# **Supporting Information**

# Mechanistic and Kinetic Insights into the Ligand-Promoted Depassivation of Bimetallic Zero-Valent Iron Nanoparticles

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Contents: 2 tables and 1 figure

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Section S1. Dissolution of nZVI under anaerobic conditions



**SI Figure S1.** Dissolution of nZVI under anaerobic conditions. Symbols are experimental data; lines are model predictions based on Eqs 1-3 in Table 1.

## Section S2. Stability Constant Calculation

In order to apply stability constants to high ionic strength (I = 0.5) solutions, the mean ion activity coefficient was determined from Davies equation:

$$\log f_{\pm} = -AZ_i^2 \left(\frac{I^{1/2}}{1 + I^{1/2}} - bI\right)$$
(S1)

where *I* is ionic strength and *A* and *b* are constants in Davies equation (A = 0.5 and  $b = 0.24^{1}$ ). The values of ion activity coefficients at I = 0.5 as a function of charges are shown in SI Table S1.

**SI Table S1.** Ion activity coefficients for dissolved ionic species at I = 0.5

$Z_i$	$-\log f_{\pm}$
±1	0.15
$\pm 2$	0.59
$\pm 3$	1.32
±4	2.35

#### Section S3. Calculation of Outer-Sphere Complex Stability Constants

A theoretical expression for outer-sphere complex stability constant ( $K_{os}$ ), derived from statistical considerations and including both the electrostatic interaction of the ions and the effect of ionic strength on those interactions, is given by<sup>2</sup>

$$K_{\rm OS} = \frac{4000\pi Na^3 f_{\pm}^2}{3} \exp(\frac{-Z_{\rm M} Z_{\rm EDTA} e^2}{4\pi\varepsilon_0 \varepsilon k Ta})$$
(S8)

where *e* is the elementary charge of an electron ( $1.6 \times 10^{-19}$  C), *N* is the Avogadro constant ( $6.0 \times 10^{23}$  mol-1), k is the Boltzmann constant ( $1.4 \times 10^{-23}$  J K-1), *T* is the absolute temperature (298 K),  $\varepsilon_0$  is the vacuum permittivity ( $8.85 \times 10^{-12}$  C),  $\varepsilon$  is the relative permittivity of water at 25 °C (78.5), *a* is the distance of closest approach of the ions (assumed to be  $5.0 \times 10^{-10}$  m),  $Z_{\rm m}$  and  $Z_{\rm EDTA}$  are the charges of the individual metal and EDTA species, respectively, and  $f_{\pm}$  is the mean ionic activity coefficient,

$$\log f_{\pm} = A Z_{\rm M} Z_{\rm EDTA} \left( \frac{I^{1/2}}{1 + I^{1/2}} - bI \right)$$
(S9)

where *I* is ionic strength and *A* and *b* are constants in Davies equation (A = 0.5 and  $b = 0.24^{1}$ ). The values of ion activity coefficients and outer-sphere stability constants as a function of charges at I = 0.5 are shown in SI Table S3. As such, the complex formation rate constants can be calculated according to Eq. S7, as demonstrated in SI Table S4.

$Z_{\rm M}Z_{\rm EDTA}$	$f_{\pm}^{2}$		K <sub>os</sub>	
	I = 0	I = 0.5	$I = 0^{a}$	I = 0.5
0	1	1	0.32	0.32
-1	1	0.51	1.32	0.41
-2	1	0.26	5.50	0.52
-3	1	0.13	22.9	0.67
-4	1	6.66×10 <sup>-2</sup>	95.5	0.87
-6	1	1.72×10 <sup>-2</sup>	1.66×10 <sup>3</sup>	1.44
-8	1	4.43×10 <sup>-3</sup>	$2.88 \times 10^{4}$	2.38

**SI Table S3**. Correction of outer-sphere stability constants to I = 0.5.

<sup>a</sup>Morel and Hering<sup>1</sup>

### REFERENCES

1. Morel, F. M. M.; Hering, J. G., *Principles and Applications of Aquatic Chemistry*. John Wiley & Sons: 1993.

2. Fujii, M.; Rose, A. L.; Waite, T. D.; Omura, T., Effect of divalent cations on the kinetics of Fe(III) complexation by organic ligands in natural waters. *Geochim. Cosmo. Acta* **2008**, *72*, (5), 1335-1349.