

Ionic strength dependence of transition and heavy metal adsorption onto metal oxides

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Transition and heavy metal adsorption onto metal oxides influences the global cycling of metals, plays a role in the formation of enriched metal deposits, and filters natural and waste waters in the subsurface environment. The ionic strength dependence of metal adsorption is important to geochemists because natural waters are composed of different electrolyte types and vary widely in ionic strength. It is generally accepted that transition and heavy metal adsorption onto metal oxides does not exhibit an ionic strength dependence and that this behaviour indicates that metals bind to solid surfaces as inner-sphere complexes. However, Fig. 1 illustrates that while Cd adsorption from NaNO_3 solutions onto goethite (Hayes and Leckie, 1987) does not exhibit major variations with ionic strength, Cd adsorption from NaCl solutions onto γ -alumina (Kosmulski, 1996) progressively decreases with increasing ionic strength, and Cd adsorption from NaClO_4 solutions onto γ -alumina (Kosmulski, 1996) may increase with increasing ionic strength. An analysis of these datasets and many others reported in the literature indicates that transition and heavy metal adsorption is very strongly dependent on the nature of the electrolyte, and may increase, decrease, or exhibit little variation with increases in the ionic strength of the solution.

In this study, experimental data for the adsorption of numerous transition and heavy metals onto quartz, silica, alumina, corundum, goethite, anatase, magnetite and manganese dioxide, from NaClO_4 , NaNO_3 , KNO_3 , and NaCl solutions, over a wide range of ionic strengths, have been fit using the triple layer model of Sahai and Sverjensky (1997), and at most two metal surface complexes. This model accounts for the ionic strength dependence of aqueous ion activity coefficients through the use of the extended Debye-Huckel expression. It is accompanied by a database of surface site densities, capacitances, and equilibrium constants for surface protonation, deprotonation, and electrolyte adsorption, which was modified to accommodate reported surface titration data and experimentally-determined points of zero charge.

Recent applications of the triple layer model have suggested that divalent transition and heavy metals (M^{2+}) form simple surface species such as >SOM^+ in nitrate solutions (Hayes and Leckie, 1987; Katz and Hayes, 1995). However, using the triple-layer model of Sahai and Sverjensky (1997), surface complexes of the form $\text{>SOHM}^{2+}\text{NO}_3^-$, where M^{2+} is bound to a neutral surface site (>SOH) on the 0-plane of the triple layer model and NO_3^- is on the β -plane, are found to best fit data collected over a wide range of ionic strengths for Cd and Pb adsorption onto goethite (Hayes and Leckie, 1987) and Co adsorption onto corundum (Katz and Hayes, 1995). A similar type of surface complex $\text{>SOM}^+\text{NO}_3^-$ fits the adsorption data for UO_2 onto hydrous ferric oxide at pH values where the system can be assumed to be depleted in CO_2 . A combination of two complexes, including $\text{>SOHM}^{2+}\text{NO}_3^-$ was found to fit Zn adsorption onto anatase (James and MacNaughton, 1977).

In addition to sharing a common electrolyte, the systems described above have several other common characteristics: (a) the solids have intermediate-range dielectric constants between 10 and 22, (2) metal adsorption occurs on positively-charged surfaces, and (3) MNO_3^+ is the predominant aqueous complex over the pH range of adsorption and the range of ionic strengths studied. The one exception to (3) is Zn adsorption onto anatase, which required a second surface complex, >SOZnOH , to fit the adsorption data at low ionic strengths, where ZnOH^+ is the predominant aqueous complex. Adsorption of the predominant aqueous complex rather than the more abundant bare metal ion may be favoured because the free energy of solvation is smaller for a monovalent cationic complex (e.g. MNO_3^+ or MOH^+) than for a divalent cation (i.e. M^{2+}) (James and Healy, 1972). Metal-ligand complexation is also favoured in low dielectric constant environments like the interface.

Metal adsorption data over a wide range of ionic strengths in NaCl and NaClO_4 solutions are more limited. Calculations for Cd adsorption from NaCl and NaClO_4 solutions onto γ -alumina are best matched by calculations using the surface complexes,

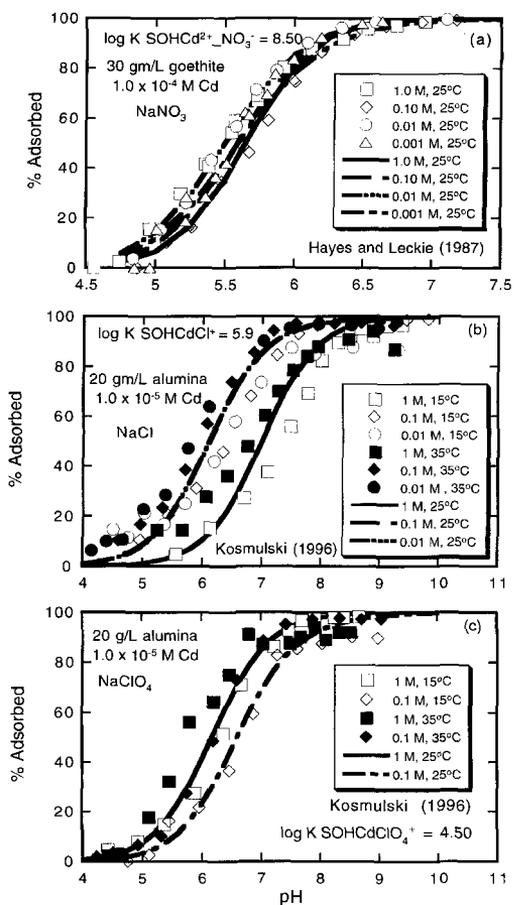


FIG. 1. The ionic strength dependence of Cd adsorption. For Kosmulski (1996) data, the open symbols indicate data collected at 15°C and the closed symbols indicate data collected at 35°C. In all cases, the symbols represent experimental data and the lines represent model calculations at 25°C.

$>\text{SOHCdCl}^+$ and $>\text{SOHCdClO}_4^+$, respectively. The predominant aqueous cadmium complex in a 0.01 M NaCl solution is CdCl^+ , and cadmium chloride complexes are more abundant than the bare metal ion, Cd^{2+} , at higher ionic strengths. However, cadmium perchlorate complexes do not form readily in aqueous solution. Therefore, these complexes must form at the interface. Due to its large size, the perchlorate anion is less solvated than

either Cl^- or NO_3^- , and will therefore adsorb preferentially to the surface.

It appears that transition and heavy metal adsorption onto intermediate-range dielectric constant solids with positively-charged surfaces often occurs in combination with the adsorption of the electrolyte anion. However, metal adsorption onto negatively-charged, low dielectric constant solids like quartz and silica, is not always accompanied by the electrolyte anion. Instead, the metal adsorption edges for these minerals are usually best fit by a bare metal or metal hydroxide complex. The large solvation effects and the negative charge of these solids may inhibit the adsorption of the electrolyte anion.

In summary, from the simple systems examined that contain a transition metal, solid, and 1:1 electrolyte, transition and heavy metals often adsorb in combination with the electrolyte anion. Although transition and heavy metal adsorption can exhibit an ionic strength dependence, this variation can be accounted for by adsorption onto the 0-plane of the triple-layer model, in a manner that is consistent with the concept that transition and heavy metals adsorb as inner-sphere complexes. However, on positively-charged, intermediate-range dielectric constant solids like goethite and corundum, the electrolyte anion adsorbs with the metal, either together as an aqueous metal-ligand complex, or separately forming a metal-ligand complex at the interface. On silica and quartz, adsorption of the bare metal ion or metal hydroxide is preferred. In the future, additional experiments should be conducted to study the ionic strength behaviour of metal adsorption in different electrolytes and, particularly, in electrolytes more similar to those found in nature.

References

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