Effect of temperature on selenate adsorption by goethite

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ABSTRACT: Experimental closed-system ΔT acid-base titrations between 20 and 75°C were used to constrain a temperature-dependent basic Stern model (BSM) of the surface properties of goethite. Modeling was performed using the new Gibbs-energy-minimization model GEMS. With the latter, S^o_{298} and Cp^o_{298} values could be fitted for the goethite surface acidity and background electrolyte outer-sphere complexes. Based on these BSM parameters, an adsorption model could be established for the pH-dependent selenate sorption continuum involving both an inner- and outer-sphere surface complex, where only the latter is affected by ionic strength and temperature.

1 INTRODUCTION

Despite a growing number of studies on surface complexation modeling, not much is known about the effect of temperature on oxide surface properties and ion adsorption, especially that of oxyanions. The purposes of this study were first to better understand the temperature changes in pH_{zpc} and surface acidity of goethite, and second, to evaluate the effect of increasing temperature on adsorption of selenate. Selenate, SeO_4^{-2}, was selected because of its potentially harmful pollutant behaviour. This oxoanion is also known to form both an inner- and outer-sphere surface complex on goethite. This continuum of adsorption mechanisms is strongly affected by both pH and ionic strength (Peak and Sparks, 2002), but no data yet exist on temperature effects.

2 EXPERIMENTS

The goethite sorbent was prepared from ferric nitrate solution under highly alkaline conditions at elevated temperature (Gerth 1990). 50 mL of a 1 M ferric nitrate solution was rapidly admixed to 650 mL of NaOH solution heated to 70°C to give a final OH⁻ concentration of 0.5 M. The suspension was kept at 90°C for 7 days, shaken up once per day, and ultimately dialyzed in cellulose tubing with deionized boiled water at room temperature during further 7 days until Na concentration was less than 0.1 mg/L. All chemicals were stored in plastic bottles, and all experiments were carried out in plastic vessels under bubbling argon in order to minimize silica and car-bonate contamination. BET surface area of the thus produced goethite was 20 ± 2 m²/g indicating well crystallized material. Additional acid leaching for removing of amorphous hydroxide coatings was therefore avoided. For the batch titration and adsorption experiments, suspensions with varying goethite concentrations of 5, 10, and 30 g/L were prepared. Background electrolyte concentrations of 0.01, 0.05, and 0.1 M were fixed using $NaNO_3$. In each of the 50 mL polypropylene bottles, 30 mL of suspension was filled with argon in the headspace, and heated in a water bath to the desired temperature of 20°C to 70°C in steps of 10°C.

The effect of temperature on the pH_{zpc} was determined in closed systems by the ΔT titration approach introduced by Fokkink et al. (1989). The suspension was first adjusted to its original pH_{zpc} at room temperature (or any other pH value between 5 and 10) by adding HNO_3 or NaOH to the suspension), then the temperature was raised rapidly to the desired value, and pH was measured carefully again to a precision of 0.01 units. Selenate adsorption experiments were performed on goethite suspensions of lower s/w ratio (1 g/L). The dissolved adsorbate concentrations in membrane-filtered (0.2 μm) solutions were analyzed by the conventional hydride generation method coupled to AAS.

3 RESULTS AND MODELING

For all batch systems, the pH_{zpc} is continuously decreasing from the starting value at 20°C to an about 0.3 to 0.5 pH unit lower value at the maximum

70°C. This pH decrease occurred along a gentle, almost straight curve (Fig. 1). Upon cooling the system back again to room temperature, the same pH_{zpc} could be measured, suggesting that dissolution of the goethite was negligible, and that the system behaved effectively reversible.

The closed-system data were modeled with the basic Stern model (BSM) using the Gibbs energy minimization code GEMS, with the built-in Nagra-PSI 01/01 data base (Hummel et al., 2002), merged with HKF EoS data from the SUPCRT92-98 data base to provide better temperature corrections up to 150°C (http://les.web.psi.ch/software/GEMS-PSI).

For the GEMS-BSM model runs, the surface acidity constants of goethite at standard conditions (25°C, 1 bar) were fixed at pH_{zpc} = 9.1, ΔpK_A = 4.2, ΔpK_E = 2.0, and C_1 = 0.7. At the beginning of each of the 9 GEMS-BSM runs, pH was adjusted to 25°C (a linear average between that measured at the 20°C and 30°C temperature steps) by adding some amount of HNO_3 or NaOH to the model system. Initially, values of S^o_{298} and Cp^o_{298} for the $> O_{0.5}^-Na^+$ complex were taken the same as for this complex on rutile (Kulik 2000). Temperature-dependent H^+ adsorption data allow simultaneous adjustment of S^o_{298} and Cp^o_{298} values of both outer-sphere complexes. This is because the respective properties of $> OH_2^+$ and $> O^-$ species can be predicted, and all these properties seem to be connected through the "zero-term" isocoulombic reaction:

$>O_{0.5}H_2^+NO_3- + >O_{0.5}^- + Na^+ \Leftrightarrow >O_{0.5}^-Na^+ + >O_{0.5}H_2^+ + NO_3^-$ (1)
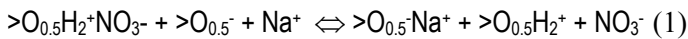
Such isocoulombic reactions are a prerequisite for modeling of temperature effects (Schoonen 1994, Kulik 2000). S^o_{298} and Cp^o_{298} values for the $>O_{0.5}^-Na^+$ complex could be found via this reaction (having all effects zero) after adjustment of the respective thermodynamic parameters of accompanying $>O_{0.5}H_2^+NO_3-$ complex, which prevails at pH < pH_{PZC}. All initial modeling runs underestimated pH at elevated temperatures. Better fits were obtained after fixing S^o_{298} for the $>O_{0.5}H_2^+NO_3^-$ complex at 262.5 J/K/mol. The Cp^o_{298} value for the same complex was set to 200 J/K/mol, but a variation of Cp^o_{298} within ±50 J/K/mol did not change the fits significantly, i.e. the experimental 50°C temperature interval is too short to adjust Cp^o_{298} unequivocally.

The initial BSM model, set up with an inner capacitance density C_1 parameter independent of temperature, predicted a steep increase in density of adsorbed electrolyte species already at moderate temperatures (50 to 80°C) and ionic strength (0.1 M) (not shown). The systematic bias points to the fact that this initial assumption does not seem to be realistic. Kulik (2000) has found that on rutile, C_1 should increase approximately by 0.1 to 0.15 F/m² from 25°C to 50°C, and by 0.1 F/m² from 50 to 100°C. Though the reasons for such an increase are not yet quite clear, this effect can be modeled using the following equation:

$$C_1(T) = C_1(T_0) + 0.003(T-T_0) \qquad (2)$$

where temperature T is taken in centigrade, T_0 = 25°C, and $C_1(T_0)$ = 0.7 F/m². Accordingly, the absolute values of S^o_{298} and Cp^o_{298} could have been decreased to avoid over-prediction of pH at elevated temperatures (i.e. to make the increase of electrolyte adsorption with temperature less steep). The best fits to closed-system experiments could be obtained using S^o_{298} and Cp^o_{298} values listed in Table 1 below.

Table 1. Thermodynamic BSM parameters for goethite surface complexes (in J/mol and J/K/mol).

Species	$logK_{298}$	G^o_{298}	S^o_{298}	Cp^o_{298}
$>O_{0.5}H^o$	1.74436*	-128548	68.36	37.68
$>O_{0.5}H_2^+$	-7.00	-168504	68.36	37.68
$>O_{0.5}^-$	-11.2	-64618	21.12	-136.3
$>O_{0.5}H_2^+NO_3^-$	-8.10	-285688	215.3	194.9
$>O_{0.5}-Na^+$	-10.1	-332778	79.8	125.8

*for Reaction $0.5H_2O \Leftrightarrow >O_{0.5}H^o$ (Kulik 2000). C_1 varied according to equation (2). All constants refer to the unimolal standard state at reference site density Γ_o = 20 μmol·m⁻² and reference state of full coverage at Γ_o ($>O_{0.5}H^o$), and of infinite dilution on the surface.
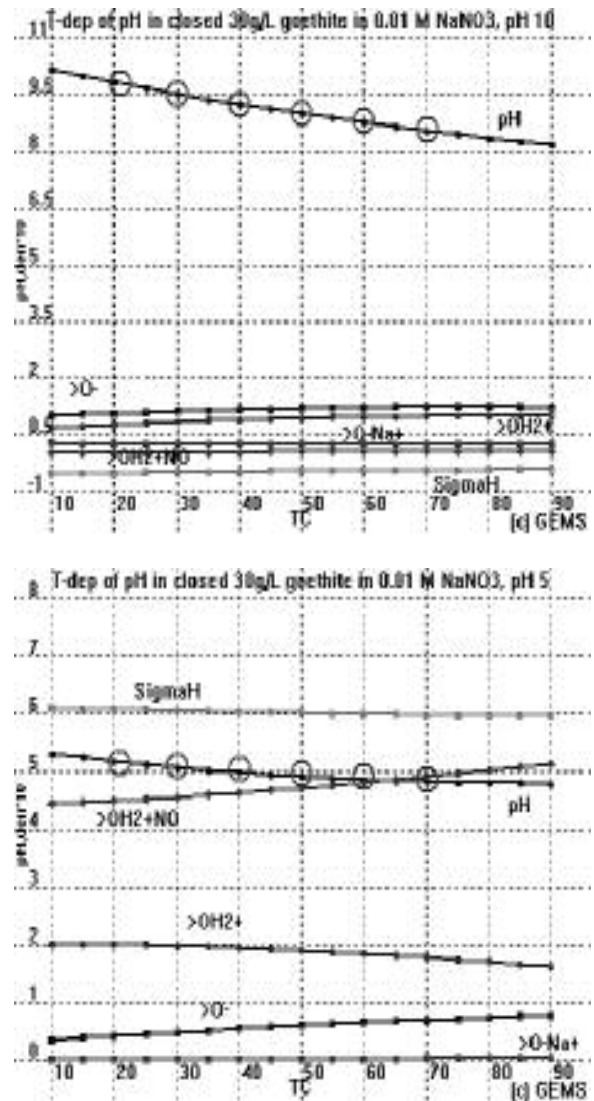
Figure 1. Densities of surface species and charge (in nm⁻²·10) vs. temperature (T in °C) for pH 10 (top) and pH 5 (bottom). Lines on these GEMS screenshots are BSM model predictions, while open circles represent the experimental data.

Among the nine experimental data sets modeled, Figure 1 represents two extreme cases, where adsorption is dominated by the $>O^-$ species near pH$_{PZC}$ (at initial pH = 10), and by the outer-sphere nitrate complex far from pH$_{PZC}$ (initial pH = 5), respectively, at both highest goethite concentration and lowest ionic strength. The model fit is good in both cases. Note that all properties defining temperature corrections for the $>O^-$ and $>OH_2^+$ surface species were predicted, not fitted, so a good fit at pH = 10 corroborates the general validity of such predictions (by the way, insensitive to C_1 parameter). The above results point to a considerable but yet unleashed potential in the closed-system adsorption experiments.

At acidic to neutral solution conditions, selenate adsorption was found to increase with decreasing concentration, and to decrease with increasing ionic strength.–A significant decrease of adsorption with increasing temperature was also observed.

In order to account for all three effects, first both an inner- ($>SeIS$) and outer-surface ($>SeOS$) complex was introduced (Fig. 2), where the former is dominating in the acidic range only, just as evidenced recently by EXAFS measurements (Peak and Sparks, 2002). The adsorption of selenate was modeled first at 20°C assuming that the outer-sphere surface complex is prevalent and all other BSM parameters were kept as fixed on the previous stage. This complex can be constructed using the reaction:

$$>O_{0.5}H_{2.5}^{+0.5}SeO_4^{-1.5} \Leftrightarrow >O_{0.5}H^0 + SeO_4^- + 1.5H^+ \quad (3)$$
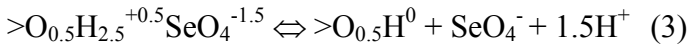
with equilibrium constant $\log K_{OS,Se}$ = -14.1 ± 0.2 (at 25°C, 1 bar). This complex approximately corresponds in the effective outer-sphere charge of -1.5 (with 0.5 on the zero-plane, and -1.5 on the beta-plane) to that for selenate or sulfate in the CD-MUSIC model (z_1 = -1.6 to -1.4: Rietra et al., 2001). The outer-sphere selenate complex is mainly relevant at higher total selenate concentrations. In order to account for the higher ionic strength and lower selenate concentrations, a second albeit relatively weak monodentate inner-sphere selenate complex of ligand exchange type needs to be introduced, with a maximum site density of about 0.2 nm^{-1}. Assuming that in this case the selenate ion replaces the "surface water" ligand $>O_{0.5}H^0$, the formation reaction can be written as:

$$>O_{0.5}H^0 + SeO_4^{-2} \Leftrightarrow >SeO_4^{-2} + 0.5H_2O \quad (4)$$

with equilibrium constant $\log K_{OS,Se}$ = -4.6 ± 0.6 (at 25°C, 1 bar). Relatively large uncertainty is due to the minor role of this surface complex except at low pH, low total selenate, and higher ionic strength. As shown in Fig. 2, ionic strength affects only the outer-sphere complex. Note that there is an increasing competition between this complex and the outer-sphere nitrate complex at decreasing pH values. In

fact, surface complexes other than $>SeO_4^{-2}$ were all subject to the competitive SAT at common maximum site density $\Gamma_{C,max}$ = 3 nm^{-2}. Practically the same curves were obtained at greater values of $\Gamma_{C,max}$.

Modeling of pH adsorption edges for selenate at 50°C and 75°C has shown that no serious temperature corrections are needed. For the outer-sphere selenate complex (3), the following best-fit parameters were obtained: $\Delta_r H^o_{298}$ = 71.54 ± 3 kJ/mol and $\Delta_r S^o_{298}$ = -30 ± 10 J/K/mol. The $\Delta_r Cp^o_{298}$ was set to zero, and no adjustment was necessary (note again, however, that the temperature interval is too short to define this parameter with uncertainty less than ±50 units). Hence, the temperature correction for $K_{OS,Se}$ is provided by a two-term (Van't Hoff) approximation:

$$\log K_{OS,Se} = -1.567 - 3737/T \quad (5)$$

Note that this temperature correction is consistent with a C_1 parameter increasing with temperature according to equation (2), but remains independent of the electrolyte concentration at constant temperature. For the inner-sphere selenate complex (4), the following parameters were found: $\Delta_r H^o_{298}$ = 50.11 ± 9 kJ/mol and $\Delta_r S^o_{298}$ = 80 ± 30 J/K/mol; $\Delta_r Cp^o_{298}$ was set to zero again. The respective two-term correction equation is analog to (5):

$$\log K_{IS,Se} = 4.179 - 2617/T \quad (6)$$

The quality of fits is in general good, and even improved with increasing temperature (cf. Fig. 3 for an example). The thermodynamic data for both selenate surface species are compiled in Table 2. The larger scatter for the second inner-sphere surface complex is due to uncertainty in the generally minor contribution of this complex to total adsorbed selenate.

Table 2. Thermodynamic BSM parameters for surface complexation of selenate on goethite (in J/mol or J/K/mol).

Species	G^o_{298}	S^o_{298}	Cp^o_{298}
$>O_{0.5}H_{2.5}^{+0.5}SeO_4^{-1.5}$	-659795	152.3±10	-193.7
$>SeO_4^{-2}$	-434463	167.4±30	-231.3

4 CONCLUSION

Our results suggest that the ΔT titration technique is helpful in characterizing temperature effects on surface acidity. The model fits indicate that the selenate inner-sphere surface complex on goethite is affected by concentration only, while the outer-sphere complex is also affected by ionic strength and temperature. A drawback for fit quality is that BSM use only one capacitance parameter C_1 having the same value for outer-sphere cations and anions. Perhaps, better fits could be obtained with CD-MUSIC type models, which are not yet implemented in GEMS.
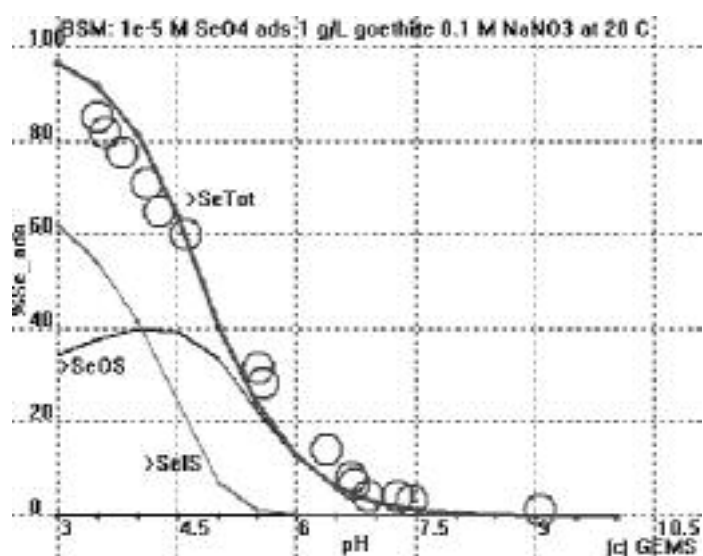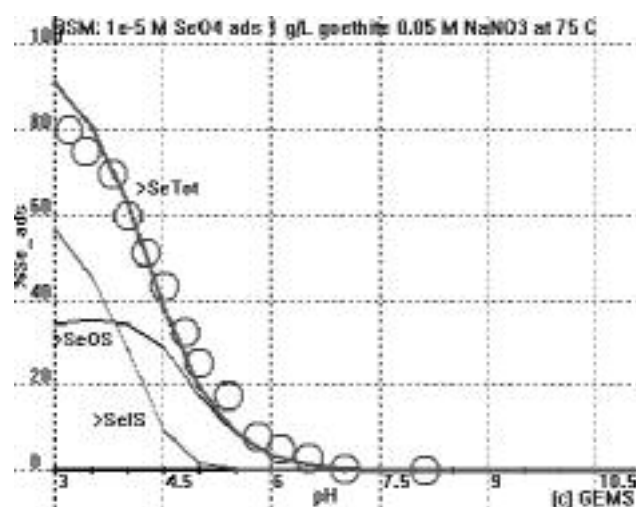
Figure 3. GEMS screen plots, with experimental circles and model curves, showing adsorption of selenate onto goethite surface at constant ionic strength (0.05 M NaNO$_3$), but different pH and temperatures (50°C and 75°C, for 20°C see left side).
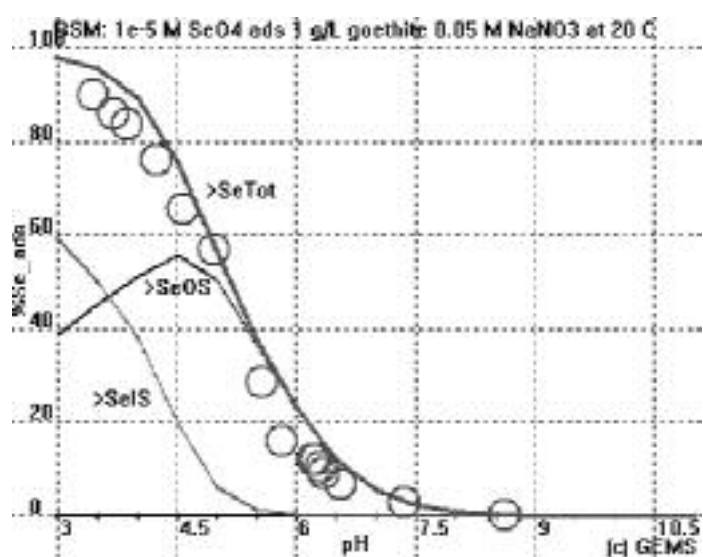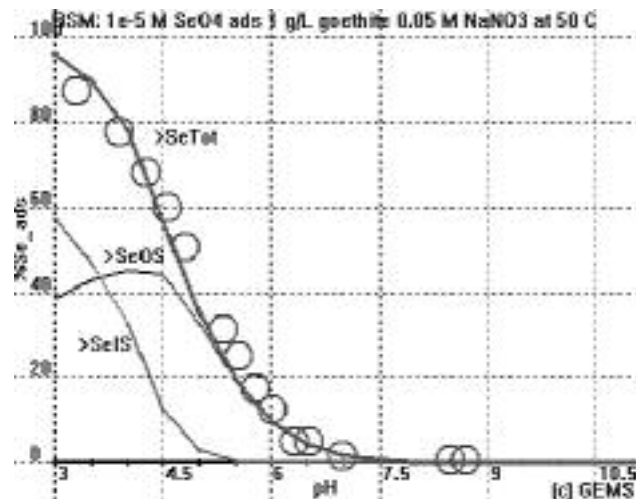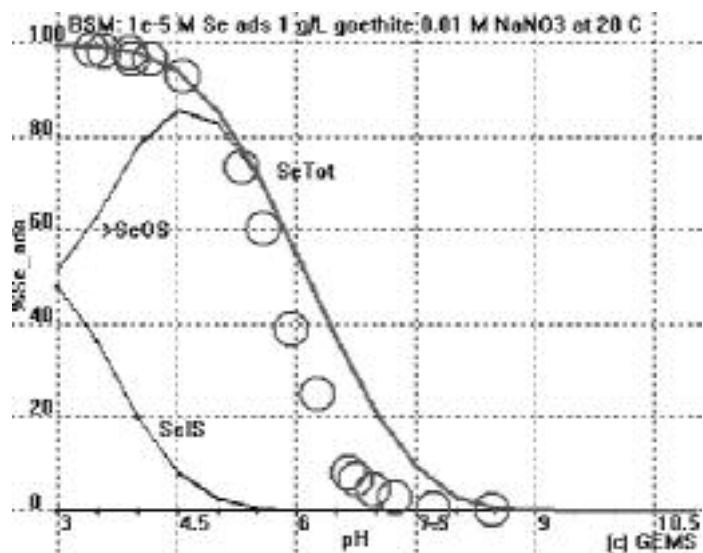

Figure 2. GEMS screen plots, with experimental circles and model curves, showing adsorption of selenate onto goethite surface at constant temperature (20°C), but different ionic strengths (0.01, 0.05, and 0.1 M NaNO$_3$) and pH values.

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