^0C$ due to the dehydroxylation of the octahedral layer.
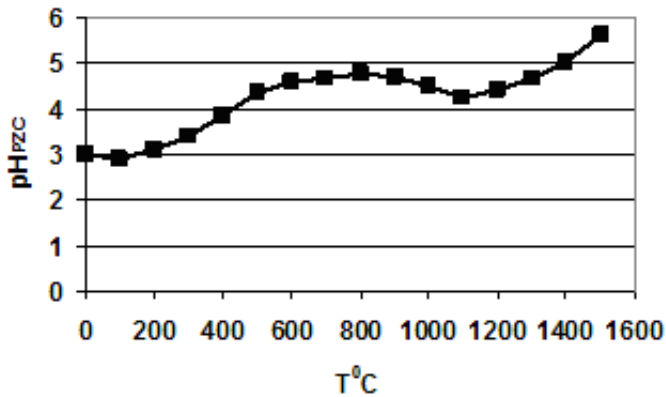

Fig. 4 The relation between pH_{PZC} and temperature for kaolinite (Tschapek et al., 1974)

Further on, the pH_{PZC} value increases up to 4.7 between $800-900^0C$, due to the formation of metakaolinite and afterwards of free γ-Al_2O_3. The formation of the mullite beside the appearance of free SiO_2 begins at 900^0C. The pH_{PZC} value of SiO_2 is up to 3, consequently the pH_{PZC} of the mixture (mullite+SiO_2) should be less than the pH_{PZC} of pure mullite (pH_{PZC} for mullite is around 8). The decrease of pH_{PZC} for temperature more than 900^0C is not so large with the appearance of γ-Al_2O_3. If γ-Al_2O_3 is present, the pH_{PZC} should be increased, although it is not impossible for γ-Al_2O_3 to form a limited specific surface. The increase of pH_{PZC} for kaolinite for temperature more than 1200^0C can be explained as follow: at T > 1200^0C the crystallization of free SiO_2 into cristobalite begins, meaning that the specific surface decreases. The role of SiO_2 in the mixture is less than before and consequently, there appears an increase of pH_{PZC} for the mixture. As a result, the temperature treatment of the sample increases the Al_2O_3 in kaolinite, facilitating its pH_{PZC} without its protonization (Tschapek et al., 1974).

The characteristics of surface charge for any minerals are essentially for the determination of the mechanism of its reactions with soluble compounds and for the orientation of the pathways of its weathering reactions in rocks and soils. As we know, the density of surface charge is created by isomorphic substitutions in the mineral structure

(denoted σ_0) and, consequently, reactions of adsorption-desorption of protons appear at the interface with the solution (denoted σ_H). For kaolinite the sign of σ_0 is negative, arising either directly for Al(III) substitution with Si(IV) in the tetrahedral sheet of mineral, or indirectly from isomorphic substitution in 2:1 layer type clay mineral inclusions (White, 2005). The sign of σ_H varies with the pH value for aqueous solutions, being positive at low pH values and negative at higher pH values.

The surface charge density for two kaolinite samples was determined as a function of pH by potentiometric titration in 10^{-2} M LiCl like electrolyte by Schroth and Sposito (1997). The equilibrium values were 3.6 and 3.5, respectively, in good agreement with previous studies of the authors. A wide range of data is present in the published literature and significant names are denoted for this property; the point of zero charge is an important property of a mineral in aquatic systems. A good review of pH_{PZC} for kaolinite was realized by Schroth and Sposito (1997). The authors found that for kaolinites, the isoelectric point is ranged from 3 to 5, while the pH_{PZC} vary from 3 to 7. The differences are attributed to the sample preparation and to the different models used to data interpretation.

In the literature, the values for pH_{PZC} for different minerals were obtained by means of other methods or were reported without explicitly stating the experimental method. Table 2 lists some value of the point of zero charge for some mineral oxides or silicate minerals. The values of point of zero charge cover almost all the pH domain, from acidic to alkaline domain and for the same oxide the values can differ from an author to another.

Tab. 2 Values of point of zero charge for same metallic oxides (from Schroth and Sposito, 1997; White, 2005; Railsback, 2006)

Oxide mineral	pH_{PZC}	Oxide mineral	pH_{PZC}
TiO_2 (anatase)	$5.8 - 7.2$	Manganese dioxide, δ-MnO_2	$2.8 - 4.5$
TiO_2 (rutile)	6.7	Manganese dioxide, β-MnO_2	7.2
Alumina, Al_2O_3	$6.8 - 9.3$	Tin dioxide, SnO_2	5.5
Gibbsite, $Al(OH)_3$	8.2	Sillimanite (Al_2SiO_5)	4.9
SiO_2 (quartz)	$2 - 3$	Sanidine ($KAlSi_3O_8$)	6.1
SiO_2 (gel)	$1.5 - 2.5$	Albite ($NaAlSi_3O_8$)	5.2
Hematite, α –Fe_2O_3	$6.5 - 8.5$	Anorthite ($CaAl_2Si_2O_6$)	5.6
Ferrihydrite, $Fe_2O_3 \cdot nH_2O$	8.5	Andalusite (Al_2SiO_5)	6.9
Goethite, $FeOOH$	$7.6 - 8.3$	Periclase (MgO)	12.2
Ag_2O	12	Kaolinite ($Al_2Si_2O_5(OH)_4$)	5.0-5.4

Generally, the chemical interaction of kaolinite with acid and alkaline solutions is a proton adsorption-desorption process and it is easy to find the equilibrium constant at pH_{PZC}.

$$RO^- + 2H^+ \Leftrightarrow ROH_2^+, \qquad K_{pH_{PZC}} = \frac{a_{ROH_2^+}}{a_{RO^-} \cdot a_{H^+}^2} \qquad (4)$$
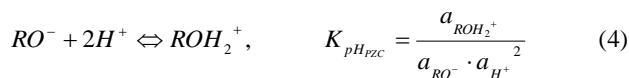
where a_X represents the chemical activity of the species mentioned above. At pH_{PZC}, $a_{ROH_2^+} = a_{RO^-}$, therefore $K_{pH_{PZC}} = \left(a_{H^+}\right)^{-2}$. The constant equilibrium value of kaolinite is $K_{pH_{PZC}} = (10^{-4.2})^2 = 3.96 \cdot 10^{-9}$. This value shows that the process of H^+ adsorption-desorption is a slow one. Knowledge of the equilibrium constant K, permits to calculate the standard free energy, which accompanies the charging of kaolinite by adsorption-desorption of H^+.

The point of zero charge, pH_{PZC}, for alumina was assessed to vary from 7 to 10, depending on the type of alumina. Relevant data for this oxide were obtained in another place and the results show that for alumina powders the pH_{PZC} value is 7.2 (Gavriloaiei and Gavriloaiei, 2007). Ntalikwa (2007) observed that below pH_{PZC} of minerals, σ_o increases with the increase in electrolyte concentration (C_o), whereas above PZC, σ_o decreases with the increase in C_o. It was concluded that σ_o of this material is a function of pH and C_o and that its polarity can be varied through zero by varying these parameters.

Many authors considered that the cation adsorption by kaolinite surface depends on the cation concentration in the solution, on the nature of the electrolyte and on the pH value. Most of the negative or positive surface charge for kaolinite is pH dependent and is likely to be due to isomorphous substitution. The specific edge area of kaolinite is not known and has to be estimated. Morphologically, kaolinites exist as thin platelets, whose edge area is small compared with their basal surface. The surface area of the edges was found to be in between 7-14% of the total surface area (after Zhou and Gunter, 1992). The surface charge density for kaolinite of the edges is greater with one order of magnitude than that of either alumina or silica in the same conditions. From the consideration of surface charge density, it is obvious that the ionization of edges cannot explain the magnitude of the changes in the cation exchange capacity and surface charge observed in experiments. So, the basal surface must also contribute to these changes. The charges on the basal surface are negative but the magnitude is pH-dependent.

Conclusion

Despite the differences between the methods used in the laboratory practice, the acid-base method is a suitable tool for pH_{PZC} determination for mineral oxides and silicates. Initially, the method was developed for pure minerals, but further on the method was extended to contaminated minerals. In comparison with the other methods, this method is advantageous when the temperature dependency is examinate for surface charge density. The present paper evaluates the surface charge density of kaolinite (Aghireş, Romania) suspended in $NaNO_3$ electrolyte. It was observed that the value of the points of zero charge for this mineral is pH = 4.9. Results obtained for three different electrolyte solutions show that the pH_{PZC} value for mineral is in a good correlation with the data from the literature. Given the precision of the experiment, the pH_{PZC} value calculated from graphical method, demonstrate the internal consistency of the titration and ion adsorption data. Further determinations, will show that surface charge density increase with mixing time of minerals.

Although is not reported, a possible explanation for these results is that usual equilibrium time for most of the experiments is on the order of minutes, since the authors performed a continuous titration.

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