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 0.05M 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 Na^+ cations. Fitting the SIP data using the mechanistic model of Leroy et al. (Leroy, Revil 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 $26.9 \times 10^{16} \text{ sites m}^{-2}$. 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 11.2×10^{16} sites 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.

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 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,b).

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 ($\sigma'' = \omega\epsilon$), ω is the angular frequency of the electric field, and $i = \sqrt{-1}$. Polarization of a porous media is of

71 particular interest here as this phenomenon is closely related to surface geochemical properties
72 and likely to be useful for in-situ monitoring of contaminants (Lesmes and Frye, 2001).

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

87 Vaudelet et al. demonstrated the sensitivity of SIP measurements to the sorption of
88 copper, lead, sodium and zinc to the surface of a silica sand (Vaudelet et al., 2011a,b). Schwartz
89 et al. (2014) studied the SIP response caused by acidifying a mineral soil using an organic acid
90 and found substantial effects on both the real and imaginary conductivity. These authors
91 attributed some of these effects, however, to dissolution of the mineral structure under acidic
92 conditions leading to shifts in the soil's formation factor with pH. Notably, Lesmes and Freye
93 (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 Figure 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 β -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.

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

pH-dependent changes in the fixed charge of the silica gel surface, i.e., within the *o*-plane, result from addition or removal of hydrogen ions from silanol groups ($\equiv SiOH^0$, where $\equiv$ refers to the terminal surface of the silica gel). These groups are protonated in acidic solutions where the pH is below the point of zero charge (PZC), giving the surface a net positive charge and allowing for adsorption of anions. In contrast, sites that have lost a hydrogen ion will dominate when the solution pH is above the PZC and cations are adsorbed to balance the surface charge. The complexation reactions can be written as:

$$pH(pzc) = \frac{1}{2}(\log K^- + \log K^+) \quad (6)$$

where K^+ , K^- , K_{Na} , and K_{Cl} are the associated equilibrium constants for the different reactions described above.

The pH-dependent changes in fixed charge resulting from these complexation reactions at the interface between the solid and liquid controls ion sorption at the mineral surface. The distribution of ions near the surface can be described using three charge densities (C/m^2): (i) the net charge immediately at the surface in the *o*-plane (Q_o), (ii) ions that are strongly bound to the surface within the Stern layer are represented by charge accumulated at the β -plane (Q_β), and (iii) the charge density at the *d*-plane (Q_d) is used to represent ion accumulation in the diffuse layer, though ions are loosely bound here and charge is distributed across the transition zone as the ionic composition approaches that of the bulk solution. In the triple-layer model, the Stern

layer is used to separate the solid surface from the diffuse layer and the charge densities on the surface are evaluated by enumerating the net number of hydrogen ions consumed by all surface reactions (Davis et al. 1978):

$$Q_o = F([\text{SiOH}_2^+] + [\text{SiOH}_2^+\text{-Cl}^-] - [\text{SiO}^-] - [\text{SiO}^-\text{-Na}^+]) / A \quad (7)$$

where F is the Faraday constant ($9.65 \times 10^4 \text{ C mol}^{-1}$), A is the surface area of the suspension ($\text{m}^2 \text{ L}^{-1}$) which is given by the product of the specific surface area of the particles (m^2/g) and the concentration of particles in the liquid (g/L), and [j] is the concentration of species j (moles L^{-1}). For a solution containing only NaCl, the charge balanced by ions in Stern layer is given by:

$$Q_\beta = F([\text{SiO}^-\text{-Na}^+] - [\text{SiOH}_2^+\text{-Cl}^-]) / A \quad (8)$$

According to the Gouy-Chapman theory (Davis et al., 1977; Leroy and Revil, 2004), the diffuse layer charge density is:

$$Q_d = -(8000\epsilon_f k T N_A C_f)^{\frac{1}{2}} \sinh\left(\frac{e\Psi_d}{2kT}\right) \approx 0.118\sqrt{C_f} \sinh\left(\frac{e\Psi_d}{2kT}\right) \text{ at } 25^\circ\text{C} \quad (9)$$

where C_f is the bulk concentration of the counter ion in the diffuse layer (mol L^{-1}), N_A is Avogadro's number ($6.022 \times 10^{23} \text{ atoms mol}^{-1}$), ϵ_f is the relative dielectric constant of the electrolyte solution (for water we use $\epsilon_f = 81\epsilon_0$), ϵ_0 is the absolute permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$), k is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$), T is the temperature (K), e is the elementary charge ($1.6 \times 10^{-19} \text{ C}$), and Ψ_d is the mean electrostatic potential at the outer Helmholtz plane; in some studies, Ψ_d is assumed to be equal to the zeta potential at the shear plane (Leroy et al., 2008). Based on the requirement for net charge balance:

$$Q_o + Q_\beta + Q_d = 0 \quad (10)$$

Sorption of ions to the surface is limited by the total surface site density for all functional groups on the silica gel, Γ_T (sites m^{-2}), which is given by (Sahai and Sverjensky 1997):

$$\Gamma_T = \frac{([\text{SiOH}^0] + [\text{SiOH}_2^+] + [\text{SiOH}_2^+ \text{Cl}^-] + [\text{SiO}^-] + [\text{SiO}^- \text{Na}^+]) \cdot N_A}{A} \quad (11)$$

Note that the site density (Γ) and charge density (Q) are related via the elementary charge, e . The proportional contribution of each functional group to the total site density is controlled by pH. Since in this study we only consider pH conditions which are higher than the point of zero charge ($\text{pH} > \text{PZC}$), we assume that adsorption of Na onto the surface of silica gel has the largest contribution to the surface ion density (i.e., $[\text{SiO}^- \text{Na}^+] \gg [\text{SiOH}_2^+] + [\text{SiOH}_2^+ \text{Cl}^-]$). The ion density for the Stern layer is then given by Γ_{SiONa}^s and that for the diffuse layer is Γ_{Na}^d . Based on the triple layer model, programs like FITEQL can be used to estimate the adsorbed counter ions in the Stern and diffuse layers as a function of pH and ionic strength (Hayes et al., 1991; Westall, 1982).

2.2 Electrochemical polarization model

When an external alternating electrical field is applied to a porous media, the charged ions in both the Stern and diffuse layers may migrate. The ions in the Stern layer are thought to move tangentially along the surface of grain as a result of the stronger electrostatic attraction to the surface in this region (Schwarz, 1962). In contrast, the ions in the diffuse layer are less strongly bound to the grain and their contribution to the polarization signal depends on their ability to bridge between grains, in which case they contribute to DC electrical conductivity rather than polarization.

An early complex conductivity model developed by Schwarz (1962), focused on the electrical response of non-interacting spherical grains. Lesmes and Morgan (2001) built on this model to capture the influences of the Stern layer, diffuse layer, and interfacial (Maxwell-

Wagner) polarization effects in a porous media. The Lesmes and Morgan model assumes the form of a Debye relaxation (Eq.12), where the frequency dependent conductivity σ_s (S/m) and permittivity ϵ_s (F/m) responses of the Stern layer are given as a function of the dielectric permittivity of the grain ϵ_g (F/m) and a time constant τ (s).

$$\sigma_s = \frac{\epsilon_g \omega^2 \tau}{1 + \omega^2 \tau^2}, \quad \epsilon_s = \frac{\epsilon_g}{1 + \omega^2 \tau^2} \quad (12)$$

Here ω (Hz) is the angular frequency of the applied electric field. The grain permittivity is dependent on the particle radius R (m) and charge density of the Stern layer Q_β (Eq.13). The relaxation time of the polarization τ is additionally dependent on the mobility μ ($\text{m}^2\text{s}^{-1}\text{V}^{-1}$), or diffusion coefficient D (m^2/s), of counter ions in the Stern layer:

$$\epsilon_g = \frac{eRQ_\beta}{kT} \quad (13a)$$

$$\tau = \frac{R^2}{2\mu kT} = \frac{R^2}{2D} \quad (13b)$$

Because *Schwarz's* model did not consider DC surface conductivity (σ_f^{DC}) when the grains are in contact with each other, *Lesmes* and *Morgan* applied *O'Konski's* theory (O'Konski 1960) to generalize the conductivity of a single grain σ_s^* (S/m):

$$\sigma_s^* = [\sigma_s + \sigma_f^{DC}] + i\omega\epsilon_s$$

$$\sigma_s^* = \left[\frac{\epsilon_g \omega^2 \tau}{1 + \omega^2 \tau^2} + \sigma_f^{DC} \right] + i\omega \frac{\epsilon_g}{1 + \omega^2 \tau^2} \quad (14)$$

where

$$\sigma_f^{DC} = \frac{\epsilon_g}{\tau} \quad (15)$$

The contribution of the diffuse layer was captured independently by these authors using Fixman's theory, which produces a spectral response that is broader than a typical Debye relaxation (Fixman, 1980).

Building on these efforts, Leroy et al. (2008) derived a similar polarization model for a spherical grain from first principles that accounts specifically for the surface chemistry of silica grains and sorption of a monovalent cation within the triple layer. For a non-conductive mineral grain, the net complex conductivity is given by Equation 16, where the permittivity of the solid mineral is ϵ_m (note that the mineral grain is assumed to be an insulator, i.e., $\sigma_m=0$ S/m) and the overall contribution of the triple layer is given by the complex conductivity $\tilde{\sigma}_s$ (S/m). Notably, mobile cations in the diffuse layer are assumed to contribute only to the DC conductivity (i.e., Γ_{Na}^d is the equilibrium surface site density of adsorbed sodium ions in the diffuse layer). Following Leroy et al. (2008), we also assume that the ion mobility in the diffuse layer is equal to that in the Stern layer. Protons associated with water adsorbed to the mineral surface also contribute to the net DC conductivity (with an assumed contribution to the surface conductivity of $\sigma_s^0(H^+) = 2.4 \times 10^{-9}$ S at 25°C) (Revil and Glover, 1997; Leroy et al., 2008). Surface contributions to polarization (i.e., the imaginary conductivity) in this model are therefore related only to the density of cations bound within the Stern layer (i.e., Γ_{SiONa}^s).

$$\sigma_s^* = \tilde{\sigma}_s + i\omega\epsilon_m \quad (16)$$

$$\tilde{\sigma}_s = \frac{2}{R} [\mu e \Gamma_{SiONa}^s \frac{i\omega\tau}{1+i\omega\tau} + \mu e \Gamma_{Na}^d + \sigma_s^0(H^+)] \quad (17)$$

Equations 14 and 16 represent the complex conductivity of a single grain. To upscale these models to represent the net polarization response of a porous medium, the models must be convolved with the grain size distribution of the medium (Börner et al., 1996; Lesmes and Morgan, 2001). Additionally, interfacial polarization effects of the Maxwell-Wagner type must be accounted for, e.g., by applying the *Bruggeman-Hanai-Sen* (BHS) effective medium theory

(Bruggeman, 1935; Hanai, 1960; Sen et al., 1981; Lesmes and Morgan, 2001; Leroy et al., 2008):

$$\frac{\sigma^* - \hat{\sigma}_s^*}{\sigma_f^* - \hat{\sigma}_s^*} \left(\frac{\sigma_f^*}{\sigma^*} \right)^\delta = \varphi \quad (18)$$

where σ^* is the net complex conductivity of the porous medium, $\hat{\sigma}_s^*$ is the size-averaged complex conductivity of an individual grain, σ_f^* is the complex conductivity of the pore fluid, φ is the medium porosity, and δ is a polarization exponent accounting for the shape of the grain (equal to 1/3 for spherical grains).

3. Materials and Methods

3.1 Experimental Setup

A sketch of the column (length = 4.5cm, inner diameter = 2.54cm) used for our experiments is shown in Figure 2. The column was packed with silica gel (Sigma-Aldrich 236802, Grade 636), which the manufacturer specifications indicate has a grain size of 250-500 μ m and an internal pore diameter of 60Å. The surface area of the silica gel was independently determined to be $511.51 \pm 5.90 \text{ m}^2 \text{ g}^{-1}$ using the BET (Brunauer-Emmett-Teller) nitrogen adsorption method (Lowell, 2004). Before packing the silica gel into the column, it was soaked for 12 hours in a pH = 7, 50mM NaCl solution and was degassed in a vacuum chamber. The silica gel was carefully wet packed in the column with a 50mM NaCl solution to make sure the column was saturated and did not contain air bubbles. The porosity of the column was estimated to be around 68% from wet and dry weight measurements, thus resulting in a pore volume of about 14.4mL. However, the top and bottom chambers of the column contribute an addition 45mL of pore space, making the total column volume equal to 104.4mL.

The spectral induced polarization measurements are presented schematically in Figure 2. Electrical measurements of both phase and magnitude were collected using a dynamic signal analyzer (*PCI-4461*, National Instruments, Austin, TX) operated over the frequency range of 0.01-1000Hz. Channel 1 was designated to record the current waveform by measuring the voltage response across a precision reference resistor in series with the column, whereas Channel 2 recorded the potential response of the sample. Both current injection and potential measurement electrodes were made from non-polarizing silver wires (~Gauge 12) coated with silver chloride. The general procedure is similar to that described by Ntarlagiannis et al. (2005).

Figure 2 Schematic diagram of the experimental setup showing column design with electrode configurations

3.2 Experimental Procedures

After packing the column, a constant flow rate of 0.5mL/min was applied to the bottom inlet using a peristaltic pump, thus complete replacement of one pore volume of the column (including the reservoirs) requires approximately four hours, and the residence time within the

silica gel packed column region is around 30 minutes. For the first three days of the experiment, a solution containing 50 mM NaCl with a pH of 7.0 was injected to the column. Sodium hydroxide (NaOH) was then used to adjust the pH of the influent solution to 8.0 for 3 days, after which it was further increased to a pH of 10 for the remainder of the experiment. The entire experiment lasted for 46 days with a total of 258 pore volumes eluted through the column (or almost 4000 pore volumes considering only the silica gel sample). SIP measurements were performed every two hours throughout the experiment. The pH and electrical conductivity of the inflow and outflow were recorded using pH and conductivity electrodes.

Independent of the flow experiment, potentiometric titrations were performed on the silica gel for three different ionic strengths of the NaCl solution (0.005M, 0.05M and 0.5M) in the pH range 5-10. Titrations were performed using 1 g L⁻¹ suspensions of silica gel in the desired ionic strength background. A N_{2(g)} purge of the headspace was maintained throughout the experiment to minimize the impact of dissolved carbonate. At the start of the titration, one large aliquot of 10 mM HCl was added to the sample to lower the pH. The suspension was stirred for 1 hour prior to the start of a base titration with 10 mM NaOH. During the titration 0.1 mL increments of NaOH were added successively to the sample, where the time between additions was defined by the period required to reach an electrode stability of 0.1 mV min⁻¹ with a maximum delay time of 60 minutes prior to the next addition.

We subsequently used the program FITEQL to fit the titration data with a triple layer model, allowing us to determine the number of Na⁺ occupied sites on the silica gel surface. A total site density of 5 sites nm⁻² was assumed in the model consistent with the data from Leroy and Revil (2008). However, capacitance values for the outer and inner Helmholtz layers were

fixed at 0.8 F m^{-2} and 1.7 F m^{-2} , respectively, as opposed to the values of 0.2 F m^{-2} and 1.2 F m^{-2} used by Leroy and Revil (2008).

4. Experimental Results

4.1 Column Influent and Effluent Observations

Figure 3 shows the measured pH and electrical conductivity of the column influent and effluent throughout the experiment. Figure 3a shows that the mean fluid conductivity of the influent and effluent solutions (i.e., $5610 \pm 35 \mu\text{S/cm}$ and $5485 \pm 53 \mu\text{S/cm}$, respectively) were within 2.5% of each other and stable over the course of the experiment. This observation is important as it indicates that changes in the complex conductivity are not associated with changes in the electrical conductivity of the bulk pore fluid. In contrast, Figure 3b shows that as the influent pH was increased from 7 to 10, the effluent pH remained at values around 8 until the end of the experiment. This pH response may indicate a strong buffering effect by the silica gel as hydrogen ions on the surface are consumed, allowing for enhanced sodium sorption on the surface (Eq.4). Notably, however, the measured outflow pH approaches a maximum of around 8.5, which is substantially lower than the inflow value. At face value, this observation suggests that equilibrium was not reached in the column. While the silica gel buffering effect is one possible explanation for this observation, we also point out that the influent solution was not initially equilibrated with atmospheric CO_2 . It is therefore possible that carbon dioxide gas diffused into the effluent solution as it was being collected, thus causing an apparent suppression of the pH that is not representative of the actual conditions within the column. Regardless of whether these outflow pH values represent the true internal condition of the column or an artifact of the outflow measurements, it is clear from the effluent data that a change of at least 1.5pH units was achieved within the silica gel column.

Figure 3 The pH and electrical conductivity responses of the influents and effluents: (a) fluid electrical conductivity and (b) pH.

4.2 Transient SIP Spectral Responses

The real and imaginary part of the complex conductivity spectra are shown for representative times throughout the experiment in Figure 4. Both the real and imaginary conductivities increase substantially over the course of the experiment. These increases in complex conductivity are consistent with an increase in sodium sorption on the silica gel surface as the pH change drives deprotonation of silanol groups. In other words, we attribute the increase in both the real and imaginary conductivity to increases in the charge density on the silica gel surface caused by the pH change; this interpretation is consistent with theoretical

models for grain polarization (e.g., Leroy et al., 2008). The rate of change of the real and imaginary conductivity is approximately constant throughout most of the experiment, though it is clear from Figure 5a that the rate was slower in the initial phase while the influent pH was still below 10. After approximately 225 pore volumes have been eluted through the column (i.e., about 40 days into the experiment) both the real and imaginary conductivity stabilize (Figure 5), indicating that the silica gel surfaces reach equilibrium with the resident pH of the injected fluid.

Figure 4 The imaginary and real conductivity responses of certain days: (a) imaginary conductivity; (b) real conductivity.

Figure 5 The peak of imaginary conductivity and the averaged real conductivity responses dependent on pore volume: (a) peak of imaginary conductivity; (b) averaged real conductivity.

Figure 6 The frequency of the peak of imaginary conductivity response with pore volumes

One interesting trend in the SIP measurements noted over the course of the experiment was a gradual shift in the frequency at which the peak of the imaginary conductivity spectra occurs towards higher frequencies (Figures 4 and 6), which implies a reduced relaxation time. According to Eq .13, the relaxation time is dependent on the length scale of polarization (i.e., grain size) and ion mobility within the Stern layer. One possible explanation for the observed frequency behavior is a decrease of sodium mobility in the Stern layer as the pH and, therefore, fixed charge of the surface increase, causing the ions to be held more tightly. Another potential explanation for the frequency shift could be related to the substantial intragranular porosity of the silica gel used in this experiment. Fluids within the small diameter micropores (60 Å) of the silica gel would be largely immobile. It is therefore likely that the surfaces first exposed to the pH change would be associated with the intergranular porosity between grains where the fluid is mobile. Diffusion into the silica gel grains will limit the rate at which deprotonation and sodium sorption may occur at the silanol sites in these regions. Even though the actual grain size of the

silica gel did not change over time, our data suggest that the average grain size contributing to the SIP measurement decreased over time as a larger and larger portion of the intra-granular surface area was brought to equilibrium. Additional studies investigating the role of mass transfer between the mobile and immobile regions of the pore space and the kinetics of these processes should be performed to further evaluate the cause of this frequency phenomenon.

SIP data for four representative pH values, along with the best fit of the Leroy et al. (2008) model to the data, are shown in Figure 7. The model is able to fit the shapes and magnitudes of the spectra well and the fitted values of the Stern and diffuse layer site densities are given in Table 1. However, the position and width of the spectra shifted and broadened with pH requiring an increase in the log-normal variance of the grain size distribution to fit the data (reported as a unitless log-parameter in Table 1). The resulting shift in the mean of the grain size distribution to higher values, which is the opposite of the micropore activation discussed previously, may present a limitation of the Leroy et al. (2008) model. Lesmes and Morgan (2001), for instance, noted that polarization contributions from the diffuse layer could cause broadening of the spectra, but this effect is not accounted for in the Leroy et al. model. The apparent shift in the grain sizes may therefore be an artifact caused by fitting of the model.

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Figure 7 Comparison of SIP result (dots) with electrochemical polarization Model fit result (solid): (a) imaginary conductivity and (b) real conductivity

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4.3 Acid-Base Titrations and Comparison to SIP Results

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In order to test our hypothesis that the observed SIP response is caused by deprotonation of the silanol sites and sorption of Na^+ , we performed an independent acid-base titration of the silica gel to develop a geochemical model of the surface site distribution. We performed a set of acid-base titrations on the silica gel for three different ionic strengths ($[\text{NaCl}] = 0.005\text{M}, 0.05\text{M}$

and 0.5M) and fit the data to a triple layer model of the surface using the nonlinear, least-squares fitting program FITEQL.

The triple-layer model includes five parameters: K^- , K^+ , inner layer and outer layer capacitances (C_1 and C_2), and total site concentration. Hayes et al. (1991) report that the inner layer capacitance C_1 should be kept in the range of 0.1 to 2.0 F/m². The silanol site density for silica is assumed to be 4.6/nm² from ³H-exchange experiments (Sahai and Sverjensky, 1997; Yates et al., 1974). For both fitting the titration data with FITEQL and predicting site density changes with pH, we assumed that all the available surface sites on silica gel surface are occupied by adsorbed H⁺ and OH⁻ (Sahai and Sverjensky, 1997). Our data were fit as shown in Figure 8 using the parameter values: log K^+ =2.29 (Eq. 2), log K^- =-7.60 (Eq. 3), C_1 =1.7 F/m², and C_2 =0.8 F/m².

Figure 8 FITEQL model fit to surface titration data on silica gel in 0.005M- 0.5M NaCl. Values for log K^+ =2.29 and log K^- =-7.60

Figure 9 FITEQL estimated surface stern layer and diffuse layer of Na⁺ bound site density response with pH

Given the geochemical model of surface speciation obtained by fitting the acid-base titration data, the density of sodium sorption sites in the Stern and diffuse layer can be estimated based on Eqs. 7-10 (shown in Figure 9). These parameter values can then be used within the complex conductivity model of Leroy et al. (2008) to predict the SIP response of the silica gel. Comparisons between the geochemically predicted SIP spectra and the observed spectra are shown in Figures 10 and 11. It is clear that the predictions and observations do not match. The real conductivities are over-predicted by the titration data at low pH and the imaginary conductivities are under-predicted at high pH. Direct comparisons between the observed and predicted values of the peak imaginary conductivity and average real conductivity are shown as a function of pore volume in Figure 12. This figure also emphasizes the systematic failure of the prediction of the imaginary conductivities, though this problem may be associated with the potential issues in measuring the outflow pH of the column discussed earlier. The relative

insensitivity of the real conductivity to pH in the FITEQL model indicates that the diffuse layer site density, which mainly contributes to the real imaginary response, is not well captured by the geochemical titration data. This is proposed to be due to potential differences between the theoretical basis of the model assuming electrostatic interactions of Na^+ ions compared with a more realistic description wherein the Na^+ ions within the double layer have a range of distances from the silica gel terminal surface. Several demonstrations of this phenomena have recently been described for monovalent ion interactions with mica surfaces (Fenter et al., 2007, 2008; Lee et al., 2012). However, to capture this distribution, an alternative ion sorption model is needed.

Figure 10 Comparison between the SIP measurements (dots) and FITEQL prediction (solid) of the (a) imaginary conductivity and (b) real conductivity for pH values: 6.9, 7.5, 8.0 and 8.5.

Figure 11 Correlations between the peak of the imaginary conductivity (a) and average real conductivity (b) at each measurement point for the SIP and FITEQL predicted responses. The dashed line indicates the observed correlation, whereas the solid line indicates perfect correlation (i.e., 1:1 line).

Figure 12 Comparison SIP measurement of peak of imaginary conductivity (a) and average real conductivity (b) response with FITEQL predicted

A comparison between the Na^+ ion bound surface site densities obtained by fitting the SIP data to the Leroy et al. (2008) model versus that obtained from the acid-based titration is given in Table 3.1. The Na^+ ion bound site density of the Stern layer is overestimated by the titration data relative to the SIP data at low pH, but underestimated at high pH. It is likely this is an artifact of the model not accounting for specific surface complexation of Na^+ ions with increasing pH. This difference is the explanation for the mismatch between the imaginary conductivity spectra predicted using the FITEQL model versus the spectra measured by SIP in Figure 10. In contrast, the diffuse layer density estimated by the titration data is always higher than that obtained from the SIP data for all pH values and shows a small degree of variability (Table 1). Again, this is consistent with the mismatch observed for the real conductivity spectra in Figure 10 and is indicative of the insensitivity of the acid-base titrations to the diffuse layer site density.

Table 1 Comparison of Calculated from titration and expected parameter values for the SIP model

Experiment condition	Stern Layer(Sites/m ²)		Diffuse Layer(Sites/m ²)		Grain Variance
	SIP	Titration	SIP	Titration	
Start(pH 7.0)	8.00E+15	9.12E+15	1.45E+18	2.87E+18	3.00E-1
pH7.5	1.29E+16	2.92E+16	1.55E+18	2.91E+18	3.2E-1
pH 8.0	7.6E+16	6.57E+16	1.85E+18	2.94E+18	3.85E-1
End(pH 8.5)	2.77E+17	1.32E+17	2.84E+18	2.97E+18	4.61E-1

5. Conclusions

This study investigated whether SIP measurements can be used to capture equivalent information to that obtained from geochemical sorption experiments – specifically an acid-base titration. SIP measurements successfully monitored the surface adsorption of sodium cations as

the influent pH was raised during a column flow experiment with silica gel. These measurements were fit well by Leroy et al. (2008) model for complex conductivity. In contrast, we found that predictions of the SIP spectra using the Leroy et al. model with parameters estimated by acid-base titration of the silica gel produced a poor match to the measured SIP data. However, in this particular experiment, we experienced a problem with directly evaluating the pH within the column, which may explain systematic errors observed in matching the imaginary conductivities. The sorption model developed from the titration data was insensitive to changes in the diffuse layer site density, which led to a lack of change in the predictions of the SIP response. This is in direct contrast to the SIP measurements, where an increase in the real conductivity of the silica gel with pH was clearly apparent and, as shown from independent measurements of the column influent and effluent, was not associated with changes in pore fluid conductivity. Our results therefore suggest that polarization measurements made with SIP are able to capture changes associated with ions that are tightly bound to the mineral surface, i.e., are bound to the surface as inner sphere complexes within the Stern layer. Changes in ion density within the diffuse layer, which contribute to the DC real conductivity of in SIP measurements, are not captured by the acid-base titration. Our work therefore suggests that SIP data may not only provide information relevant to geochemical modelers, but it may in fact provide meaningful information about surface processes that are not captured by the sorption model developed from potentiometric titration data in this work. Additional studies examining specific binding of ions at mineral-water interfaces (i.e. formation of inner versus outer sphere complexes or the distribution between the two) are needed to further refine these models.

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