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# SPECIFIC ADSORPTION OF CARBONATE IONS AT THE HEMATITE /AQUEOUS ELECTROLYTE SOLUTION INTERFACE

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A study on adsorption of carbonate ions at the α-$Fe_2O_3$/aqueous solution of $NaClO_4$ interface is presented. The concentration range of carbonate ions was from $1.00 \cdot 10^{-6}$ to $1.00 \cdot 10^{-3}$ M. The shape of carbonate ion adsorption plot vs. pH is characteristic for anions adsorption onto metal oxides and is called "adsorption envelope". To prevent carbon dioxide access to the solution, all measurements were conducted in a special chamber in nitrogen atmosphere.

*keywords: carbonate ions, adsorption, hematite*

## 1. INTRODUCTION

Adsorption of ions at the metal oxide/electrolyte solution interface results in changes of charge density distribution in the electrical double layer in such system. The triple layer model of the electrical double layer assumes that the cation specific adsorption leads to an increase of negatively charged groups ($SO^-Ct^+$) at the surface, whereas adsorption of anions causes an increase of positively charged groups ($SOH_2^+An^-$) (James and Parks, 1982; Schindler, 1981). Practical application is the most important aspect for experimental study of properties of the electrical double

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layer (edl). Zeta potential measurements give important information concerning the properties of the diffuse part of the edl. Very interesting aspects of ion adsorption at the metal oxide/electrolyte solution interface are systems where anions that form bidentate surface complexes and multivalent cations are presented (Collins et al., 1999).

Hematite is a commonly occurring natural form of iron oxide (Davis and Bhatanagar, 1995). Synthetic iron oxide pigments are of great economical importance due to their stability and their relatively low production costs (Eggleston and Stack, 2003). In order to obtain precise experimental results, the measurements were carried out on α-$Fe_2O_3$ with rigorously defined properties (Schwertmann and Cornell 1991).

Adsorption of ions at the metal oxide/water solution interface and its influence on edl is well described in literature. However in real dispersed systems, for instance in many technological processes and aqueous environment, the solid phase as well as of solution are rich in many organic and inorganic impurities.

## 2. MATERIALS AND METHODS

All measurements were carried out with hematite prepared according to the Matijevic's procedure (Matijevic, 1993) (acidic hydrolysis of $FeCl_3$). The powder specific surface, determined by the Braunauer-Emmet-Teller (BET) method (nitrogen adsorption - desorption) was 63.5 $m^2/g$. Polydispersity coefficient (PCS method) was 0.22, meaning that the investigated hematite was monodispersed. X-ray diffraction data confirmed its crystalline structure. NaOH and sodium carbonate were supplied by Polskie Odczynniki Chemiczne (Gliwice, Poland) and $NaClO_4$ by Aldrich. They were dispersed in doubly-distilled water. The surface charge of hematite was calculated by comparison of the potentiometric titrations curve of the oxide suspension and background electrolyte. The titrations of oxide suspensions were carried out in a thermostatic Teflon vessel in free of $CO_2$ nitrogen atmosphere at 25ºC with 0.1ºC accuracy using Julabo Refrigerated/Heating Circulator model F10 kept in a special chamber that isolated the titration vessel from the outer environment. During experiments nitrogen pressure in the chamber was slightly higher than that outside the chamber.

The measurements were performed using a PHM 240 Radiometer Research pH-meter with a glass and calomel reference electrode. The whole titration procedure (e.g. addition of titrant by Dosimat 665) and data acquisition from the pH-meter during measurement was computer-controlled. Potentiometric titration was carried out with the use of an automatic burette (Dosimat 665, Metrohm). For adsorption and potentiometric titration experiments the sample of α-$Fe_2O_3$ (1.0 g) was added to 50 $cm^3$ of solution.

The background electrolyte concentrations were $1.00\cdot10^{-1}$, $1.00\cdot10^{-2}$ and

$1.00{\cdot}10^{-3}$M respectively. The concentration range of carbonate ions in the system was from $1.00{\cdot}10^{-6}$ to $1.00{\cdot}10^{-3}$ M. The adsorption measurements of carbonate ions from the $NaClO_4$ solution were carried out with $^{14}C$ isotope as the radiotracer. The radioactivity of samples was measured by the LS5000 TD Beckman beta counter. The pH range was from 3 to 10.

The ζ potential measurements were carried out for concentration of electrolyte ranging from $1.00{\cdot}10^{-6}$ to $1.00{\cdot}10^{-3}$ M using the Malvern 3000 Standard Zetasizer. Each measurement of the ζ potential was repeated five times.

## 3. RESULTS AND DISSCUSSION

The surface charge is formed on the metal oxide as a result of ionization and complexation reactions of surface hydroxyl groups. Surface charge density as a function of pH is very important feature of surface properties of metal oxide/electrolyte solution systems. The $pH_{pzc}$ position depends on the alkaline-acidic character of the surface hydroxyl groups. For hematite this parameter is from 7.0 to 9.0 (Kosmulski, 2001).

The surface charge density dependence on pH for the α-$Fe_2O_3$/aqueous $NaClO_4$ solution indicates that the $pH_{pzc}$ is equal to 8.53. However, the ζ potential shows that $pH_{iep}$ = 8.7 – 9.0 (Fig. 1). The difference between these values may arise from α-$Fe_2O_3$ particle size fractions used in the potentiometric titration and electrophoretic measurements. In the latter method fine particles was used while in the potentiometric titrations fine particles as well as hematite aggregates were applied.

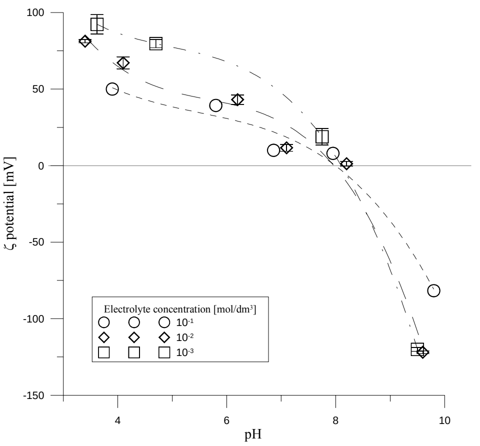

Fig. 1. ζ potential of α-$Fe_2O_3$ as a function of pH

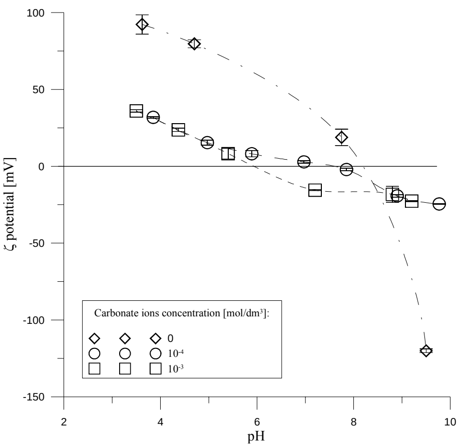

Fig. 2. ζ potential of α-$Fe_2O_3$ as a function of pH in $1.00{\cdot}10^{-3}$M $NaClO_4$ solution in the presence of carbonate ions

The ζ potential of α-$Fe_2O_3$ as a function of pH in the presence of carbonate ions is shown in Fig. 2. One can see that the isoelectric point of α-$Fe_2O_3$ is equal to pH=8.3 in the absence of carbonate ions and is shifted towards lower pH in the presence of carbonate ions with the increase of their concentration. At the initial concentration of $1.0\cdot10^{-3}$M carbonate ions the $pH_{iep}$ is equal to 6.2.

Specific adsorption of anions at the metal oxide/electrolyte interface leads to a decrease of $pH_{iep}$ due to the increase of concentration, complexed by anions, positively charged groups at the α-$Fe_2O_3$/electrolyte interface and simultaneous decrease of concentration of ionized positively charged forms. Because the diffuse layer charge is proportional to the algebraic sum of negatively and positively charged groups, the decrease of concentration of positively charged groups leads to majority of negative charged ones, and decrease of zeta potential making a shift of $pH_{iep}$ towards lower pH.

The adsorption densities and equilibrium concentrations of carbonate ions as a function of pH are depicted in Figs 3, 4, 5 and 6.

The initial concentration of carbonate ions was from $1.00\cdot10^{-3}$ M to $1.00\cdot10^{-6}$ M respectively. The shapes of adsorption of carbonate ions plot vs. pH are characteristic for anions adsorption onto metal oxides and are called “adsorption envelope”. One can observe an increase of adsorption and decrease of concentration of carbonate ions with a decrease of pH of the electrolyte. Such progress of adsorption is characteristic for specific anion’s adsorption onto metal oxides. The edge of adsorption moves to acidic environment with the increase of the concentration of carbonate ions. It means that carbonate ions adsorption may go through exchange of hydroxyl groups with inner-sphere complex formation or through decreasing hydrogen ions population with outer-sphere complex formation.

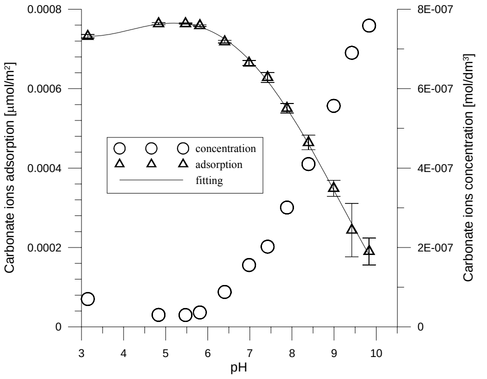

Fig. 3. Adsorption density as a function of solution pH for α-$Fe_2O_3$/$1.00\cdot10^{-3}$ M $NaClO_4$ + $1.00\cdot10^{-6}$ M $HCO_3^-$ system. Fitting curve for pK = 3.685 and n = 0.46

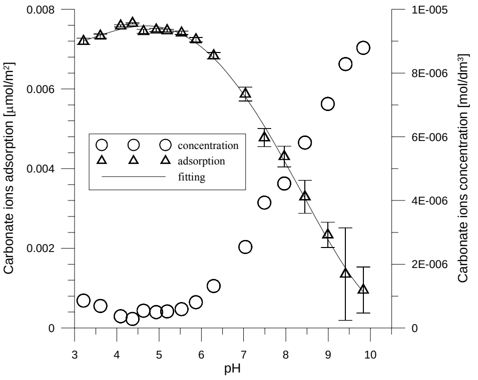

Fig. 4. Adsorption density as a function of solution pH for α-$Fe_2O_3$/$1.00\cdot10^{-3}$ M $NaClO_4$ + $1.00\cdot10^{-5}$ M $HCO_3^-$ system. Fitting curve for pK = 3.685 and n = 0.46

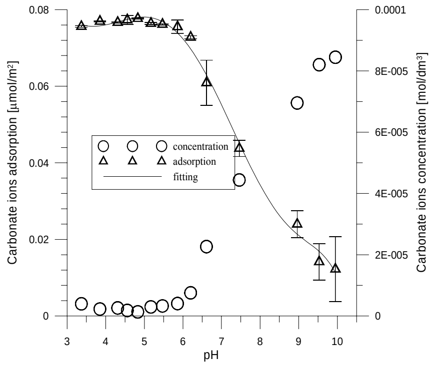

Fig. 5. Adsorption density as a function of solution pH for $\alpha$-$Fe_2O_3/1.00 \cdot 10^{-3}$ M $NaClO_4$ + $1.00 \cdot 10^{-4}$ M $HCO_3^-$ system. Fitting curve for pK = 3.684 and n = 0.52

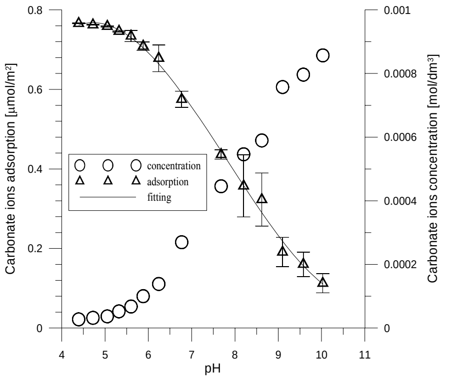

Fig. 6. Adsorption density as a function of pH solution for $\alpha$-$Fe_2O_3/1.00 \cdot 10^{-3}$ M $NaClO_4$ + $1.00 \cdot 10^{-3}$ M $HCO_3^-$ system. Fitting curve for pK = 3.685 and n = 0.46

Table 1. Parameters calculated from adsorption data

| Initial concentration of carbonate ions mol/dm$^3$ | pK | n | $pH_{50\%}$ | $\Delta pH_{10\text{-}90\%}$ |
|---|---|---|---|---|
| $1.00 \cdot 10^{-6}$ | 3.685 | 0.46 | 8.025 | 4.175 |
| $1.00 \cdot 10^{-5}$ | 3.685 | 0.46 | 8.049 | 4.107 |
| $1.00 \cdot 10^{-4}$ | 3.684 | 0.52 | 8.172 | 3.706 |
| $1.00 \cdot 10^{-3}$ | 3.685 | 0.46 | 8.025 | 4.175 |

where: pK – is the constant of the reaction; n – is the number of OH- released per carbonate ion; $pH_{50\%}$ and $\Delta pH_{10\text{-}90\%}$ - are the parameters of edge of adsorption

Table 2. Comparison of specific surface of hematite before and after adsorption measurements

| Parameter | Hematite | Hematite after carbonate ions adsorption | |
|---|---|---|---|
| | | Initial concentration $1.0 \cdot 10^{-4}$ M | Initial concentration $1.0 \cdot 10^{-3}$ M |
| BET surface area | 63.5 m$^2$/g | 125.2 m$^2$/g | 127.9 m$^2$/g |
| BJH cumulative adsorption surface area of pores between 1.7nm<d<300nm | 0.2 cm$^3$/g | 0.4 cm$^3$/g | 0.4 cm$^3$/g |
| BJH cumulative desorption surface area of pores between 1.7nm<d<300nm | 0.2 cm$^3$/g | 0.4 cm$^3$/g | 0.4 cm$^3$/g |

One can see that the values of equilibrium constants do not depend on the initial concentration of carbonate ions. It means that there is no influence of the electrostatic component on adsorption. The quantity of freed $OH^-$ ions is also unchanged and is smaller than 1. As a consequence the adsorption edge parameters are constant. From these data one can conclude that alkaline iron carbonates can be formed on the α-$Fe_2O_3$ surface.

In order to verified the changes that took place on the surface of the oxide after adsorption, iron oxide was examined and the results were compared. One can conclude from Table 2 that not only BJH cumulative adsorption surface area of pores but also BET surface area increased. It can be explained by the formation of carbonate layer on the surface of α-$Fe_2O_3$.

Figure 7 shows changes in the size distribution of hematite after adsorption of carbonate ions. These results were confirmed by the AFM (Atomic Force Microscopy) method (Fig. 8).

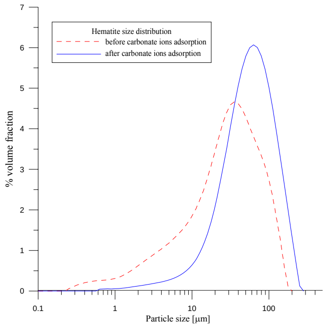

Fig. 7. Size distribution of hematite before and after adsorption measurements by Static Light Scattering

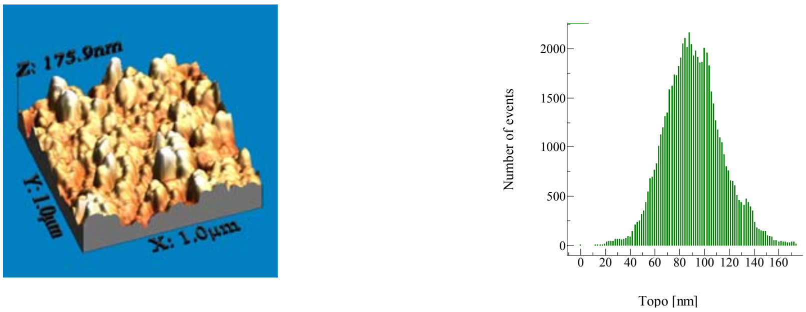

Fig. 8a. 3D image and roughness histogram before adsorption of carbonate ions

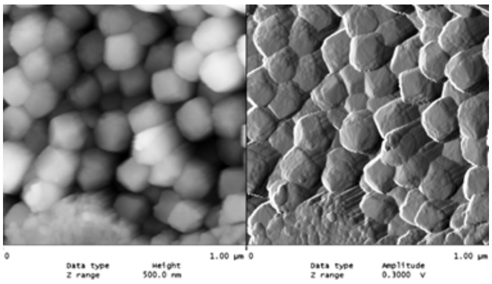

Fig. 8b. AFM pictures of hematite samples before adsorption of carbonate ions

Fig. 8c. 3D image and roughness histogram after adsorption of carbonate ions

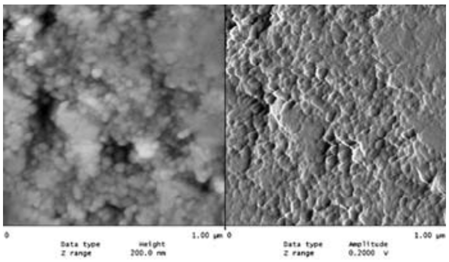

Fig. 8d. AFM pictures of hematite samples after adsorption of carbonate ions

Comparing the above results one can conclude that there are clear differences in shape and size of hematite crystallites. Hematite sample after adsorption is more crumbled and crystallites are more oval in the shape. The surface becomes smoother. It was confirmed by the RSM roughness parameter equal to 23.4 before and to 8.1 after adsorption measurements.

The IR spectroscopy revealed that two new peaks were present after adsorption measurements. The broad and intense band at 3444 cm$^{-1}$ can be ascribed to the stretching mode of hydroxyl group and water molecule. The peaks at 1320 - 1630 cm$^{-1}$ correspond to stretching mode in the carbonate molecule (Frost and Dickfos, 2007, Ferretto and Glisenti, 2008; de Faria and Lopes, 2007).

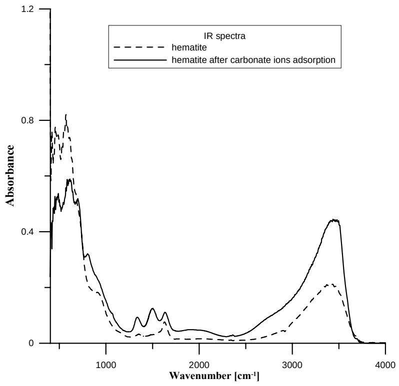

Fig. 9. IR spectra of hematite before and after adsorption measurements

## 3. CONCLUSIONS

Carbonate ions adsorption leads to an exchange of surface hydroxyl with carbonate groups that causes an increase of negatively charged groups on the hematite surface and, in consequence, a decrease of $\zeta$. The shapes of the carbonate ions adsorption vs. pH plot are characteristic for anions adsorption onto metal oxides and are called “adsorption envelope”. One can observe an increase of adsorption and decrease of concentration of carbonate ions in solution with a decrease of pH of the electrolyte. Carbonate ions cause also changes of the surface properties of the oxide.

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Adsorpcja jonów węglanowych powoduje zwiększenie negatywnie naładowanych grup powierzchniowych obecnych na powierzchni hematytu i w konsekwencji spadek potencjału dzeta. Kształt krzywych adsorpcji jest charakterystyczny dla adsorpcji anionów na tlenkach metali. Obserwowane są ponadto zmiany we właściwościach powierzchniowych, np. wzrost powierzchni właściwej hematytu po adsorpcji jonów węglanowych, zmiany w rozkładzie ziarnowym, czy zmiany w widmach IR.

*słowa kluczowe: jony węglanowe, hematyt, adsorpcja*