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Influence of kinetics on the determination of the surface reactivity of oxide suspensions by acid–base titration

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Abstract

The effect of acid–base titration protocol and speed on pH measurement and surface charge calculation was studied on suspensions of γ-alumina, hematite, goethite, and silica, whose size and porosity have been well characterized. The titration protocol has an important effect on surface charge calculation as well as on acid–base constants obtained by fitting of the titration curves. Variations of pH versus time after addition of acid or base to the suspension were interpreted as diffusion processes. Resulting apparent diffusion coefficients depend on the nature of the oxide and on its porosity.

Keywords: Acid–base titration; Surface charge; Oxides; Titration kinetics; Surface acid–base constants; Surface complexation

1. Introduction

The sorption properties of metal oxides and hydroxides have been the subject of many investigations during recent years because they play an important role in the transport of toxic and radioactive species in the environment, in catalytic processes, in corrosion inhibition, etc. The sorption properties of such compounds are generally described by the acid–base behavior of superficial hydroxyl groups using one of the surface complexation models (1-pK [1] or 2-pK [2] monosite models, 1-pK multisite model [3,4]). The acid–base properties are defined by several parameters whose number depends on the model used: surface site density, acidity constants, and electrostatic parameters. All these parameters are generally determined by fitting the data acquired from titration experiments, in which a suspension of the solid is titrated in order to determine the quantity of acid or base necessary to protonate or deprotonate the surface hydroxyl groups. Hence, the accuracy of the determination of acido-basic parameters depends on the accuracy of the titration experiments. The quality of titration data can be affected by several factors. A number of errors are associated with instrumentation and measurements methods: poor calibration and drift of electrodes, junction potentials, underestimated activity coefficients, and effect of suspension on electrode response [5]. Other sources are intrinsic to the solid: solubility, presence of impurities, kinetics of the processes at the interface, and evolution of the solid. In previous investigations, we have evidenced that transformation of γ-alumina into bayerite in aqueous solutions results in a continuous modification of the acid–base parameters of the solid [6]. We also showed that the solubility has a large effect on the calculated surface charge of alumina and a correction method was developed [7]. All these factors may explain why a large scatter is observed for acid–base parameters obtained by different authors on oxides with the same chemical composition [8].

The present study is devoted to the kinetic aspect of titration. Some authors have already drawn attention to this effect [9,10]. Sorption of protons during titration of oxides is often described as a two-step process: a fast initial uptake followed

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by a slower process [11]. The fast step is attributed to the reaction of protons with the superficial hydroxyl groups and the time necessary to reach equilibrium is often considered to be less than a few minutes. The slower process is poorly understood and numerous assumptions have been published, such as a rearrangement of protons at the surface [11], their diffusion into micropores [10] or macropores [12], in the lattice of the oxide [13], or in the hydrated layer formed on the surface [10], and also the diffusion of oxygen ions from the bulk of the solid to its surface [13].

In order to circumvent the slower step, "fast" titrations with a short delay between each addition of acid or base were proposed for nonporous solids (ZnO [14,15] or α-Fe_2O_3 [10], for example). Thus, the titration curve should only correspond to the reaction with surface hydroxyl groups. However, the appropriate time necessary to separate the fast and the slow steps cannot be easily determined.

The present study was initiated after several observations during titration experiments performed with aluminum, silicon, and iron oxides. Titration curves depend, often strongly, on the titration speed: time interval between the addition of each aliquot of acid and base, and volume of each aliquot. Most often a hysteresis appears when a reverse titration is performed. As a consequence, titration speed has an influence on the calculated acid–base constants and site density, denoting that equilibrium, which is supposed to be met in surface complexation models, is not achieved.

The aim of the present work was to study in detail the effect of kinetics on the validity of the data obtained by titration, to determine the procedures leading to minimum errors, and to understand, when possible, the causes of the kinetic effects observed. Several oxi-hydroxides, largely studied in the literature and with different morphologies were chosen: γ-alumina, goethite, hematite, and silica. For this purpose, acid–base titrations with various speeds and procedures were performed. The influence of equilibration time on surface charge calculation was studied. Modeling of charge vs pH curves was undertaken to estimate the influence of experimental procedures on calculated acidity constants. In order to associate the results with the characteristics of the solids, we used chemical analysis, X-ray diffraction, high-resolution scanning electron microscope, surface area and porosity measurements, and X-ray photoelectron spectroscopy.

2. Materials and methods

2.1. Chemicals and solutions

The solids used in this study were γ-alumina (Merck 90), goethite (BASF), hematite (two samples from Alfa of 99.8 and 99.945% purity), and silica (Merck 100) (Table 1). A hydration period of 1 day (ferric oxi-hydroxides and silica) or 15 days (γ-alumina) was performed prior to titration. In the case of γ-alumina, a previous study [6] has shown that hydration leads to an evolution of the surface reactivity by transformation into bayerite. This evolution is fast in the first days of hydration, and then slows down. We have chosen a hydration time of 15 days, so that the effect of evolution on surface reactivity will be negligible during the time required for titration or batch experiments.

Other reagents were HNO_3 and NaOH 0.1 M (Normadose, Prolabo), sodium nitrate p.a. (Prolabo), and deionized water (resistivity $> 16\ \text{M}\Omega$).

2.2. Titration methods

"Continuous" titrations were performed using a Metrohm automatic system monitored by a homemade software, with a combined Ag/AgCl glass electrode (Metrohm) calibrated with disposable standard buffer solutions (Centipur, Merck). The test solution vessel (100-mL PE bottle) with alumina (0.1 g), goethite (0.3 g), hematite (0.5 g), or silica (0.05 g) equilibrated with 50 mL of 0.1 M $NaNO_3$, with a continuous flow of argon to prevent CO_2 uptake, was immersed in a water bath thermostated at $25.0 \pm 0.1\,^\circ\text{C}$. The solid/solution ratio was chosen to obtain the same order of magnitude for surface area in all suspensions (ca. 5 to 15 m^2). The added volumes of acid or base and equilibration time before the next addition were varied according to the pH value since the stabilization of the measured potential was faster for pH values far from the neutral range. Three protocols of such titration methods were used (Table 2).

Continuous titrations with longer and constant intervals (1 h) between each addition of acid or base were also used.

"Batch" titrations were performed with γ-alumina by stirring 100 mg of powder in 50 mL of a 0.1 M $NaNO_3$ solution at $25 \pm 1\,^\circ\text{C}$ during time intervals of 7, 18, and 48 h. The initial pH was adjusted by addition of NaOH or HNO_3. After the

Table 1
Morphological characteristics of the solids used in the study

	Alumina	Goethite	Hematite, 99.8%	Hematite, 99.945%	Silica
SEM observation	Agglomerates 50–100 µm	Acicular crystals	Spheroidal crystals	Spheroidal crystals	Agglomerates 100–200 µm
Crystal dimensions (nm)	3–4	≈600 × 50 × 50	50–100	50–100	[a]
BET surface area (m^2/g)	152	20	7.7	9.4	296
t-plot surface area (m^2/g)	167	21	10	12	261
t-plot micropore volume (mL/g)	0	0.0003	0	0	0.012
Langmuir surface area (m^2/g)	139	20	6.2	7.9	287
BJH pore volume (mL/g)	0.21	0.054	0.034	0.039	1.06
BJH desorption size distribution	<8 nm: 76% 20–80 nm: 9%	<8 nm: 11% 20–80 nm: 57%	<8 nm: 4% 20–80 nm: 51%	<8 nm: 5% 20–80 nm: 52%	<8 nm: 11% 10–20 nm: 75%

[a] Unavailable data (amorphous solid).