



# Mineral surface charge development in mixed electrolyte solutions



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## ABSTRACT

Effects of competing counterions with different charge-to-size ratios on potential-determining ion (*pdi*;  $H^+$ ,  $OH^-$ ) adsorption at mineral/water interfaces were resolved in mixtures of aqueous solutions of NaCl and  $NaClO_4$  solutions. These effects were monitored on two synthetic goethite ( $\alpha$ -FeOOH) particle preparations with distinct charge uptake capacities arising from differences in surface roughness. Charge development at these mineral surfaces was chiefly explored by high precision potentiometric titrations at 25 °C. These measurements confirmed that the greater charge-to-size ratio chloride ion not only promoted greater surface charge, but also had pronounced effects in perchlorate-dominated solutions. Cryogenic X-ray photoelectron spectroscopic measurements confirmed that perchlorate retains significant loadings at the goethite surface, even in the presence of chloride. Molecular dynamics simulations of the (110) plane of goethite exposed to these mixed solutions showed that chloride compressed the interfacial region containing electrolyte ions. Perchlorate, on the other hand, is not only present over a thicker region of the interface but also promotes an additional outer-sphere sodium species.

These findings were used to develop a thermodynamic adsorption model predicting charge development at these mineral surfaces. The model involves a new formulation accounting for coexisting ion-specific regions each with their distinct compact plane capacitance values. The model can predict charge development in any mixtures of NaCl and  $NaClO_4$  contacted with goethite particles of contrasting charge uptake capacities without any additional parameters. This model can also be applied to a broader range of material surfaces.

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## 1. Introduction

Reactions at mineral particle surfaces contacted with aqueous media have been the object of a variety of studies due to the abundance and reactivity of these compounds in natural and technological systems [1–4]. Mineral particle surfaces expose various types of (hydr)oxo functional groups capable of adsorbing and exchanging with ions, and of developing surface charge manifested as interfacial electrostatic potentials. Surface charge development principally arises from the adsorption of potential-determining ions (*pdi*;  $H^+$ ,  $OH^-$ ), the charges of which are counterbalanced by oppositely charged electrolyte counterions. The extent of mineral surface charge development is notably related to the identity of the counterions, one that can *a priori* be rationalized on the basis of the charge-to-size ratio, as for example seen in the order  $ClO_4^- < NO_3^- < Cl^-$  [5]. This order conveys the notion that smaller counterions of the same charge are more effective charge-neutralizing agents than bigger ones [6].

Studies dedicated to mineral surface charge development predominantly involve one type of environmentally relevant

background electrolyte [7,8], which is often considered to be inert, although more recent efforts have been pointing to the contrary in some cases [9,10]. Effects of mixed electrolyte are, on the other hand, scarcely considered [11,12], despite their importance in colloidal and environmental chemistry, as well as geochemistry. For example, such systems are of great interest for natural and agricultural soils, where organic and inorganic ions typically coexist [13–15]. Much uncertainty however lies on the impact of coexisting electrolyte ions, and particularly those of different size-to-charge ratios, on mineral surface charge development and electric double layer (EDL) properties.

This study has therefore been devised to address this issue further by resolving the competitive effects of two counteranions of considerably different charge-to-size ratios ( $5.98 \times 10^{-3}$  1/pm for  $Cl^-$  and  $3.47 \times 10^{-3}$  1/pm for  $ClO_4^-$ ) on mineral surface charge development. Two types of goethite ( $\alpha$ -FeOOH) particles with distinct sizes, specific surface area and surface roughness were considered, notably to address effects of micropores excluding the larger  $ClO_4^-$  anion in this process. Surface charge was investigated by high precision potentiometric titrations and zeta potential measurements in mixed aqueous solutions of  $NaClO_4$  and NaCl. Molecular dynamics (MD) simulations of the representative (110) plane of goethite were also carried out to resolve molecular-scale aspects

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of these mixed systems. A thermodynamic modeling strategy that can effectively account for these phenomena, and that is consistent with concepts derived from molecular simulations, was developed to predict all experimental data.

## 2. Materials and methods

### 2.1. Mineral synthesis

All mineral particles and titrants were prepared under conditions aimed at minimizing adventitious contaminations. Suspensions and solutions were prepared with deionized (DI) (MilliQ) water and stored in sealed polyethylene bottles to avoid sample contamination with silica and carbonate. NaOH titrants were freshly prepared from carbonate-free 50% (w/w) solutions of NaOH. All experimental procedures were performed under an atmosphere of N<sub>2</sub>(g) to minimize CO<sub>2</sub>(g) contamination. Although CO<sub>2</sub>(g) could not be strictly eliminated from some of the steps of suspension preparation, such as washing, carbonate contamination mostly occurred at particle surfaces only. These impurities were generally removed by exhaustive degassing sessions under acidic (pH 3–4) conditions prior the onset of the experiments. Overhead propeller stirrers were used instead of magnetic stirrers throughout the synthesis procedures to minimize damaging of mineral particles. All synthesis procedures were conducted at 25 °C.

A suspension of goethite particles with a specific surface area of 66 m<sup>2</sup>/g (GT66) was prepared by drop-wise addition of 2.5 M NaOH to a vigorously stirred 0.15 M Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution until the suspension reached a pH of 12 [16]. The resulting product was placed into an oven and converted to goethite at 50 °C for 24 h. Synthesis of goethite particles with a specific surface area of 122 m<sup>2</sup>/g (GT122) was prepared by drop-wise addition of a 1.0 L solution of 0.5 M NaHCO<sub>3</sub> to a vigorously stirred 1.0 L solution of 0.4 M Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O [17]. During this procedure, the solution color turned from orange to brownish red with no visible precipitate. It was sonicated for 60 s to promote particle homogeneity and dispersity, then cooled to 15 °C to prevent conversion to other undesirable iron (oxy)hydroxide phases. The suspension was then dialyzed at 25 °C for the 3 following days, with the dialysis water changed 3 times a day. The pH of the resulting ferrihydrite suspension was adjusted to pH 12 by drop-wise addition of 5 M NaOH to the continuously stirred suspension, resulting in color change from brownish red to brown. The suspension was thereafter heated at 90 °C for 24 h, forming a light orange precipitate. All mineral suspensions were washed with DI water, then dialyzed. Dialysis water was changed three times per day until its conductivity was on the same order of magnitude as that of DI water.

### 2.2. Particle characterization

Portions of all dialyzed suspensions were dried in an oven at 40 °C for 24 h. The resulting powders were ground in an agate mortar and used for structure determination using powder X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Particle specific surface area and porosity were, respectively, measured by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, based on 90-point N<sub>2</sub>(g) adsorption–desorption isotherms. Particle shape was determined by transmission electron microscopy (TEM). Salient physico-chemical attributes of the particles are reported in Table 1.

XRD measurements were carried out on a Bruker D8 Advance device working in  $\theta$ – $\theta$  mode using Cu K $\alpha$  radiation. FTIR spectra (Bruker Vertex 70/V equipped with DLaTGS detector at 298 K) were collected on dry mineral powders pressed on an attenuated

**Table 1**

The surface characteristics of synthetic FeOOH particles.

Properties	GT66	GT122
Length (nm) <sup>a</sup>	82–358 (218)	52–118 (77)
Width (nm) <sup>a</sup>	12–34 (22)	7–22 (12)
BET (m <sup>2</sup> /g) <sup>b</sup>	66	122
BJH pore diameter (nm) <sup>c</sup>	20.8	10
BJH pore volume (cm <sup>3</sup> /g) <sup>c</sup>	0.42	0.39
t-Plot micropore area (m <sup>2</sup> /g) <sup>c</sup>	4.90	5.76
Major crystal plane	90–95% (110)	92–94% (110)
Minor crystal plane	5–10% (021)	6–9% (021)
–OH (sites/nm <sup>2</sup> ) <sup>d</sup>	3.25–3.48	3.31–3.39
$\mu$ -OH (sites/nm <sup>2</sup> ) <sup>d</sup>	3.25–3.48	3.31–3.39
$\mu_3$ -OH (sites/nm <sup>2</sup> ) <sup>d</sup>	8.18–8.63	8.37–8.54

<sup>a</sup> Particle dimensions were estimated from TEM imaging, the values within the parenthesis were obtained as a mean value of all obtained results.

<sup>b</sup> Determined from BET analysis.

<sup>c</sup> Determined from BJH analysis; <sup>d</sup> Total surface site densities over all surface area.

total reflectance cell (Golden Gate, single bounce diamond) under vacuum. Characteristic O–H stretching and bending modes were observed to identify the present crystallographic phases. All characteristic XPS spectra were collected with a Kratos Axis Ultra electron spectrometer equipped with a delay line detector. A monochromatic Al K $\alpha$  radiation source operated at the power of 150 W, and a hybrid lens system with a magnetic lens and a charge neutralizer were used during measurements. Specific surface area and porosity determinations were conducted on 90-point N<sub>2</sub>(g) adsorption/desorption isotherms (Tristar, Micrometrics). These measurements were performed on the powders previously dried overnight at 110 °C under a flow of dry N<sub>2</sub>(g). This drying temperature was sufficiently high to desorb surface water while not altering bulk structure. Lastly, TEM was used for particle imaging of air-dried samples placed on a copper grid and covered with formvar film. Imaging was carried out with a JEOL-1230 instrument working at 80 kV and a point resolution of around 3.4 Å.

### 2.3. Potentiometric titrations

Potentiometric titrations were performed in ionic strengths of 3, 10 and 100 mM under an atmosphere of humidified N<sub>2</sub>(g) and at a constant temperature of 25 °C. This ionic strength was achieved by addition of dry NaCl or NaClO<sub>4</sub> salts to the corresponding mineral suspensions or titrant solutions (e.g. 10 mM acid in 90 mM electrolyte for  $I = 100$  mM). Titrations in mixed NaCl/NaClO<sub>4</sub> electrolyte solutions were carried out at a total ionic strength of  $I = 100$  mM using titrants made in either NaCl or NaClO<sub>4</sub>. Exact ionic compositions were tracked for each experimental data point and fully taken in account in the thermodynamic modeling calculations to be described in Section 3.

All suspensions ( $\sim 400$  m<sup>2</sup>/L) were first acidified to pH 3–3.5 and stirred in an atmosphere of humidified N<sub>2</sub>(g) for several hours to evacuate dissolved and adsorbed carbonate ions. Alkalimetric titrations were thereafter carried out using an automated system whereby 5–20 electromotive force (*e.m.f.*) measurements of the glass pH electrode were carried out at a 300 s interval. The titrant was added only when the *e.m.f.* drift was less than 0.6 mV/h, or if the measurement time exceeded 100 min. This experimental protocol ensured that (near) equilibrium with respect to proton adsorption was reached at every point. All titrations were complete within 3000 min.

The electrochemical cell consists of a Metrohm 6.0133.100 pH electrode and 6.0726.100 Ag|AgCl reference electrode filled with 100 mM NaCl solution. This set-up minimized variations in liquid junction potential during the titrations. The cell was also re-calibrated after each titration in the ionic medium of interest to verify

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