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SURFACE COMPLEXATION MODELING

Hydrous Ferric Oxide

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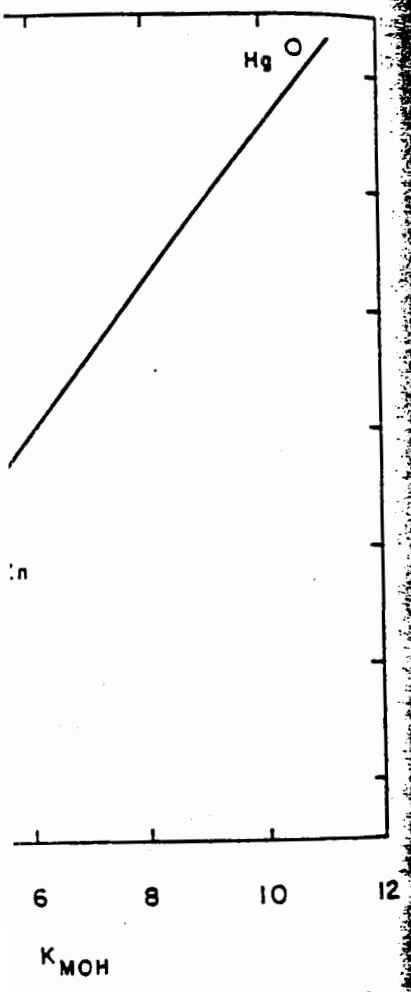

st hydrolysis constants for six cations
ons corresponding to K_2^{int}.) The fitted
393, and is the result of a linear least
es correspond to 95% confidence limits

)ugger et al., 1964; Schindler et al.

complexation constants for binding
≡FeOM⁺) are plotted against th
ons. Both correlations are good wit
iting perhaps that surface hydrox
n solution.
id 10.2 can be used to predict surf
it cations for which limited or

sorption data exist. This has been done for several cations and the results are reported in Table 10.5. For example, the sorption constants for Mn^{2+} are estimated at $10^{-0.4}$ and $10^{-3.5}$, slightly weaker than those for Co^{2+}.

The plots of $\log K_1^{int}$ and $\log K_2^{int}$ versus $\log K_{MOH}$ are the graphical representations of one of the several linear free-energy relationships discussed by Irving and Rossotti (1956). The derivation of such LFERs consists of (1) expressing the log K values as differences in the standard molar free energies (μ° values) of reactants and products,

$$RT \ln K^{int} = \mu^\circ_{\equiv FeOH} + \mu^\circ_M - \mu^\circ_{\equiv FeOM} - \mu^\circ_H \tag{10.3a}$$

$$RT \ln K_{MOH} = \mu^\circ_{OH} + \mu^\circ_M - \mu^\circ_{MOH} \tag{10.3b}$$

TABLE 10.5 Derived and Estimated Surface Complexation Constants for Some Cations[a]

Ion	$\log K_{MOH}$[b]	$\log K_1^{int}$	$\log K_2^{int}$
Ba^{2+}	0.53	5.46	−7.2[c]
Sr^{2+}	0.71	5.01	−6.58
Ca^{2+}	1.15	4.97	−5.85
Mg^{2+}	2.56	[d]	−4.6[c]
Ag^+	2.0	−0.72	−5.3[c]
Mn^{2+}	3.41	−0.4[e]	−3.5[c]
Co^{2+}	4.35	−0.46	−3.01
Ni^{2+}	4.14	0.37	−2.5[c]
Cd^{2+}	3.92	0.47	−2.90
Zn^{2+}	5.04	0.99	−1.99
Cu^{2+}	6.5	2.89	0.6[c]
Pb^{2+}	6.29	4.65	0.3[c,f]
UO_2^{2+}	8.2	5.2[e]	2.8[c]
PuO_2^{2+}	8.4	5.4[e]	3.0[c]
Be^{2+}	8.60	5.7[e]	3.3[c]
NpO_2^{2+}	8.83	5.9[e]	3.6[c]
Hg^{2+}	10.60	7.76	6.45
Sn^{2+}	10.60	8.0[e]	5.9[c]
Pd^{2+}	12.0	9.6[e]	7.7[c]

[a]This represents a completion and extension of Tables 10.1 and 10.2; see those tables for the reactions corresponding to K_1^{int} and K_2^{int}.
[b]From Baes and Mesmer (1976), except for Cu^{2+}, which is from Smith and Martell (1976).
[c]Estimated using the LFER in Figure 10.2.
[d]An LFER cannot be established relating $\log K_1^{int}$ to $\log K_{MOH}$ for Ba^{2+}, Sr^{2+}, and Ca^{2+}; hence $\log K_1^{int}$ for Mg^{2+} cannot be established.
[e]Estimated using the LFER in Figure 10.1.
[f]Probably an underestimate.