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Discussion on: "A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part I: Titration and sorption measurements. Part II: Modelling" by Bart Baeyens and Michael H. Bradbury

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Praise and thanks must be addressed first to Baeyens and Bradbury for performing such a careful experimental and modelling study of trace metal sorption on montmorillonite and for writing such detailed and didactic papers, and then to Marsily for inviting and publishing this work and its comments. A simple measure of the methodical approach of the authors and the generosity of the editor is given by the number of figures in the second paper: it is certainly now uncommon to read an article with 28 figures; we can only hope that it is not beyond the fortitude of too many readers.

I believe that these articles will advance two important scientific and pedagogical goals. Scientifically they begin verifying the hypothesis that trace metal sorption on clays may be understood and modelled as the superposition of simple ion exchange and surface complexation processes. Pedagogically they provide for the readers of the *Journal of Contaminant Hydrology* (JCH) a clear and systematic introduction to the somewhat arcane but important topic of surface complexation modelling.

With praise necessarily come criticisms of which I have two. One is the absence of an explanation for the decrease in metal sorption at high pH predicted by the model(s), or equivalently for the maximum in sorption at pH values of 8–9, whose position is a matter of some concern to the authors. After reflection, I presume this predicted decrease results from the calculated formation of dissolved hydrolysis metal species. Such a prediction is made problematic by the possible concomitant formation of insoluble hydrolysis species, possibly as surface precipitates, which, I presume, has not been included in the model. For example, I doubt that the large decrease in the partitioning between the solid and dissolved phases predicted for nickel in Fig. II-12 at

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high pH values could ever be measured under the conditions of those experiments. But I am not sure, and this brings me to my second criticism: the absence of important specific information, something particularly surprising in such detailed papers. My attempt at understanding quantitatively the reasons for the predicted decrease in (Ni) sorption at high pH was hindered by, for example, the absence of a list of all the important reactions considered (e.g. $NiOH^+$ formation?) along with their constants, and the difficulty in finding the exact values of such parameters as the solid/liquid ratio or the total metal (Ni) concentrations in the experiment. It would also have helped if Fig. II-12 and similar figures had a second, more obvious, ordinate than R_d, such as:

$$\frac{C_{\mathrm{init}} - C_{\mathrm{eq}}}{C_{\mathrm{init}}} = \frac{(\equiv \mathrm{SOM}^+)}{M_{\mathrm{tot}}}$$

Praise and criticisms aside, a fundamental question is raised by the authors' results: why is a coulombic term not required in their adsorption model and why does the inclusion of such a term render the model unable to fit the experimental data. Before attempting to find an explanation in some fundamental differences between the surface complexation properties of clays and those of oxides (for which the electrostatic models have been developed), we can examine in some detail why the removal of the coulombic term helped Bradbury and Baeyens in their data-fitting exercise and the general role of the coulombic term in surface complexation modelling.

Bradbury and Baeyens's iterative scheme for fitting their experimental data is best exemplified by the progress from Fig. II-4 to Fig. II-6 to Fig. II-8. Having noted the poor model fit of Fig. II-4, the authors explain: "the curve shape can be changed..... but only by radically altering the values of $K_{\mathrm{int}}(+)$, $K_{\mathrm{int}}(-)$ and the total site capacity. This, however, leads to unacceptable fits to the titration data." They then proceed in the modelling of Fig. II-6, to radically alter $K_{\mathrm{int}}(+)$ and $K_{\mathrm{int}}(-)$ and to (temporarily) accept an unacceptable fit of the titration data (Fig. II-5). The fact is, I believe that the spacing of the two $\mathrm{p}K_a$ values by 2.25 rather than 1.05 pH units on either side of the PZC (5 and 9.5 rather than 6.2 and 8.3) is mostly responsible for the improved fit rather than the elimination of the coulombic term. Had it been included, the coulombic term would have played much less of a role in Fig. II-6 than in Fig. II-4, simply because the surface would have been less charged at the relevant pH values.

In the next step, despite appearances to the contrary, the improvement in model fit from Fig. II-6 to Fig. II-8 is not the result of considering two types of low metal affinity acid–base groups on the surface ($S^{W1}OH$ and $S^{W2}OH$). The addition of these acid–base groups improves the fit of the acid–base titration data (Fig. II-7) but can have no influence on the calculated Zn sorption since: (1) only the high affinity sites (S^SOH) actually bind Zn at trace concentrations, and (2) the coupling between the weak and strong sorbing sites provided by the coulombic interactions has now been eliminated. In fact the improvement in fit between Fig. II-6 and Fig. II-8 results from the choice of totally different protonation constants for the strong sorbing sites as compared to the weak sorbing sites. (In other words the fit of Fig. II-8 has been optimized on three — $K_{\mathrm{int}}(+)$, $K_{\mathrm{int}}(-)$ and ${}^{S}K_{\mathrm{int}}$ — rather than one parameter, ${}^{S}K_{\mathrm{int}}$). I believe that an equally good fit could have been obtained in Fig. II-4 if the $\mathrm{p}K_a$ values of the high affinity sites had been similarly allowed to vary independently from those of the low affinity sites.

I conclude this examination of Bradbury and Baeyens' fitting procedure with a double bet (how about some fine Swiss chocolate?).

Bet #1. Including a coulombic term in the model of Fig. II-8 or in some kindred model, would provide equally good fits of the data.

Bet #2. By including a coulombic term, a model with two fewer fitting parameters (than that of Fig. II-8) would provide an equally good fit of the data. Such a model would need to include only one type of low metal affinity acid groups (thus only two pK_a values for these), but allow different pK_a values for the high metal affinity groups (as in Fig. II-8).

I have just argued that including a coulombic term probably would allow as good a model fit of the data as excluding it, and perhaps with fewer parameters. This does not address the more basic question of why such a term, which is fundamental to surface complexation models [1], is not in fact necessary to model Baeyens and Bradbury's data. From a practical data-fitting point of view (rather than a theoretical physical or thermodynamic one) a coulombic term allows one to fit parsimoniously three important features of the data regarding surface reactions on oxides: (i) the ionic strength dependence of the acid–base titrations, (ii) the smoothness of the acid–base titration curves, and (iii) the independence of cation sorption on ionic strength.

The first of these is clearly the most important since the coulombic term accounts for the fanning out of the acid–base titration curves around the PZC as a function of I, one of the most remarkable experimental features of such titrations in oxide suspensions. This of course is hardly necessary in the Baeyens and Bradbury study since the experimental acid–base titrations do not exhibit any measurable separation as a function of ionic strength (Fig. I-4). This may well be explained by the relatively small experimental range in ionic strengths: 0.1 and 0.5 M. If one had titration data for montmorillonite at low ionic strengths and could adequately take into account the extent of H^+ exchange in the clay lattice (probably a difficult thing) then either the necessity of a coulombic term to model the data would become apparent, or the differences with the behavior of oxides would provide an important clue as to the physical difference between clays and oxides.

The necessity to smooth out titration curves is well illustrated in Fig. II-5: a diprotic acid titration curve simply cannot fit the experimental data. Besides the introduction of a coulombic term, there are of course other means to obtain a smooth fit, such as adding more pK_a values to the model or including a continuous distribution of pK_a values as is often done for humic acids. Having included four different pK_a values in their final model (actually six if one counts those of the high affinity sites), the authors, unsurprisingly, obtain a smooth fit of the titration curve without the need for a coulombic term.

Finally the role of the coulombic term in balancing out the effects of the activity coefficients of dissolved cations is one of the more intriguing features of surface complexation modelling. Typically the decreased (re)activity of a metal ion as ionic

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[1] What follows is largely inspired from Chapter 9 of Dzombak and Morel (1990), which I presumed to have been read only by a handful of courageous scientists.

strength increases is balanced out by the decreasing repulsion from the positive surface charge (due to shielding by counter ions). The result is to predict no effect of I on metal sorption as is seen in the data. An examination of the data from Fig. I-5 of Baeyens and Bradbury's study shows that this effect may be of little practical importance in clays: as the ionic strength decreases, the ion exchange of the metal (Ni) in the lattice of montmorillonite increases drastically, but it is difficult to tell if the chemical sorption on the edge sites is also affected. According to the model of Bradbury and Baeyens it should be (see Fig. II-12); according to a model that included a coulombic term, it should not.

In short, Baeyens and Bradbury were able to fit their data without including a coulombic term in their model because either their experimental data on clays do not show the features that make it necessary in the case of oxides, or they achieved the desired modeling result by other means.

This comment is quite detailed, perhaps nit-picky in its criticisms, and only a few readers of JCH will wish to follow the specifics of the arguments or even perhaps care what coulombic terms do or do not do. I believe, however, that we need to examine the problem at this level if we are to make the necessary progress. The specific challenge before us is to obtain a sound thermodynamic description of the coordinative properties of the solid–water interface, now for materials as complex as clays. The validity and practical utilities of such mathematical devices as coulombic interaction terms are at the heart of the issue. We must resolve it if we are to do more than fit data empirically with an increasing number of ad-hoc parameters and obtain useful predictive capabilities. There are other ways to address the electrostatic modelling of metal coordination by clays than to superpose a distribution coefficient for ion-exchange with surface complexation (see, for example, Dzombak and Hudson, 1995). Clearly this multi-disciplinary problem will be solved through the joint effort of many types of scientists who must learn from each other. I have learned a great deal from reading Baeyens and Bradbury's work, I have also learned from writing this comment, and I will surely learn from reading the authors' response. I hope the readers of JCH will as well.

References

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