

## DETERMINATION OF SURFACE CHARGE FOR METAL OXIDES

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### Abstract

The behavior of aqueous dispersion of inorganic oxides is of great importance in industrial and laboratory applications. Point of zero charge is of fundamental importance in surface sciences; for example, in the field of environmental science, it determines how easily a solid substrate is able to adsorb potentially ions. It also has applications in colloids science, e.g., flotation of minerals. Point of zero charge ( $pH_{PZC}$ ) for a given oxide 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 oxide surface will have a positive charge in the acid pH domain (and the value is less than the point of zero charge) and a negative charge in the alkaline pH domain.

The point of zero charge ( $pH_{PZC}$ ) for titanium dioxide reported in the literature cover almost all pH domain, from 2 to almost 9. In this paper, we used the acid-base titration method to determine the  $pH_{PZC}$  for a  $TiO_2$  sample. Results obtained for three different electrolyte solutions show that the value of point of zero charge is 5.5, in a very good correlation with the data from the literature.

**Keywords:** point of zero charge, titanium dioxide, acid-base titration method

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## Introduction

The mobility of ions in the aquatic environments is controlled by adsorption processes at the interface and by the competition among various chemical species for surface binding sites. Adsorption at solid-liquid interface is important in technological processes like corrosion, catalysis, nanoparticles, water treatment and purification or surfactants. Physical and chemical properties of the interface are a topic in numerous processes ranging from minerals to detergency, including some applications as water treatment or soil remediation.

Titanium dioxide (called also *titania*),  $\text{TiO}_2$  is the naturally occurring oxide of titanium and a useful adsorbent for studies on the relationship between the surface charge and the ions concentrations from bulk solution. Its point of zero charge ( $\text{pH}_{\text{PZC}}$ ) is in the middle of the pH scale and this fact makes possible to study adsorption on positively and/or negatively charged surface of  $\text{TiO}_2$  over a large range of pH and ionic strength. The applications of  $\text{TiO}_2$  are numerous (e.g. as pigment in paint industry, catalyst support in different industrial processes) and its surface properties have been extensively studied. Titanium dioxide presents two isomorphous forms: *rutile* is thermodynamically stable at room temperature, and *anatase* is kinetically stable (the transformation into rutile at room temperature is so slow, that practically does not occur). There is also another form of  $\text{TiO}_2$ , namely *brookite*, but until now the surface properties of brookite has not been extensively studied.

The most common form is rutile and the other two forms (anatase and brookite) can convert to rutile upon heating. It is used as pigment because of its brightness and very high refractive index ( $n=2.7$ ), in which it is surpassed only by some materials. Every year almost 4 million tons of pigmentary  $\text{TiO}_2$  are consumed in the world. Titanium dioxide is also an effective opacifier in powder form, where it is employed as a pigment to provide whiteness and opacity to products such as paints, coatings, plastics, papers, inks, foods, medicines or toothpastes. In ceramics glazes titanium dioxide acts as an opacifier and seeds crystal formation. In almost every sunscreen with a physical blocker, titanium dioxide is found because of its high refractive index and its resistance to discolouration under UV light. Anatase form of titanium dioxide is a photocatalyst under UV light. Titanium dioxide is added to paints, cements, windows, tiles, deodorizing or sterilizing products; titanium dioxide has potential for use in energy production.

The chemical processes between the oxide surface and dissolved species from the bulk solution have great importance in the interface chemistry. Because these reactions depend on the pH values, we can say that the surface charge is pH dependent. Depending on the pH value, the  $\text{TiO}_2$  surface can be protonated (positive charge of the protons) or deprotonated/hydroxylated (negative charge of hydroxyl ions). **Point of zero charge** ( $\text{pH}_{\text{PZC}}$ ) for a given mineral surface is the pH value at which this surface has a net neutral charge (or the number of positive ions,  $\text{H}^+$  is equal with the number of negative ions,  $\text{HO}^-$ ). The significance of the  $\text{pH}_{\text{PZC}}$  value is that a given mineral surface will have a

positive charge in the acid pH and the value is less than the point of zero charge. The same mineral surface will have a negative charge in the alkaline pH and the value is greater than the point of zero charge. Somewhere in between these two values, there is a point where the surface charge is zero and this point is called **point of zero charge** ( $\text{pH}_{\text{PZC}}$ ). The value of pH is used to describe the point of zero charge only for systems in which  $\text{H}^+/\text{HO}^-$  are the potential determining ions (most cases). When the pH is lower than the  $\text{pH}_{\text{PZC}}$  value, the system is said to be below the  $\text{pH}_{\text{PZC}}$  (figure 1). The position of the  $\text{pH}_{\text{PZC}}$  differs for various minerals. Some other authors define the *net density of electric charge*,  $\sigma_{\text{net}}$  function by the intrinsic surface charge ( $\sigma_0$ ) due to lattice imperfections, the net proton charge ( $\sigma_{\text{H}}$ ) due to binding of  $\text{H}^+$  or  $\text{HO}^-$  and the charge due to other surface complex ( $\sigma_{\text{SC}}$ ) (after White, 2005). Usually, the surface charge is measured in coulombs per square meter ( $\text{C}/\text{m}^2$ ).

$$\sigma_{\text{net}} = \sigma_0 + \sigma_{\text{H}} + \sigma_{\text{SC}} \quad (1)$$

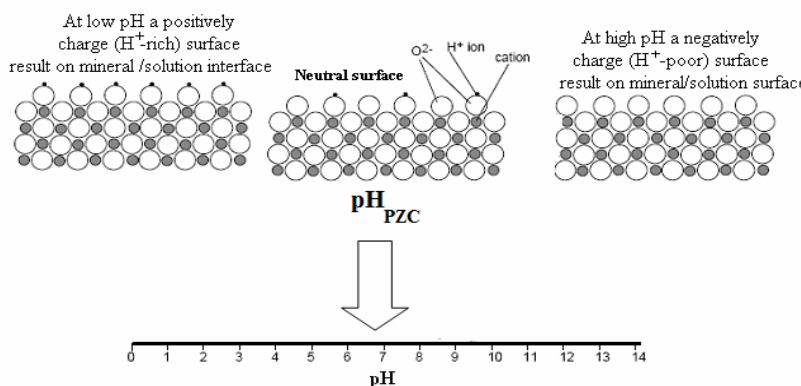


Fig. 1 Configuration of protonated/deprotonated oxide surface and the position of point of zero charge for an unknown substrate (in the upper part, it is represented the structure of the mineral surface in the acidic, neutral and alkaline pH domain) (after Railsback, 2006)

## Method and materials

In order to determine the  $\text{pH}_{\text{PZC}}$  value, a commercial sample of titania,  $\text{TiO}_2$  p.a. (0.063 mm) was used, with a specific surface area of  $200 \text{ m}^2 \cdot \text{g}^{-1}$  (Barringer and Bowen, 1985). The surface charge density of titania in aqueous solutions was determined by the acid-base titration method. Two titrations were carried out (Milonjic et al., 1983, Todorovic and Milonjic, 2004): the first one in the presence of titanium dioxide (1 g  $\text{TiO}_2$  in  $200 \text{ cm}^3$  of electrolyte aqueous solution) and the other one, with the same

electrolyte solution, but in the absence of titania (blank). The electrolyte solution was  $\text{KNO}_3$  of  $10^{-1}$ ,  $10^{-2}$  and  $10^{-3}$  M aqueous solution, respectively. Small volumes (0.1 mL) of solution of either HCl or NaOH (both of  $10^{-1}$  M) were added as titrant, to cover the pH range from 2 to 10. The mixture was shaken on a magnetic stirrer (3 min.) and after a period of homogenization, the pH value was recorded (using a Corning Pinnacle 555 pH-meter device). The temperature was kept almost constant at  $25 \pm 1^\circ\text{C}$ .

The surface charge density ( $\sigma_0$  in  $\mu\text{C}\cdot\text{cm}^{-2}$ ) was calculated from the following equation (Todorovic and Milonjic, 2004):

$$\sigma_0 = \frac{\Delta v \cdot M \cdot F}{S \cdot A \cdot V} \cdot 100 \quad (2)$$

where  $\Delta v$  ( $\text{cm}^3$ ) = 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),  $S$  ( $\text{m}^2\cdot\text{g}^{-1}$ ) = the specific surface area of titanium dioxide,  $A$  ( $\text{g}\cdot\text{dm}^{-3}$ ) = the amount of oxide used for the titration, and  $V$  ( $\text{cm}^3$ ) = the volume of the electrolyte used for the titration.

## Results

The acid-base titration method was found to be suitable in the determination of  $\text{pH}_{\text{PZC}}$  for contaminated oxide minerals (Kosmulski and Saneluta, 2004). Generally, it needs to perform different volume of electrolyte solution to a constant mass of titanium dioxide. The inflexion point of the graph  $\sigma = f(\text{pH})$  give informations about the  $\text{pH}_{\text{PZC}}$ . The pH dependency of surface charge for different mineral oxides is illustrated in the figure 2.

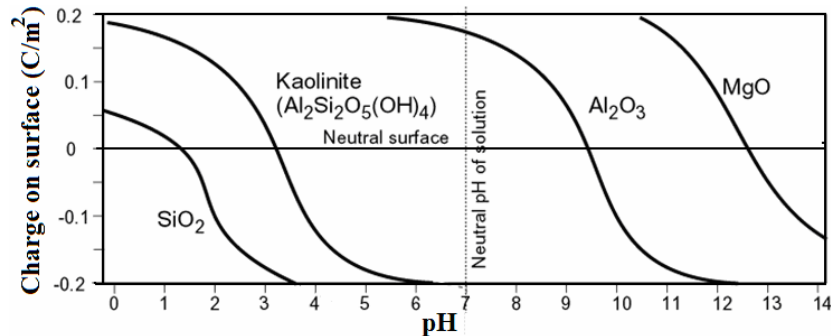


Fig. 2 Surface charge of some mineral oxides as a function of pH (the intersection point represents the value for  $\text{pH}_{\text{PZC}}$ ) (after Railsback, 2006)

This method need a comparison with a blank sample in the absence of mineral oxide and for different ionic strengths to localize the value for  $\text{pH}_{\text{PZC}}$ . Surface charge depends on the nature of the surface and on the ionic strength of the working solution. The experimental value of the  $\text{pH}_{\text{PZC}}$  is independent of the ionic strength, as in figure 3.

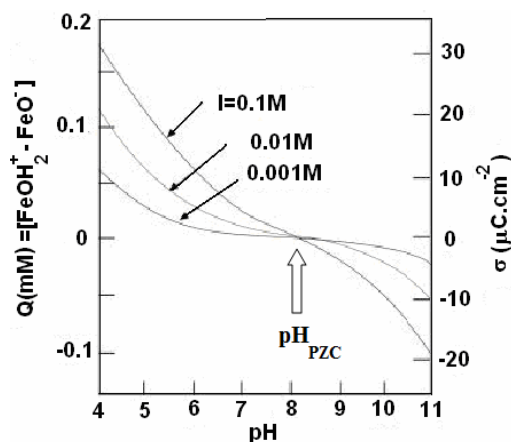


Fig. 3 Surface charge of goethite as a function of pH for different ionic strength of a 1:1 electrolyte solution (Dzombak and Morel, 1990, after White, 2005)

The surface charge densities as a function of  $\text{KNO}_3$  electrolyte concentration and pH, calculated from the equation above are presented in figure 4. The curves obtained with these ionic strengths intersect the pH axis at  $\text{pH}=5.5$ , which represents the *point of zero charge* of the titanium dioxide (figure 5). The obtained  $\text{pH}_{\text{PZC}}$  value is in good agreement with the other values, determined through both methods (acid-base titration or mass titration). A good survey of  $\text{pH}_{\text{PZC}}$  of titanium dioxide was realised by Kosmulski, 2002. He reported the values for point of zero charge of titania in a short interval of values for a set of 138 samples of  $\text{TiO}_2$ . The values for anatase were between 5.9 and 6.0 slightly higher than for rutile, where the values were between 5.4 and 5.5. The results show that anatase has a median  $\text{pH}_{\text{PZC}}$  higher with approximately 0.5 pH unit than rutile.

In the literature, the values for  $\text{pH}_{\text{PZC}}$  for titania were obtained by means of other methods or were reported without explicitly stating the experimental method. Table 1 lists some value of the point of zero charge for some mineral oxides. 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. In other paper, the curves

obtained with other samples (alumina) intersect the pH axis at  $\text{pH}=7.2$  which represents the *point of zero charge* of the alumina (Gavriiloaiei and Gavriiloaiei, in press). The obtained  $\text{pH}_{\text{PZC}}$  value was in good agreement with the other values, determined by both methods (acid-base titration or mass titration). According to Todorovic and Milonjic, 2004, the value of the  $\text{pH}_{\text{PZC}}$  for oxides minerals depends on the alumina/solution ratio: increasing the alumina/solution ration leads to an increase in the  $\text{pH}_{\text{PZC}}$  value. The point of zero charge,  $\text{pH}_{\text{PZC}}$ , of alumina was assessed to vary from 7 to 10, depending on the type of alumina.

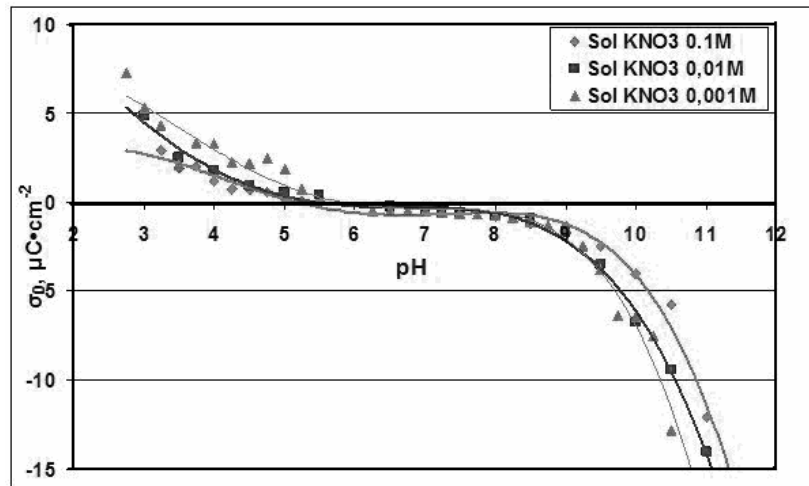


Fig. 4 Surface charge density obtained for titanium dioxide

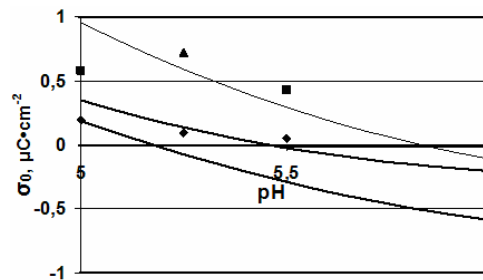


Fig. 5 Surface charge density for titanium dioxide obtained for pH 5 to pH 6 domain

Tab. 1 Values of point of zero charge for same metallic oxides (from White, 2005)

Oxide	pH <sub>PZC</sub>
TiO <sub>2</sub> (anatase)	5.8 – 7.2
TiO <sub>2</sub> (rutile)	6.7
Alumina, Al <sub>2</sub> O <sub>3</sub>	6.8 – 9.3
Gibbsite, Al(OH) <sub>3</sub>	8.2
SiO <sub>2</sub> (quartz)	2 – 3
SiO <sub>2</sub> (gel)	1.5 – 2.5
Hematite, $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	6.5 – 8.5
Ferrihidrite, Fe <sub>2</sub> O <sub>3</sub> ·nH <sub>2</sub> O	8.5
Manganese dioxide, $\delta$ -MnO <sub>2</sub>	2.8 – 4.5
Manganese dioxide, $\beta$ -MnO <sub>2</sub>	7.2
Stanium dioxide, SnO <sub>2</sub>	5.5
Goethite, FeOOH	7.6 – 8.3
Ag <sub>2</sub> O	12

## Conclusions

In conclusion, the acid-base titration method was found to be a “suitable” tool in the determination of point of zero charge for mineral oxides. The method was developed for pure metal oxides and was extended for contaminated samples. Some authors recommended that for the case of contamination samples, is better to use an acid-base titration method for the oxide suspension and the inflexion point provides the information about the pH<sub>PZC</sub> value. The advantage of the other methods was demonstrated when it is examine the temperature dependency of the point of zero charge.

Despite of these differences, the present paper measured the pH<sub>PZC</sub> for titanium dioxides (TiO<sub>2</sub>) using KNO<sub>3</sub> like electrolyte solution of different concentrations. The pH<sub>PZC</sub> value for TiO<sub>2</sub> was found to be 5.5, in a very good correlation with the data from the literature.

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