# The Adsorption of 2-Ketogluconate by Goethite

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## SUMMARY

Low-molecular-mass-organic acids play an important role in many soil processes, including mineral dissolution and nutrient mobilization and uptake. One such organic acid is 2-ketogluconate (kG). This substance is a microbial exudate that has been shown to enhance the solubility of gibbsite and goethite, form stable aqueous complexes with Al, Fe, and Ca metal species, and to compete with $PO_4$, $AsO_4$, and $SO_4$ ligands for adsorption sites on gibbsite and kaolinite. This study examines the adsorption of kG by goethite, as influenced by temperature (T), pH, and ionic strength ($I_S$). Adsorption edge studies showed that kG adsorption was a function of pH, but independent of $I_S$. Ketogluconate adsorption also resulted in a negative shift in the surface charge characteristics of goethite. The inclusion of $PO_4$ and $AsO_4$ ligands decreased kG adsorption throughout the pH 4 to 10 range. However, $SO_4$ only decreased kG retention in the pH < 6 range. The 1-pK basic Stern surface complexation model, coupled with a chemical model that considered the monodentate $\equiv FeOkG^{0.5-}(s)$ and the bidentate $\equiv Fe_2O_2H_{-1}kG^-(s)$ surface species was used to successfully describe the experimental adsorption data. In general, the kG adsorption isotherms were H-type, and they were well-described by the Langmuir and the Dubinin-Radushkevich (D-R) isotherm models. The adsorption of kG increased with increasing T and increasing IS. Adsorption was endothermic and entropically-driven, and the computed $\Delta H_{ad}$ values were similar to those reported for other specifically-adsorbed ligands, ranging from 22.32 to 53.7 kJ mol$^{-1}$. The energy of adsorption computed from the D-R isotherm model ranged from 12.84 to 18.33 kJ mol$^{-1}$, indicating chemical adsorption. Results from this study are consistent with those of previous research, indicating that kG is retained at the goethite surface via inner-sphere mechanisms, and that kG may play an important role in soil chemical processes.

## OBJECTIVES

To conduct adsorption edge and adsorption isotherm studies and examine the influence of pH, $I_S$, T, and competing ligands on the adsorption of kG by goethite, and to generate evidence for determining the adsorption mechanism of kG by variable-charge soil minerals.

pK$_a$ = 11.97

pK$_a$ = 3.00

Structure of 2-keto-D-gluconate at circumneutral pH

## MATERIALS AND METHODS

_Adsorption Envelopes_ Adsorption envelopes were determined in triplicate batch systems. Suspensions containing 0.2 g goethite were equilibrated for 72 h at ambient T (20°C -22°C) with 20 mL of pH-adjusted solutions in either 0.01 M or 0.001 M NaCl. The initial concentration of all adsorbates was 0.1 mM. After equilibration, the liquid and solid phases were separated by centrifugation. Aliquots of the supernatant were withdrawn for ligand analysis by ion chromatography, and the remaining supernatant was used for pH determinations. The adsorbed concentrations of kG, $PO_4$, $AsO_4$, and $SO_4$ (q) were computed by difference between the initial adsorbate concentration ($c_{in}$) and the equilibrium concentration ($c_{eq}$).

_Surface Complexation Modeling_ The q vs. pH adsorption edge data were employed to develop a chemical model that describe kG adsorption. The 1-pK$_a$ formulation of the basic Stern surface complexation model was used. The model computations and optimizations were performed using FITEQL 4.0 software. Input parameters required for the computations, e.g., surface hydrolysis, electrolyte adsorption, and ion association constants, were obtained from literature sources. The goodness-of-fit parameter computed by FITEQL is the weighted sum of squares of residuals divided by the degrees of freedom (WSOS/DF).

## MATERIALS AND METHODS

_Adsorption Isotherms_ kG adsorption isotherms (q vs. $c_{eq}$) were determined in triplicate batch systems as a function of $I_S$ (0.01 or 0.1 M NaNO$_3$), pH (5 or 9), and T (7, 25, and 45°C). Suspensions containing 0.2 g goethite were equilibrated with 20 mL of pH-adjusted solutions in either 0.01 M or 0.1 M NaNO$_3$ at the desired T (± 0.1°C) for 16 h. Ketogluconate was then added to achieve initial concentrations ($c_{in}$) that ranged from 0.02 to 0.1 mM kG. The batch systems were equilibrated for an additional 72 h at T. After equilibration, the liquid and solid phases were separated by centrifugation. Aliquots of the supernatant were withdrawn for kG analysis by ion chromatography, and the remaining supernatant was used for pH determinations. The adsorbed concentrations of kG (q) were computed by difference between the initial ($c_{in}$) and equilibrium concentrations ($c_{eq}$).

The Langmuir:

$$q_{kG} = \frac{bK_L c_{eq}}{(1 + K_L c_{eq})}$$

and the Dubinin-Radushkevich (D-R):

$$q_{kG} = b \exp\left[-k\left\{RT \ln\left(1 + \frac{1}{c_{eq}}\right)\right\}^2\right]$$

models where used to describe the kG adsorption isotherms. In these expressions, b is the adsorption maximum, $K_L$ is the Langmuir constant ($bK_L$ is the effective Henry's Law constant, $k_H$), k is related to the mean energy of adsorption ($E = (2k)^{-0.5}$), R is the gas constant, and T is the temperature.

_Thermodynamic evaluations_ The van't Hoff equation was used to determine the enthalpy ($\Delta H_{ad}$) and entropy ($\Delta S_{ad}$) of adsorption:

$$\ln k_H = -\frac{\Delta H_{ad}}{RT} + \frac{\Delta S_{ad}}{R}$$

This equation assumes that $\Delta H_{ad}$ and $\Delta S_{ad}$ are constant and independent of T. Thus, the variation of ln $k_H$ as a function of $T^{-1}$ may be used to determine $\Delta H_{ad}$ and $\Delta S_{ad}$ values. Further, the Gibbs free energy of adsorption ($\Delta G_{ad}$) may be determined by: $\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad}$.

### Solid and Suspension Properties Used to Model kG Adsorption by Goethite

| Parameter | Value |
|---|---|
| $S_A$, surface area (m$^2$ g$^{-1}$) | 35 |
| $n_{sA}$, Type A site density (nm$^{-1}$) | 0.13 |
| $S_{TA}$, Type A total site concentration (×10$^{-5}$ mol L$^{-1}$) | 7.5 |
| C, capacitance (F m$^{-2}$) | 0.9 |
| a, suspension density (g L$^{-1}$) | 10 |
| Background electrolyte (M NaCl) | 0.001 or 0.01 |
| Aqueous reactions | log K |
| $H_2O = H^+ + OH^-$ | −14.00 |
| kG$^-$ + H$^+$ = HkG$^0$ | 3.00 |
| kG$^-$ = H$_{-1}$kG$^{2-}$ + H$^+$ | −11.97 |
| Surface reactions† | log K$^{int}$ |
| $\equiv FeOH^{0.5-} + H^+ = \equiv FeOH_2^{0.5+}$ | 9.5 |
| $\equiv FeOH^{0.5-} + Na^+ = \equiv FeOH^{0.5-}$–Na$^+$ | −1.0 |
| $\equiv FeOH^{0.5-} + H^+ + Cl^- = \equiv FeOH_2^{0.5+}$–Cl$^-$ | 8.5 |
| kG complexation (WSOS/DF = 6.58) | log K$^{int}$ |
| $FeOH^{0.5-} + H^+ + kG^- = \equiv FeOkG^{0.5-} + H_2O$ | 16.09 |
| $2FeOH^{0.5-} + H^+ + kG^- = \equiv Fe_2O_2H_{-1}kG^- + 2H_2O$ | 20.56 |

† $\equiv FeOH$ represents the singly-coordinated surface hydroxyl

## RESULTS



Goethite Charging Characteristics



kG Adsorption Envelopes

## RESULTS



kG Adsorption Isotherms
[Solid lines, Langmuir model; dashed lines, D-R model]



Temperature-Dependence of the Effective Henry's Law Constant ($k_H$)

### Thermodynamic Parameters for kG Adsorption

| °C | 0.01 M NaNO$_3$ $\Delta H_{ad}$† | $\Delta S_{ad}$ | $\Delta G_{ad}$ | 0.1 M NaNO$_3$ $\Delta H_{ad}$ | $\Delta S_{ad}$ | $\Delta G_{ad}$ |
|---|---|---|---|---|---|---|
| | | | pH 5 | | | |
| 7 | | | −12.96 | | | −11.15 |
| 25 | 53.7 | 244 | −15.56 | 34.22 | 174 | −18.12 |
| 45 | | | −21.61 | | | −20.90 |
| | | | pH 9 | | | |
| 7 | | | −9.05 | | | −10.01 |
| 25 | 22.32 | 120 | −12.71 | 29.51 | 150 | −14.32 |
| 45 | | | −16.22 | | | −18.62 |

†Units are kJ mol$^{-1}$ for $\Delta H_{ad}$ and $\Delta G_{ad}$; J K$^{-1}$mol$^{-1}$ for $\Delta S_{ad}$

## CONCLUSIONS

- kG adsorption increases with increasing T, indicating an endothermic and entropically-driven adsorption process
- The magnitude of $\Delta H_{ad}$ for kG adsorption is similar to that of other specifically-adsorbed ligands

## CONCLUSIONS

- The adsorption of kG by goethite is pH-dependent and $I_S$-independent, suggesting a specific retention mechanism
- kG adsorption is reduced in the presence of $PO_4$ and $AsO_4$ throughout the pH 3 to 10 range; $SO_4$ reduces kG adsorption in pH < 6 systems (further evidence of specific kG retention)
- kG adsorption is described by a surface complexation model that includes both monodentate [$\equiv FeOkG^{0.5-}(s)$] and bidentate [$\equiv Fe_2O_2H_{-1}kG^{0.5-}(s)$] surface species