

**APPLICATIONS OF ACID-BASE TITRATION IN DETERMINATION OF
SURFACE CHARGE FOR ALUMINA**

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Abstract

The presence of alumina in the natural aquatic environments increases its applications in drinking and wastewater purification, in ceramics due to the interactions with organic and inorganic ions. The chemistry of alumina reactions in water is complex. The adsorption ability of alumina might be influenced by surface characteristics of the adsorbent (surface properties, density and pore volume, pore distribution, porosity, pH_{PZC}) as well as by the ionic strength, the pH of the solution, and the physiochemical properties of adsorbents.

The aim of the study is to evaluate the point of zero charge (pH_{PZC}) for alumina using the potentiometric “acid-base” titration and $NaNO_3$ like electrolyte solution. The pH_{PZC} for alumina was found to be 7.2, in a good correlation with the results obtained by other researchers.

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

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Introduction

The chemistry of alumina reactions in water is complex. The adsorption ability of alumina for organic or inorganic ions might be influenced by numerous factors. The mobility of cations or anions in aquatic environments is controlled by the adsorption at the solid-liquid interface and by the competition among various species for surface binding sites. This kind of processes is important in industry (corrosion, catalysis, molecular sieves, and semiconductor manufacturing). Alumina plays an important role in regulating the composition of soil–water, sediment–water and other natural aqueous systems. Active alumina, due to its high surface area, mechanical strength and thermal stability has found several applications as an adsorbent and catalyst. The acid–base properties of alumina are the main reason for its wide usage in water treatment technology, in adsorption processes (beside active carbon, silica gel and zeolites), for the removal of several organic compounds from water (organic contaminants, coagulants).

Classification of alumina

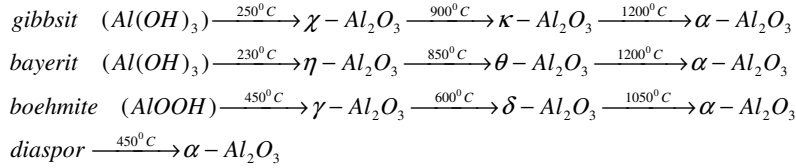
According to Haber, 1925 (after Kasprzyk-Hordern, 2004) alumina can be classified as follows:

	α - group	γ - group
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	-	gibbsit
$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	diaspor	boemite (bauxita)
Al_2O_3	corindon	γ - oxid

Aluminum trihydroxide (bayerite), which was not known in 1925 and, therefore not placed in Haber classification, should be located in γ -group beside gibbsite. The European authors use the above-mentioned classification. In the USA, the classification is as follows (after Kasprzyk-Hordern, 2004):

	α - grup	β - grup	γ - grup
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	gibbsit	bayerite	nordstrandit
$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	boemite	diaspor	-

Stumpf et al., 1950 (after Kasprzyk-Hordern, 2004) reported that apart from α - Al_2O_3 , another six crystal structures of alumina occur: γ , δ , κ , η , θ and χ - Al_2O_3 . The sequence of particular type formation under the thermal processing of gibbsite, bayerite, boehmite and diaspor is as follows:



Münster, 1957 proposed another classification, which was modified by Lippens, 1961 (after Kasprzyk-Hordern, 2004) based on the temperature of aluminium hydroxide formation. The two groups of alumina are:

- low-temperature alumina T_{low} : $Al_2O_3 \cdot nH_2O$ ($0 < n < 6$) obtained by dehydrating at temperatures not exceeding $600^\circ C$ (γ -group). This group belongs to: ρ , χ , η and γ - Al_2O_3 ;
- high-temperature alumina T_{high} : nearly anhydrous Al_2O_3 obtained at temperatures between 900 and 1000 C (δ -group). This group belongs to κ , θ and δ - Al_2O_3 .

All these structures are based on a more or less close-packed oxygen lattice with aluminum ions in the octahedral and tetrahedral interstices. In terms of catalytic activity, high-temperature alumina is less active than low-temperature alumina.

The main two parameters determining the catalytic properties of alumina are acidity and basicity. The Brönsted tip acidity – basicity is defined as the ability to release-accept protons, while Lewis acidity – basicity is the ability to release-accept electrons. Both Brönsted and Lewis acid sites are thought to be the catalytic center of alumina (fig. 1).

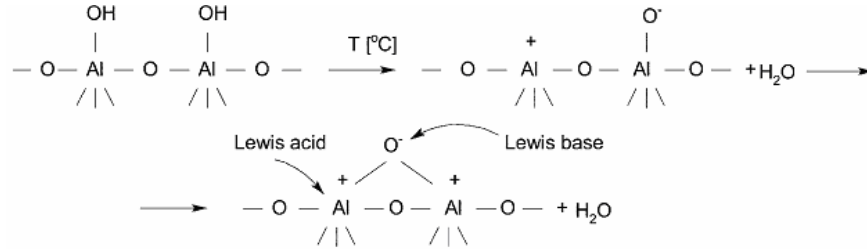


Fig. 1 The process of molecules chemisorption on the alumina surface

The point of zero charge (PZC or pH_{PZC}) is an important property of a mineral in aquatic systems. The single important parameter that describes the electric double layer of a mineral-water solution is the point of zero surface charge (PZC). By definition, the PZC point represents the pH value at which the net surface charge is zero ($\sigma_0 = 0$) (Isac et al., 1995, Preocanin and Kallay, 1998, White, 2004). This point represents the main condition in the aqueous solution at which the value of σ_0 is zero and this is determined by a particular value of the activity of the potential-determining ion. The models for the surface –OH groups of mineral oxides concerns the solid-liquid interface. Due to the

presence of water molecules, a complexity of alumina surface groups should be expected and we have to take into account the interaction of water with surface groups of minerals. In solution of alumina, an electric double layer interface is formed as a result of electrostatic interaction between the charge alumina surface and opposite ions from the bulk solution. The properties of the alumina surface depend on the pH value. In acidic medium, below pH_{PZC} , the surface is charged positively. At a basic medium ($pH > pH_{PZC}$) the surface is charge negatively (fig. 2):

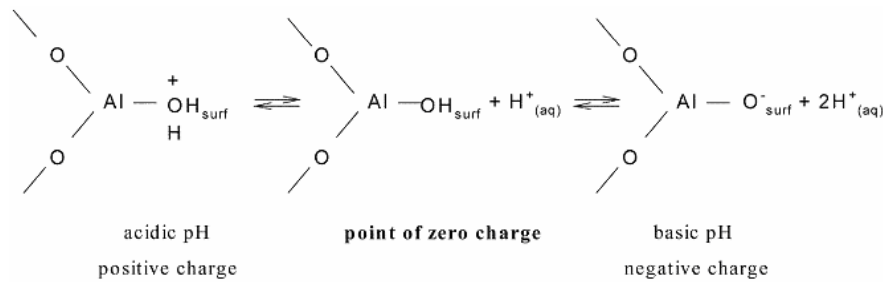
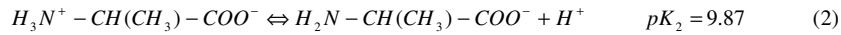
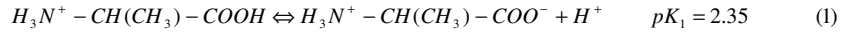


Fig. 2 The surface of alumina can be in a protonated / deprotonated status, depending on the pH value

The researchers often refer to the isoionic point (or isoionic pH,) compared by the isoelectric point (or point of zero charge) of compounds, such as proteins, amino/acids (Harris, 1998).



The isoionic point (or isoionic pH) is the pH obtained when the pure, neutral acid HA is dissolved in water. The isoelectric point (isoelectric pH or point of zero charge) is the pH at which the average charge of the acid is zero. Most of the molecules are in the uncharged form HA, and the concentrations of the ionic forms are equal to each other. For ex., when alanine is dissolved in water, the pH of the solution, by definition is the isoionic pH. Because alanine (HA) is the intermediate form of a diprotic acid (H_2A^+), the proton concentration is given by (Harris, 1998):

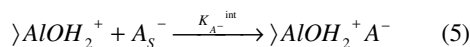
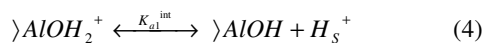
$$\text{isoionic point } [H^+] = \sqrt{\frac{K_1 K_2 c + K_1 K_w}{K_1 + c}}, \text{ where } c = \text{formal concentration of alanine.}$$

For 0.1 M alanine, the ionic pH is around $pH=6.12$. The point of zero charge is the pH at which the concentrations of H_2A^+ and A^- are equal and the average charge of

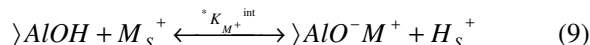
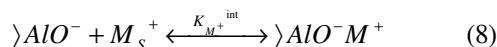
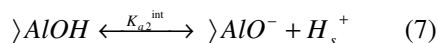
alanine is zero. The value of point of zero charge, calculated for alanine, with the equation (3) and is around pH=6.11.

$$pH = \frac{1}{2}(pK_1 + pK_2) \quad (3)$$

There are numerous models which describe adsorption/desorption process of a cation at an alumina/electrolyte interface. Among these models, we chose the model which was developed by Davies et al., 1978. According this model the reaction at the mineral/solution surface, can be describe by the following equations:



for the pH range below the point of zero charge ($pH \leq pH_{PZC}$)



for the range above pH_{PZC} ($pH \geq pH_{PZC}$). The signification of the formula above are given here: $\rangle AlOH_2^+$, $\rangle AlOH$ and $\rangle AlO^-$ represent positive, neutral and negative surface species, M^+ , A^- represent monovalent ions, $\rangle AlOH_2^+$, $\rangle AlO^- M^+$ represent surface complexes, the subscript «int» represent the intrinsic character of equilibrium constants and «s» represent the solid phase surface.

Materials and methods

In the literature, there are many methods used for the determination of pH_{PZC} . Among these, the most important are “mass titration method” and “acid-basic titration” (Preocanin and Kallay, 1998, Isac et al., 1995, Hurduc, 1979, Mândru and Ceacareanu, 1974).

In this paper, a commercial alumina (aluminum oxide for chromatography) was used for the determination of pH_{PZC} , using the acid-base titration method. The specific surface area was taken from literature (Todorovic and Milonjic, 2004) and was $110 \text{ m}^2 \cdot \text{g}^{-1}$. The electrolytic solution of NaNO_3 was obtained from commercial source.

The surface charge density of alumina in aqueous solution was determined by acid-base titration and involves two series of measurements. First series is in the presence of alumina (1.0 g of Al_2O_3 in 200 cm^3 aqueous electrolyte solution NaNO_3 of $1 \text{ mol}\cdot\text{dm}^{-3}$ concentration) and the second one with the same solution of electrolyte, but in the absence of alumina powder (blank). A solution of either HCl or NaOH (both $0.1 \text{ mol}\cdot\text{dm}^{-3}$) was used as titrant in the pH range from 3 to 10. 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. The temperature was kept almost constant at $28 \pm 1^\circ\text{C}$.

Results

The mass titration method was 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 also for contaminated samples. The principle of the method is simple: is necessary to add aliquots of metal oxides powder to the solution, which might acidified. The pH value of the solution changes gradually and approaches a constant value, which is the point of zero charge for pure oxide. If the sample is contaminated, the final pH is higher or lower than the pH_{PZC} , depending on the type and the amount of the contaminant. The method is simple from the experimental point of view and has some advantages: the experiments can be realized at an extremely low ionic strength, which cannot be achieved in the other method. This is important because only in the case of low ionic strengths the point of zero charge coincides with the isoelectric point. Also the method has the advantage that it studies the dependency of the point of zero charge with the temperature.

For the contaminated samples is better to use the acid-base titration method. The principle of the method is as follow: one needs to perform different volume of electrolyte solution to a constant mass of oxide powder. The inflexion point of the graph $\sigma = f(\text{pH})$ 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 surface charge density (σ_0 in $\mu\text{C}\cdot\text{cm}^{-2}$) was calculated from the following equation (Todorovic and Milonjic 2004):

$$\sigma_0 = \frac{\Delta v \cdot M \cdot F}{S \cdot A \cdot V} \cdot 100 \quad (10)$$

where Δv (cm^3) = the difference between the titrant volumes used for the suspension and the blank at given pH values, M = the molarity of the titrant, F = the Faraday constant (96.500 C), S ($\text{m}^2\cdot\text{g}^{-1}$) = the specific surface area of alumina ($110 \text{ m}^2\cdot\text{g}^{-1}$), A ($\text{g}\cdot\text{dm}^{-3}$) = the amount of alumina used for the titration, and V (cm^3) = the volume of the electrolyte used for the titration.

The surface charge densities as a function of NaNO_3 electrolyte concentration and pH, calculated from the equation above are presented in fig. 3.

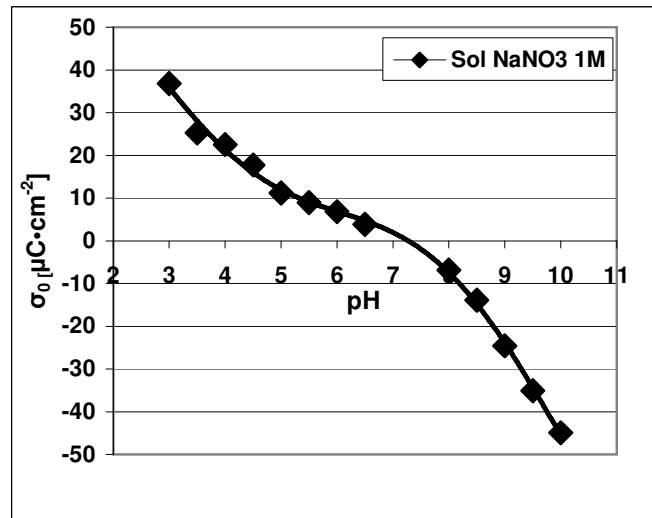


Fig. 3 Surface charge densities of alumina as a function of pH, for different ionic strengths of NaNO_3 solution, at constant temperature

The curves obtained with this ionic strength intersect the pH axis at $\text{pH}=7.2$ which represents the point of zero charge of the alumina ($\text{pH}_{\text{PZC}}=7.2$). The obtained pH_{PZC} value is 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 pH_{PZC} for oxides minerals depends on the alumina/solution ratio: increasing the alumina/solution ratio leads to an increase in the pH_{PZC} value.

The point of zero charge, pH_{PZC} , of alumina was assessed to vary from 7 to 10, depending on the type of alumina. Some relevant data for minerals are given in the tab. 1. In the literature, the pH_{PZC} values for alumina powders are very similar, indicating a small influence of the crystal structure. It has been shown (Dondur et al., 1995) that the pH_{PZC} value for AlOOH particles determined with the acid-base titration is at $\text{pH}=7.1$. This value is in good agreement with the value ($\text{pH}=7.3$) obtained by Siderova et al., 1979 for $\gamma\text{-Al}_2\text{O}_3$ in NaCl solution like electrolyte solution using the potentiometric titration method. Some results reported for Al_2O_3 minerals of varying porosity, show that the pH_{PZC} value is in the range from 6.5 to 6.9 (Goyne et al., 2002). The positive surface charge density increases with increasing ionic strength and acidity at $\text{pH} < \text{pH}_{\text{PZC}}$, while the negative surface charge density increases with increasing ionic strength and alkalinity of the solution at $\text{pH} > \text{pH}_{\text{PZC}}$ (Todorovic and Milonjic, 2004).

Tab. 1 The summary of the pH_{PZC} for alumina/hydrates alumina (Kasprzyk-Hordern, 2004)

Material	pH_{PZC}	Experimental method	Material	pH_{PZC}	Experimental method
α - Al_2O_3	8.4	Electrophoresis	γ - Al_2O_3	8.0	Electrophoresis
	9.2	Electrophoresis		9.0-9.7	Electrophoresis
	9.1	Electrophoresis		6.9	Mass titration
	9.2	Electrophoresis		8.4	Mass titration
	8.6-8.8	Stream. potential		8.0	Mass titration
	9.4	Stream. potential		7.8	Acid-base titration
	9.1	Stream. potential		8.8	-
	6.7	Electro-osmosis		8.47	-
	7.9	Mass titration		γ - $AlOOH$	9.4
	8.5	Mass titration	8.7		Potentiometric titration
	8	Electrokinetic	9.0		Potentiometric titration
	9.1	Measurement	7.7-9.4		Potentiometric titration
	8.7	-			
	8.4-9.2	-	δ - Al_2O_3	7.30	-

Conclusions

In conclusion, one may consider that the acid-base titration is a complementary method to the common mass titration for surface charge evaluation, which may have disadvantages in some specific cases. The mass titration method was found to be a “suitable” tool in the determination of point of zero charge for minerals oxides. The method was developed for pure metal oxides and was extended for contaminated samples. Despite of these differences, the present paper measured the pH_{PZC} for aluminum oxide (Al_2O_3) using $NaNO_3$ like electrolyte solution. The pH_{PZC} value for Al_2O_3 was found to be 7.2, in a very good correlation with the data from the literature.

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