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## Comparison of the surface ion density of silica gel evaluated via spectral induced polarization versus acid–base titration

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### ABSTRACT

Surface complexation models are widely used with batch adsorption experiments to characterize and predict surface geochemical processes in porous media. In contrast, the spectral induced polarization (SIP) method has recently been used to non-invasively monitor in situ subsurface chemical reactions in porous media, such as ion adsorption processes on mineral surfaces. Here we compare these tools for investigating surface site density changes during pH-dependent sodium adsorption on a silica gel. Continuous SIP measurements were conducted using a lab scale column packed with silica gel. A constant inflow of 0.05 M NaCl solution was introduced to the column while the influent pH was changed from 7.0 to 10.0 over the course of the experiment. The SIP measurements indicate that the pH change caused a  $38.49 \pm 0.30 \mu\text{S cm}^{-1}$  increase in the imaginary conductivity of the silica gel. This increase is thought to result from deprotonation of silanol groups on the silica gel surface caused by the rise in pH, followed by sorption of  $\text{Na}^+$  cations. Fitting the SIP data using the mechanistic model of Leroy et al. (Leroy et al., 2008), which is based on the triple layer model of a mineral surface, we estimated an increase in the silica gel surface site density of  $26.9 \times 10^{16}$  sites  $\text{m}^{-2}$ . We independently used a potentiometric acid–base titration data for the silica gel to calibrate the triple layer model using the software FITEQL and observed a total increase in the surface site density for sodium sorption of  $11.2 \times 10^{16}$  sites  $\text{m}^{-2}$ , which is approximately 2.4 times smaller than the value estimated using the SIP model. By simulating the SIP response based on the calibrated surface complexation model, we found a moderate association between the measured and estimated imaginary conductivity ( $R^2 = 0.65$ ). These results suggest that the surface complexation model used here does not capture all mechanisms contributing to polarization of the silica gel captured by the SIP data.

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### 1. Introduction

Investigation of sorption processes at solid–liquid interfaces is very important for understanding the fate and transport of contaminants in the subsurface. Adsorption of protons, cations, anions and organic species can be closely linked with mineral or oxide surface charges and properties (Sverjensky, 2005). Thus, understanding the electrical and chemical properties of surfaces is necessary for predicting geochemical processes.

The electrical environment near the surface of oxide minerals and colloidal particles has been investigated for many years since it plays an important role in surface reactions and interfacial electrical phenomena (Davis et al., 1978; Ohshima and Furusawa, 1998). Researchers have developed many surface complexation models (SCMs) based on different descriptions of this region, such as diffuse layer and triple layer

models which are currently widely used (Davis and Kent, 1990). These models originated to describe the equilibrium speciation of protons and metal ion adsorption to pure oxide adsorbents (Stumm et al., 1970; Huang and Stumm, 1973) and typically account for electrostatic effects. They therefore assume that the local excess charges on mineral surfaces are balanced by electrolytes to form one or more layers of adsorbed counter ions (Sahai and Sverjensky, 1997).

Researchers usually calibrate SCMs using batch studies, such as acid–base potentiometric titrations, or column flow through experiments in order to quantify sorption processes and predict the distribution of trace metals between sediment surfaces and pore fluids (Mesuere and Fish, 1992; Katz and Hayes, 1995; Davis et al., 2004; Estes et al., 2013; Zhao et al., 2014). While traditional laboratory sorption tests are commonly used to evaluate the geochemical properties of sediments, they are limited in field application and unable to provide effective properties over large areas. Furthermore, quantification of the data is dependent on the theoretical basis of the models used, which vary in terms of how the relationship between surface sorption sites and metals is conceptualized (i.e., non-electrostatic, double layer, triple layer, or charge distribution models) (Decker and Papelis, 2003; Hiemstra and

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Van Riemsdijk, 1996). Thus, the modeled parameters may not accurately reflect the physical reality of the system. In contrast, spectral induced polarization (SIP) is a minimally-invasive geophysical technique that has the potential to monitor geochemical processes over large regions of the subsurface on relatively short time scales and is sensitive to the electrical properties of mineral surfaces (Vaudelet et al., 2011a, 2011b).

Below 1 kHz, SIP measures the frequency dependent complex electrical conductivity of a porous medium  $\sigma^*(\omega)$ , which can be expressed as:

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) \quad (1)$$

where  $\sigma'(\omega)$  is the real (conductive) part of complex conductivity that captures energy losses, and  $\sigma''(\omega)$  is the imaginary (polarization) part of complex conductivity that captures energy storage, which can be equivalently written in terms of a dielectric permittivity ( $\sigma'' = \omega\epsilon$ ),  $\omega$  is the angular frequency of the electric field, and  $i = \sqrt{-1}$ . Polarization of a porous media is of particular interest here as this phenomenon is closely related to surface geochemical properties and likely to be useful for in-situ monitoring of contaminants (Lesmes and Frye, 2001).

There are two competing electrochemical polarization mechanisms used to explain SIP measurements below frequencies of 1 kHz in porous media with non-conductive minerals; note that at higher frequencies interfacial (i.e., Maxwell–Wagner) polarization typically dominates (Lesmes and Morgan, 2001). Membrane polarization results from the exclusion of ions from small pores (or pore throats) and is the classical explanation for SIP phenomena in silicate rocks (Marshall and Madden, 1959; Titov et al., 2002). Another mechanism affecting the complex conductivity of a porous medium, however, is grain polarization. This phenomenon occurs when an applied electric field causes ions bound to the grain surface to migrate tangentially to the grain surface in the Stern layer, resulting in a separation of charge across the grain (Lesmes and Morgan, 2001; Leroy et al., 2008). The ions contributing to the SIP response in the Stern layer are the same of those attracted to the surface by electrostatic sorption processes described by SCMs. The potential therefore exists to use SIP data as a surrogate for direct chemical measurements when evaluating subsurface geochemical parameters, such as the density of active exchange sites on a mineral surface.

Vaudelet et al. demonstrated the sensitivity of SIP measurements to the sorption of copper, lead, sodium and zinc to the surface of a silica sand (Vaudelet et al., 2011a, 2011b). Schwartz et al. (2014) studied the SIP response caused by acidifying a mineral soil using an organic acid and found substantial effects on both the real and imaginary conductivity. These authors attributed some of these effects, however, to dissolution of the mineral structure under acidic conditions leading to shifts in the soil's formation factor with pH. Notably, Lesmes and Frye (2001) previously indicated that such effects on the formation factor are associated with a failure to account for changes in surface conductivity in Archie's Law, suggesting that the pH influence on the SIP measurements may have been more substantial in the Schwartz et al. study than the authors presumed. Skold et al. (2011) also studied the dependence of imaginary conductivity on pH. Though these authors did not clearly demonstrate a strong pH influence on SIP data, they did demonstrate that the magnitude of the values measured were higher than those predicted from a chemical speciation (triple layer) model and suggested that accounting for the migration of hydrogen ions along the mineral surface could explain the discrepancy.

In this study, we investigate sodium sorption processes on silica gel surfaces under transient pH conditions using SIP measurements. Based on the mechanistic complex conductivity model of Leroy et al. (2008), the primary parameters controlling grain polarization in a material with uniform grain size are the surface site density of the Stern and diffuse layers. By fitting the SIP result to this model, we will estimate the

pH dependent surface site density of the silica gel. We then compare these results to estimates of surface site density obtained with the triple layer model fit to potentiometric titration data.

## 2. Theoretical background

### 2.1. Electrical triple-layer model

The Leroy et al. (2008) complex conductivity model that we use in this work is based upon the triple layer model for the electrical potential distribution near a mineral surface. In this conceptualization, illustrated in Fig. 1, three distinct planes of sorption behavior are considered. Ions in the o-plane are the potential determining ions and are closely associated with the mineral surface, may undergo sorption at specific sites through the formation of inner-sphere complexes, and are generally considered to be bonded to the surface such that the lability of the ion is controlled by the exchange rate (Davis et al., 1978; Davis and Leckie, 1980; Goldberg, 1992). This is the plane at which the pH dependent addition or removal of hydrogen ions (described below) acts to vary the net fixed charge of the surface. Ions associated with the  $\beta$ -plane, i.e., Stern layer, are hydrated and electrostatically bound to the surface as outer sphere complexes. This layer is considered to be compact as the ions are tightly bound and therefore only able to migrate tangentially to the surface. In contrast, the d-plane, also known as the outer-Helmholtz plane, marks the boundary where the diffuse layer begins and extends out into the bulk solution. This is a zone where increased concentration of counter ions occurs relative to the bulk solution, but ions move relatively freely in space and readily exchange with the bulk solution. While the triple layer model provides a useful framework for considering different types of ionic behavior near a surface, we emphasize that these models are conceptual in nature and do not necessarily capture the physical details of the ionic environment near the surface.

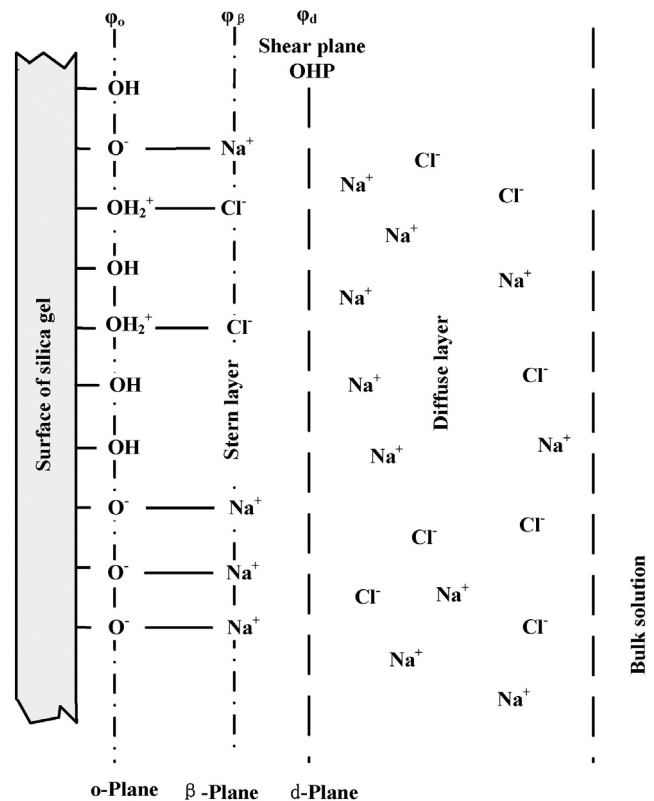


Fig. 1. Schematic description of the electrical triple layer model on silica gel surface (reproduced from Leroy et al., 2008).

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