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# Protonation enthalpies of metal oxides from high temperature electrophoresis

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ABSTRACT

Surface protonation reactions play an important role in the behavior of mineral and colloidal systems, specifically in hydrothermal aqueous environments. However, studies addressing the reactions at the solid/liquid interface at temperatures above 100 °C are scarce. In this study, newly and previously obtained high temperature electrophoresis data (up to 260 °C) – zeta potentials and isoelectric points – for metal oxides, including $SiO_2$, $SnO_2$, $ZrO_2$, $TiO_2$, and $Fe_3O_4$, were used in thermodynamic analysis to derive the standard enthalpies of their surface protonation. Two different approaches were used for calculating the protonation enthalpy: one is based on thermodynamic description of the 1-p*K*a model for surface protonation, and another one on a combination of crystal chemistry and solvation theories which link the relative permittivity of the solid phase and the ratio of the Pauling bond strength and bond length to standard protonation enthalpy. From this analysis, two expressions relating the protonation enthalpy to the relative permittivity of the solid phase were obtained.

## 1. Introduction

The processes that occur in the electrical double layer (EDL) at the interface of solid oxide and aqueous solution have a major role in the behavior of mineral and colloidal systems and their reactions [1,2]. A wide range of applications benefit from the knowledge of the surface reactions ranging from biological and geochemical to industrial systems [3–5]. Protonation of the surface is a particularly important process controlling the reactivity of minerals. Surface reactions can be expressed in the following way according to a single site model [6].

$$\mathrm{Me{-}O^- + H^+ = Me{-}OH} \quad \log K_1 \tag{1}$$

$$\mathrm{Me{-}OH + H^+ = Me{-}OH_2^+} \quad \log K_2 \tag{2}$$

$$\mathrm{Me{-}O^- + 2H^+ = Me{-}OH_2^+} \quad \log K_{pzc} \tag{3}$$

where $\mathrm{Me{-}O^-}$, Me–OH, and $\mathrm{Me{-}OH_2^+}$ represent surface species, and *pzc* stands for the point of zero charge. Electrolyte ion binding to the surface can be represented by the following reactions:

$$\mathrm{Me{-}O^- + M^+ = Me{-}O^-{-}M^+} \quad \log K_{\mathrm{M^+}} \tag{4}$$

$$\mathrm{Me{-}OH_2^+ + L^- = Me{-}OH_2^+{-}L^-} \quad \log K_{\mathrm{L^-}} \tag{5}$$

where $M^+$ and $L^-$ represent, respectively, cations and anions of a background electrolyte. Eq. (3) is often used to describe the single site 1-p*K* complexation model.

Several experimental methods exist to study the solid/aqueous interface, particularly to derive protonation constants of Eqs. (1)–(3), such as acid–base titration and particle electrophoresis [7,8]. Variation in the protonation constants with temperature allows estimating another important parameter of the solid/aqueous interface – the protonation enthalpy. Protonation enthalpies of metal oxide materials are mainly derived by two methods: calorimetric studies from titrations and heats of immersion [9–11], and from the temperature dependence of the point of zero charge (PZC) or isoelectric point (IEP) [12–16]. However, only a few PZC and IEP studies have been successful in extending the working temperature above 100 °C [12,13,17–19] for the derivation of the protonation constants. In addition, theoretical models have been developed to calculate the protonation constants and protonation enthalpy of oxides and silicates as a function of the relative permittivity (or dielectric constant) of the material, $\varepsilon_r$, and the ratio of the Pauling bond strength to bond length, $s/r_{\mathrm{Me-OH}}$ [20–22]. These models rely on the available experimental data of protonation constants and protonation enthalpies. Furthermore, surface dissolution kinetics is influenced by the magnitude and sign (i.e., endothermic or exothermic) of protonation enthalpies through the magnitude of the activation enthalpy [9].

One of the goals of this paper is to analyze all available high temperature electrophoretic data for a number of oxide materials

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and to derive the protonation enthalpies from these data. In Section 2, we present a new set of experimental data on high temperature electrophoretic mobility, zeta potential, and IEP for amorphous silica. In Section 3, we derive the protonation enthalpy for several materials using two methods: (1) thermodynamic treatment based on single site1-p*K*a model of surface complexation (Eq. (3)) [6] and (2) the model based on crystal chemistry and solvation theory [22]. In addition, we have reevaluated the expression of the protonation enthalpy and obtained two new expressions dependent on the relative permittivity of the material.

## 2. Experimental

### 2.1. High temperature electrophoresis cell

A high temperature electrophoresis cell recently developed in our laboratory was used to perform the electrophoretic mobility measurements. The system design and operation have been described in detail in our previous publications [17,18,13,19]. Briefly, this system uses the classical principle of particle electrophoresis, which implies that the velocity of charged suspended particles moving in an applied electric field is a function of the zeta potential on the particle surface. Particles were visualized inside the high temperature cell using a long focus microscope and digital camera under dark-field illumination, which allowed for sub-micron size detection. The system was able to operate at temperatures up to 260 °C and pressures up to 65 bar. The internal pressure of the system was adjusted using pressure-relief valves and kept above the gas–liquid equilibrium for water at every temperature. The particle movement was registered over the reference distance of 0.25 mm, which was calibrated with a stage micrometer (1 mm/100 divisions).

### 2.2. Materials

Amorphous silica ($SiO_2$) particle size standards (Polysciences, Inc.) – 100 ± 30 nm – were used for the electrophoresis experiments. The experimental $SiO_2$ suspensions were prepared with $1 \times 10^{-3}$ mol kg$^{-1}$ NaCl(aq) as background solution with solid loading of about 1.7 g L$^{-1}$. The suspensions were ultrasonicated for 1 h, and the size of the particles was measured at 25 °C using a dynamic light scattering instrument (Nanosizer, Malvern Instruments). All prepared suspensions showed a polydispersity index of 0.2 or less, which is indication of highly dispersed suspensions with minimal aggregation. The results of the particle size measurements are shown in Fig. 1. According to the light scattering measurements (Fig. 1), the average particle size was 115 nm for the nominal 100 nm standard.

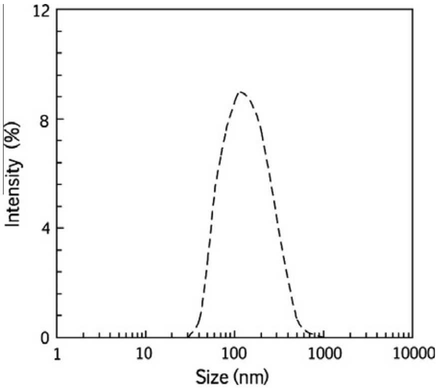

**Fig. 1.** Size distribution of $SiO_2$ particle standards by dynamic light scattering (*x*-axis is logarithmic scale).

### 2.3. Electrophoretic measurements

The electrophoretic mobility, $\mu_E$, of the $SiO_2$ particles was measured at the following state parameters: 25 °C and 20 bars, 100 °C and 20 bars, and 150 °C and 40 bars at several pH values. At these experimental conditions, the suspension was in the liquid phase at all times. The suspension pH was adjusted by titration with either HCl(aq) or NaOH(aq). Briefly, during the measurements, a constant DC potential was applied between the electrodes (usually between 5 and 9 V), the directed motion of the suspension toward one of the electrodes was visually observed, and the velocity of the movement was measured over 3–5 s. Then, polarity of the applied potential was reversed, and the velocity of the reverse movement was measured. The average value of the velocities measured in both directions was then obtained from these measurements. This procedure was repeated 20–30 times to obtain a reliable value of the standard deviation of each measurement. The electric field strength was calculated by dividing the applied electric potential by the distance between the electrodes, which was determined during the assembly of the cell. In this study, the electrophoretic mobility, $\mu_E$, was obtained from the slope of the dependence particle velocity vs. electric field at each temperature and pH according to the following expression:

$$v_T = \mu_E E + v_0 \tag{6}$$

where $v_T$ is the total velocity of the particles in m s$^{-1}$, $E$ is the applied electric field strength in V m$^{-1}$, and $v_0$ is the background velocity (noise), which may be induced by Brownian or convective motion of particles in the high temperature suspension. In the ideal case, the background velocity should be equal to zero, when the suspension is perfectly stationary. However, at elevated temperatures, thermal convection and minor pressure gradients in the cell may interfere with the velocity measurements. We found that, although minimal, some non-electrophoretic particle motion may become noticeable at temperatures above 100 °C. This influence was taken into account by measuring the particle velocity at several different values of electric field strength and applying linear fitting, according to Eq. (6). The value of electrophoretic mobility, $\mu_E$, is finally determined as the slope of this dependence. Averaging the measured particle velocity in both directions by reversing the polarity of the applied electric field helps in most cases to minimize the noise component.

### 2.4. Zeta potential calculation

The electrophoretic mobility–zeta potential relationship is known to be highly dependent on the $\kappa a$ parameter for a particular particle-electrolyte system [23–25]. The term $\kappa a$ is the product of the inverse EDL thickness, $\kappa$, and the particle radius, $a$. The value of $\kappa$ is proportional to the square root of the ionic strength of the solution and is given by $\kappa = \left(\frac{2F^2 I_m \rho}{\varepsilon_r \varepsilon_0 RT}\right)^{1/2}$, where $\rho$ is density of the solution. The Smoluchowski equation ($\zeta = \eta\mu_E/\varepsilon_r\varepsilon_0$) [23], widely used in many studies for calculating zeta potential ($\zeta$) from the electrophoretic mobility ($\mu_E$), is mainly valid for relatively high $\kappa a$ values (>500), i.e. for larger particles and thin double layer. This condition is typically met with the sizes in the order of microns and ionic strengths higher than $10^{-3}$ mol kg$^{-1}$. However, for the $SiO_2$ suspensions used in this study, the $\kappa a$ values were estimated in the range from 5 to 12, for which a more universal theory of O'Brien and White (OW) [24] should be applied. In brief, the OW approach takes into account the effect of the relaxation of the electrical double layer (EDL) around the moving particle. This relaxation effect