Further Comment: Coulombic Effects on the Adsorption of Trace Cations on Clays

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Recently Bradbury and Baeyens (B & B) published a two part experimental and modeling study of the sorption of trace metals (chiefly Zn and Ni) on montmorillonite (Bradbury and Baeyens, 1997). For their model, they combined an expression for ion exchange in the clay lattice with a surface complexation formulation for clay edges, similar to what is now commonly done for oxides. To achieve a good fit of their data, however, B & B eliminated the so-called coulombic term that is used in the surface complexation model to account for the variation in sorption energy resulting from the changes of electrostatic surface charge with pH. This ad hoc elimination was questioned by one of us (Morel, 1997). Here we examine the use of a coulombic term to model metal sorption on clay edges.

In their study, B & B observed a sorption edge for Zn with a slope of approximately unity on a log $R_d^{Zn}(= [Zn\ sorbed]/[Zn\ dissolved])$ vs. pH graph. This was inconsistent with a model which, in the pH range of interest, predicted an exchange of one proton for Zn^{2+} **and** an increasing coulombic attraction of Zn^{2+} by the increasingly negative surface at higher pH's. Thus B & B simply eliminated the coulombic term from the surface complexation model to fit their data. As can be seen in Fig. 1a, fit 1, however, by adjusting the acidity constants of the high affinity surface sites, which are effectively unconstrained, one can obtain a fair approximation of the Zn sorption data. One can in fact obtain a very satisfactory fit of the sorption edge for Zn, while keeping the coulombic term in the model, by ajusting further either the surface area (Fig. 1a, fit 2) or the concentration of high affinity sites (Fig. 1a, fit 3), both of which are poorly constrained by the available data. The acid–base titration data are then fitted with only two acidity constants for the weak sorbing sites (Fig. 1b). Thus it is indeed the change in acidity constants of the strong sorbing sites, rather than the elimination of the coulombic term per se, which was most critical in B & B's ability to fit their Zn sorption data.

Equally satisfactory fits of the Mn adsorption edge and the Zn isotherms are also readily obtained by complementing the same model parameters with appropriate sorp-

tion constants for Mn and for weak sorbing sites. It is only when considering the nickel data, simultaneously with the acid base and the Zn sorption data, that we found it more difficult to obtain a completely satisfactory fit with the traditional surface complexation model (including a coulombic term). The main difficulty there is to fit the plateau in sorption at pH = 8–10 observed in all experiments, including those at low ionic strength (0.03 and 0.01 M). By choosing appropriate (and reasonable) values for both the concentration of strong sorbing sites and the surface area, one can obtain a
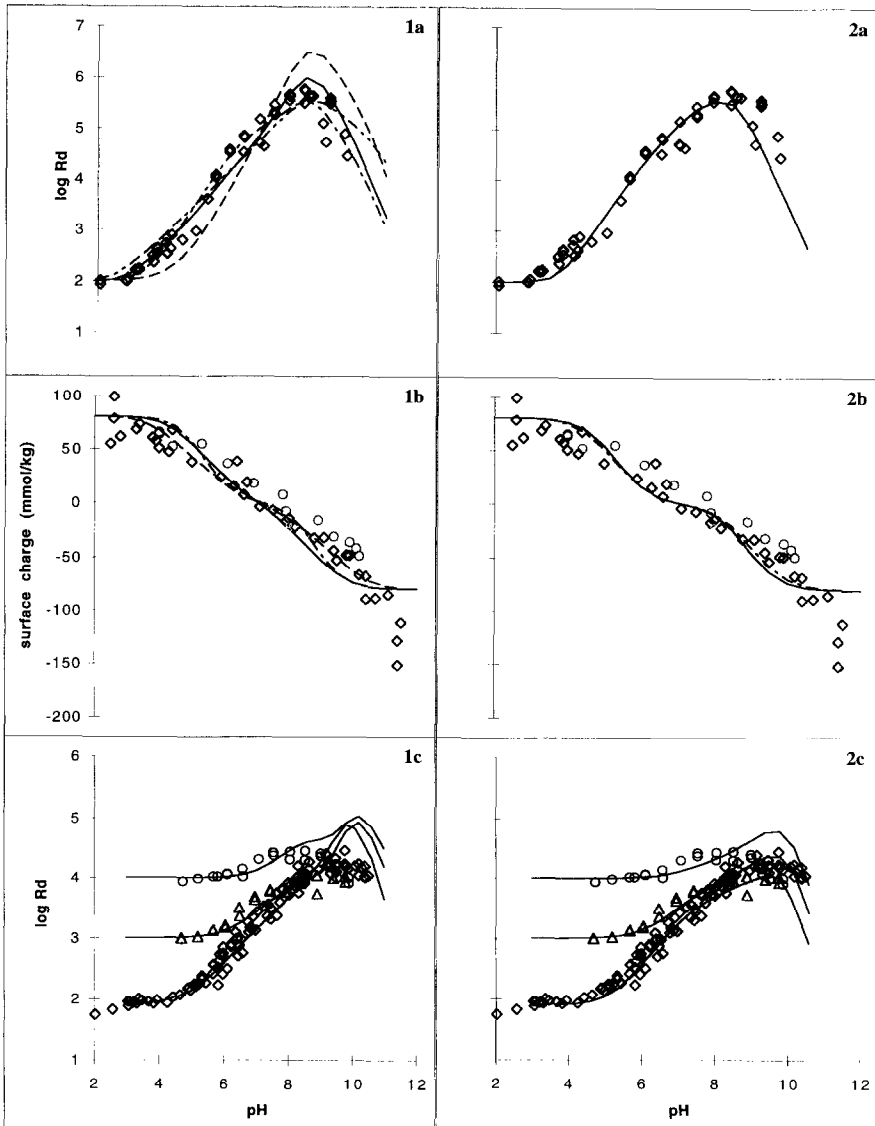
reasonable fit of the Ni sorption edges (Fig. 1c) while maintaining a good fit of the Zn sorption edge and the acid–base titration data (Fig. 1 (a) and 1 (b), fit 4). As seen in Fig. 1c, however, the model overpredicts slightly but systematically the maximum in R_d^{Ni}. The increasing coulombic attraction of Ni^{2+} by the increasingly negative surface tends to increase R_d^{Ni} before the formation of the $NiOH^+$ species in solution decreases it at higher pH. Using a low site concentration is insufficient in this case as the desorption of Zn (present as a contaminant in the solid) also increases R_d^{Ni} at pH $\simeq$ 9.

The simplest way to obtain a good fit of all the data with the surface complexation model (superposed on an ion exchange model) is to decrease the importance of the coulombic term by increasing the surface area of the sorbing solid. This may be reasonable since, depending on the exact size of the clay particles, there might not be enough possible proton exchange sites on the edges of the clay particles to account for the measured extent of proton exchange (which controls the calculated surface charge and, hence, the coulombic energy of adsorption). Many of the proton exchange sites must thus be on the faces or interlayers whose total area may be as high as 800 m^2/g (Bradbury and Baeyens, 1997). Choosing a value of 500 m^2/g, allowed us to fit all the data adequately (Fig. 2). Obviously in such a model the role of the coulombic term in the sorption of cations becomes small, though it still leads to a slight overprediction of the maximum in R_d^{Ni} at $I = 0.01$ M (Fig. 2c). The benefit, of course, is that one obtains a decent fit of the acid–base titration data with only two pK_a's for the weak sorbing sites (Fig. 2b). It is then perhaps true that cation sorption on clay edges occurs with little contribution from coulombic energy simply because the proton exchange sites are distributed over a very large effective area.

While a satisfactory fit of B & B's sorption data may be obtained in this way, upon reflexion the underlying model seems to us fundamentally unsatisfactory. As calculated, the coulombic term for the surface complexation on clay edges does not take into account the overall negative charge of the clay (caused by isomorphic replacement in the lattice) which probably imparts to them a much more negative electric potential than calculated solely from the surface charge caused by proton exchange. If one is to

Fig. 1. Sorption of cations on clays, modeled by ion exchange and surface complexation on edges with low surface area. – – – fit 1; — — —fit 2, — — – — fit 3, ——————— fit 4. a: Zn sorption edge $I = 0.1$ M. b: titration data. diamonds: $I = 0.5$ M. circles: $I = 0.1$ M. No Zn or Mn were included in the calculations for fits 1, 2 and 3. All the fits are calculated for $I = 0.5$ M. c: Ni sorption edge. diamonds: $I = 0.1$ M, triangles: $I = 0.03$ M, circles: $I = 0.01$ M.

Fig. 2. Sorption of cations on clays, modeled by ion exchange and surface complexation on edges with high surface area. ——————— fit 5. a: Zn sorption edge $I = 0.1$ M. b: titration data. Symbols: see Fig. 1b. ——————— $I = 0.5$ M, — — – — $I = 0.1$ M. c: Ni sorption edge. Symbols: see Fig. 1c. fit 1: $S = 35$ m^2/g, $(S^wOH)_T = 0.08$ mol/kg, $(S^sOH)_T = 2 \ 10^{-3}$ mol/kg, log $^wK^+ = 6.2$, log $^wK^- = -8.3$, log $^sK^+ = 4.5$, log $^sK^- = -5.5$, $(Zn)_T = 10^{-3}$ mol/kg, log $^sK_{Zn} = 3.00$. fit 2: same as fit 1, except for $S = 70$ m^2/g, log $^wK^+ = 5.61$, log $^wK^- = -8.93$. fit 3: same as fit 1, except for $(S^sOH)_T = 10^{-3}$ mol/kg and log $^sK_{Zn} = 4.70$. fit 4: $S = 70$ m^2/g, $(S^wOH)_T = 0.08$ mol/kg, $(S^sOH)_T = 1.6 \ 10^{-3}$ mol/kg, log $^wK^+ = 6.19$, log $^wK^- = -8.19$, log $^sK^+ = 4.5$, log $^sK^- = -5.5$, $(Zn)_T = 10^{-3}$ mol/kg, $(Mn)_T = 4 \ 10^{-4}$ mol/kg, log $^sK_{Zn} = 3.5$, log $^sK_{Mn} = 2.5$, $(Ni)_T = 3 \ 10^{-7}$ mol/l, log $^sK_{Ni} = 2.00$. fit 5: $S = 500$ m^2/g, $(S^wOH)_T = 0.08$ mol/kg, $(S^sOH)_T = 2 \ 10^{-3}$ mol/kg, log $^wK^+ = 5.59$, log $^wK^- = -8.97$, log $^sK^+ = 4.5$, log $^sK^- = -7.5$, $(Zn)_T = 10^{-3}$ mol/kg, $(Mn)_T = 4 \ 10^{-4}$ mol/kg, log $^sK_{Zn} = 1.8$, log $^sK_{Mn} = 0.4$, $(Ni)_T = 3 \ 10^{-7}$ mol/l, log $^sK_{Ni} = 0.00$.

calculate explicitly the coulombic energy to account for long range electrostatic forces among binding sites, it does not seem logical to consider totally separately from each other the reactions in the lattice (ion exchange on fixed charges) and at the surface (complexation by surface ligands). It thus appears that a more fundamental re-examination of the nature of trace metal sorption on clays is necessary. A successful model will presumably have to include an appropriate description of the location of the dominant acid–base groups and combine their coulombic effects on the high affinity metal sorbing sites with those of the fixed charges in the clay lattice.

References

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