

Comparison of 1-pK and 2-pK Versions of Surface Complexation Theory by the Goodness of Fit in Describing Surface Charge Data of (Hydr)oxides

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1-pK and 2-pK formulations exist in surface complexation theory with respect to the description of basic charging behavior of (hydr)oxide electrolyte interfaces. The 2-pK approach has been commonly used with at least four different electrostatic models, whereas the 1-pK model has been primarily used with only one of those electrostatic models. In this paper the 1-pK approach is combined with three more electrostatic models. The eight resulting possible combinations have been tested on several sets of data. Applying the 2-pK basic Stern model (BSM) and the triple-layer model (TLM) was not satisfactory: due to the high number of adjustable parameters involved in these model variations the optimization procedure of the applied computer codes did not converge. This was taken as an a priori justification to exclude even more complicated (four-layer) models. For the remaining six models which could be successfully applied in the present paper, the goodness of fit parameter given by a computer code was used to compare the quality of the description of the chosen experimental data by the respective models. A purely diffuse layer model (DLM) generally gave the poorest fit to experimental data when combined with the 1-pK approach and was only slightly better when combined with the 2-pK formalism. Either the 1-pK BSM or the 2-pK constant capacitance model (CCM) gave the best fit to the data in all the examples. However, it was found in two cases that some arbitrary constraint was necessary to define a unique (and thus meaningful) parameter set for the 2-pK CCM. The 1-pK TLM version allowed in more than half of the examples to determine a unique parameter set, which is impossible with the 2-pK TLM. It is concluded that the 1-pK BSM should be considered as the first choice model with respect to the goodness of fit and the uniqueness of the estimated parameters. The 2-pK CCM is still a good choice for a constant ionic strength case when the experimental data allow a determination of unique parameters and if only goodness of fit is used as a criterion.

Introduction

Processes at mineral water interfaces are of utmost importance for the fate of pollutants in the environment. It is at

these interfaces that dissolution/precipitation, redox, and sorption reactions occur. Consequently, there is a need to describe these processes. Surface complexation models allow this, and surface speciation based on such models has been used to explain the above-mentioned environmentally important processes when they were studied on lab systems. Describing basic charging (i.e., the results of pure acid–base titrations) is a prerequisite for any further purpose. Adsorption models for metal or ligand interactions in particular require a model for basic charging. Any adsorption model, which relies on linear additivity of submodels (and that is what most modelers right now practice) and goes beyond basic charging, will be dependent on the quality of the pure acid–base model.

For some 25 years surface complexation modeling has been practiced to describe the basic charging behavior of (hydr)oxides. Work by Schindler and Gamsjäger (1), Stumm et al. (2), as well as Yates et al. and Davis et al. (3) introduced the constant capacitance model (CCM), the diffuse layer model (DLM) and the triple layer model (TLM), respectively. All these models were based on the so-called 2-pK approach proposed by Parks (4). The paper by Westall and Hohl (5) gives an overview of all these versions and adds the basic Stern model (BSM). Common to these model variations are the following two surface chemical reactions between surface groups ($\equiv\text{MaOH}$) and protons near the surface (denoted by the subscript “s”):



Thus two stability constants have to be determined in some way. Quite discouraging results in the paper by Westall and Hohl (5) were that (i) the different models were equally successful in describing experimental data and (ii) the two stability constants depended on the model.

Another concept of surface complexation modeling was first introduced by Bolt and van Riemsdijk (6) and is currently referred to as the 1-pK model. This approach is based on the following surface chemical reaction.



One major advantage compared to the 2-pK model is a reduction in adjustable parameters since the stability constant appearing in eq 3 can be experimentally obtained as the pristine point of zero charge (PPZC) of a solid. Note also that compared to the 2-pK results (5), the 1-pK stability constant for eq 3 will not be dependent on the electrostatic model.

The lack of application of the 1-pK model compared to the 2-pK model may have several reasons: one might be the fact that the 2-pK approach has been applied by a wide range of scientists and thus has found its way into text books and review books dealing with surface chemistry (7). The fact that in relevant text books the existence of the 1-pK approach is sometimes not even mentioned certainly influences users in their choice of models. Another reason for the lack of application of the 1-pK approach may have been the necessity to change the commonly applied computer codes (see also next section), which are in many cases specially designed for the 2-pK approach.

The 1-pK approach has so far only been applied in combination with the BSM. There is, however, no reason it should not be combined (as the 2-pK approach) with other

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electrostatic models. The present paper does this and attempts to compare the description of the basic charging behavior of some frequently studied solids by the resulting versions of the surface complexation approach. More complex electrostatic models, exist but those will not be considered here for reasons discussed below.

Most prior comparisons of surface complexation models or parameter estimation studies (involving basic charging and in some cases ion adsorption) have unfortunately completely neglected the existence of the 1-pK approach (8, 9). In some of these 2-pK model comparisons the CCM or BSM were not considered either. The CCM cannot handle multiple ionic strength data with one comprehensive parameter set. But it can always be applied to a data set corresponding to a constant ionic medium.

A striking observation in the above-mentioned comparisons was that the DLM could describe proton stoichiometry in ion adsorption studies better than the TLM (8) although the DLM description of basic charging was in that case inferior to the TLM.

Prior comparisons between 1-pK and 2-pK models were more restricted (10) than the present paper in the sense that they would not consider all possible model variations. In some other sense, they were more comprehensive with respect to the inclusion of ion adsorption.

The present author believes that many prior comparisons of surface complexation models have not always been objective. The conclusions in the respective papers can in a way be anticipated simply by considering by whom the comparison is done, e.g., researchers from the TLM tradition favor the TLM over the DLM and vice versa. Researchers from the 2-pK tradition often neglect the existence of the 1-pK approach. It is also to be expected that the 2-pK DLM can be applied in a better way to ion adsorption than has been reported (10) simply by increasing the number of surface species, which can be justified by referring to published modeling results based on multiple data sources (data on ion uptake combined with proton uptake), e.g. ref 11, or that which has been practiced previously (8) based on uptake data only. The more variability is allowed in the calculations, the more work is necessary to accomplish an objective and complete comparison, when ion adsorption is involved.

In any case, it seems particularly difficult to find a reasonable solution with respect to the number of adjustable parameters in terms of the choice of the actual interfacial model (basic charging) and in terms of the surface species (ion adsorption). The results presented here are intended to give some guidance with respect to the first point.

Methods and Strategy

Seven data sets for basic charging of some representative sorbents were used. In the case of iron(III) (hydr)oxides comprising hydrous ferric oxide, HFO (12), goethite (13), and hematite (14), they were obtained from the literature. In the case of titanium oxides, they were taken either from the literature for anatase (15) and rutile (16) or from recent potentiometric titrations in the case of anatase (17). Data in 0.1 M media were used. This restriction arises from the conditional character of the CCM with respect to ionic strength. Data sets with few and extended numbers of experimental data points were used. The experimental data were subject to parameter estimation using a modified version of FITEQL2 (18), which in the context of the present paper has two major advantages. First, it allows the application of the 1-pK approach (also possible with FITEQL3 (19) now); second, it allows the use of known error estimates in each experimental point which are available for one of the anatase data sets. The code has other supplementary options including optimization of parameters for multisurface models (treatment of binary (hydr)oxides, consideration of different

crystal planes as is required for the MUSIC model (20)). This is described in more detail elsewhere (17).

Experimental data were used in the form protons adsorbed as a function of pH. Unless otherwise noted, experimental error estimates were not known and put to zero. The goodness of fit parameter is in this case SOS/DF (sum of squares over degrees of freedom): The lowest value for SOS/DF indicates the best fit. Setting the experimental error estimates to zero means that the weights are unity, which is in fact a special case of weighting the data points. For one set of anatase data (17), a justified weighting of experimental data was possible since experimental errors were known. In this case the goodness of fit parameter is given as WSOS/DF (weighted SOS/DF): A value close to unity will indicate that the difference between model and experiment is close to the experimental errors. Note in this context that where an objective weighting of data points is possible, the most meaningful information with respect to the optimization results is obtained. In cases where an objective weighting is not possible, such as those treated here, it can be shown that the way in which experimental data are weighted will affect the final parameters (17).

Also, weighting affects WSOS/DF, hence it is impossible to attribute a general meaning to values of this parameter as is usually done. It is only for justified weighting that the limits given by Westall (18, 19) are reasonable; this means that $WSOS/DF < 20$ is indicative of an acceptable fit to data, whereas $WSOS/DF \approx 1$ is desirable. The closer to unity $WSOS/DF$ is, the more acceptable a model becomes. It is, however, always instructive to use a graphical comparison between experiment and model, even in cases where justified weighting is possible and $WSOS/DF < 20$. Examples for this will be shown below.

Since the different models have different numbers of adjustable parameters, it is also useful to renormalize $WSOS/DF$ with respect to these numbers, which just changes the numerical values of $WSOS/DF$ but leaves the tendencies and thus the conclusions unaffected (17).

In the present parameter estimation procedure the adjustable parameters were as follows: (a) *site concentration* (all models—a fixed value of this parameter would bias results since, e.g., the 2-pK DLM requires relatively low values when applied to 2-pK TLM synthetic data to give a good fit to experimental data (17); furthermore, it is difficult to decide which value should be used, since experimentally observed proton uptake reaches, in many reported cases, some limiting value which is significantly lower than values obtained from crystallographic considerations); (b) *stability constants for basic charging* corresponding to eqs 1 and 2 (all 2-pK models); (c) *electrolyte binding constants* (all BSM and TLM versions—nonsymmetrical electrolyte binding was allowed); and (d) *capacitance values* (all CCM, BSM, and TLM versions—the outer layer capacitance (C_2) for the TLM versions was not varied in order to decrease the degrees of freedom; it was fixed to the most frequently applied value (0.2 F/m²)).

The capacitance values cannot be optimized by FITEQL codes, hence they have been systematically varied (on no more than the second decimal) to obtain $WSOS/DF$ as a function of the capacitance value. If no minimum occurs, the minimum value of ΔpK_a was arbitrarily used as an additional criterion to define a unique parameter set. Unfortunately, such a situation may occur in the application of the 2-pK CCM (17).

Apart from comparably high values of $WSOS/DF$, the fact that a unique parameter set cannot be obtained for a certain model might be considered as a criterion that allows one to reject the model. This may occur if no convergence is obtained in the optimization procedure or even if a minimum of $WSOS/DF$ as a function of some capacitance value is not observed. If a unique parameter set does not exist, there is

TABLE 1. Comparison of WSOS/DF for Surface Charge Data of Anatase Modified from Ref 17

	2-pK WSOS/DF	1-pK WSOS/DF
CCM	2.50 ^a	2.65
DLM	10.47	14.30
STERN		2.24
TLM		2.25

^a At minimum of ΔpK_a .

TABLE 2. Comparison of SOS/DF for Surface Charge Data of Anatase (15)

	2-pK SOS/DF	1-pK SOS/DF
CCM	1.53×10^{-9}	2.61×10^{-9}
DLM	9.02×10^{-9}	1.03×10^{-8}
STERN		1.09×10^{-9}
TLM		NC ^a

^a No convergence.

TABLE 3. Comparison of SOS/DF for Surface Charge Data of Rutile (16)

	2-pK SOS/DF	1-pK SOS/DF
CCM	1.03×10^{-11a}	4.10×10^{-10}
DLM	8.73×10^{-11}	2.55×10^{-10}
STERN		4.63×10^{-11}
TLM		NC ^b

^a At minimum of ΔpK_a . ^b No minimum of SOS/DF for $C_2 = 0.2 \text{ F/m}^2$.

a problem associated with the choice of parameters, since any chosen parameter set will not be very meaningful unless another criterion can help to define a unique parameter set.

Results and Discussion

The results of the modeling exercises, which were done according to the description in the previous section, are summarized in Tables 1–7 in terms of (W)SOS/DF for the relevant models.

One general difference between the 1-pK and the 2-pK approach is that for the 2-pK approach it was never possible to obtain a result for the five optimizable parameters for the BSM and the TLM versions. This is due to the high number of adjustable parameters and results in no convergence in the optimization procedure; in particular, the pure acid-base reactions and the corresponding electrolyte adsorption reactions have the same proton stoichiometry. If further parameters are systematically varied to reduce the number of parameters to be optimized, it is found that multiple parameter sets are equally successful. These two models will, therefore, not be discussed further. The results also imply that more complicated (i.e., four-layer) models will face similar problems in parameter estimation. Consequently, these have been excluded from the present discussion.

In some further cases, no SOS/DF values could be obtained: for the 2-pK DLM application to the HFO data (12) by Cox and Gosh, no convergence was obtained (Table 4); for the 1-pK TLM application to the HFO data (12) by Girvin et al., the anatase data by Sprycha (15), and the rutile data by Stiglich (16), the optimization procedure did not converge (Tables 5, 2, and 3, respectively). This was found to be due to the value of C_2 , which was fixed by definition.

TABLE 4. Comparison of SOS/DF for Surface Charge Data of HFO (12) by Cox and Gosh Modified from Ref 17

	2-pK SOS/DF	1-pK SOS/DF
CCM	4.44×10^{-10}	5.39×10^{-9}
DLM	NC ^a	9.73×10^{-9}
STERN		4.85×10^{-10}
TLM		4.87×10^{-10}

^a NC, no convergence.

TABLE 5. Comparison of SOS/DF for Surface Charge Data of HFO (12) by Girvin et al. Modified from Ref 17

	2-pK SOS/DF	1-pK SOS/DF
CCM	1.21×10^{-15}	5.22×10^{-15}
DLM	3.94×10^{-15}	8.97×10^{-15}
STERN		1.27×10^{-15}
TLM		NC ^a

^a No convergence for $C_2 = 0.2 \text{ F/m}^2$.

TABLE 6. Comparison of SOS/DF for Surface Charge Data of Goethite (14)

	2-pK SOS/DF	1-pK SOS/DF
CCM	6.45×10^{-11}	NC ^a
DLM	3.36×10^{-10}	6.30×10^{-10}
STERN		3.87×10^{-11}
TLM		5.80×10^{-11}

^a NC, no convergence.

TABLE 7. Comparison of SOS/DF for Surface Charge Data of Hematite (13)

	2-pK SOS/DF	1-pK SOS/DF
CCM	2.71×10^{-11}	9.11×10^{-11}
DLM	4.48×10^{-10}	1.46×10^{-9}
STERN		2.59×10^{-11}
TLM		2.69×10^{-11}

Also, the 1-pK CCM could not be successfully applied to Ali's goethite data (14) as indicated in Table 6.

One very promising result is that the 1-pK approach in combination with the TLM actually allowed a unique model in four of seven cases, based on surface charge data alone. Such a success has so far not been reported for the 2-pK TLM approach. It might be possible that by including variations in C_2 the 1-pK TLM is even more successful.

The following remarks can be made with respect to the results obtained for the anatase data (Table 1): All WSOS/DF values are within the range indicative of good fit. The goodness of fit parameters close to 2 for all cases except the DLM versions even indicate an excellent description of the experimental data. It is very difficult to reject any of these models by the WSOS/DF values. In Figure 1, the performance of the different 1-pK versions is compared. This figure indicates that the DLM best fit with the 1-pK approach is not able to produce a straight line as the other models do. Comparable behavior has also been reported for the 2-pK DLM (10). On the basis of WSOS/DF, the 1-pK DLM version gives the worst fit to the data. This is somewhat unfortunate since this model version has only one adjustable parameter (site concentration). It is important to note that although

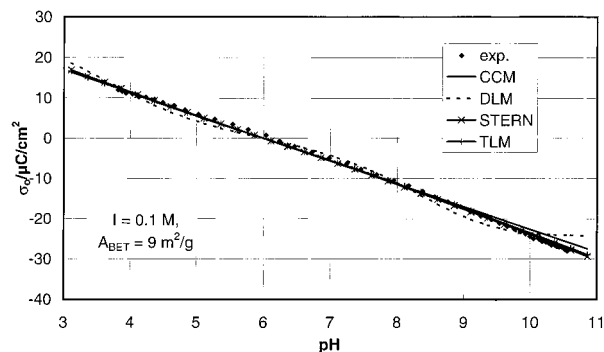


FIGURE 1. Graphical comparison of the ability of four different 1-pK models to describe the basic charging behavior of anatase. Modified from ref 17.

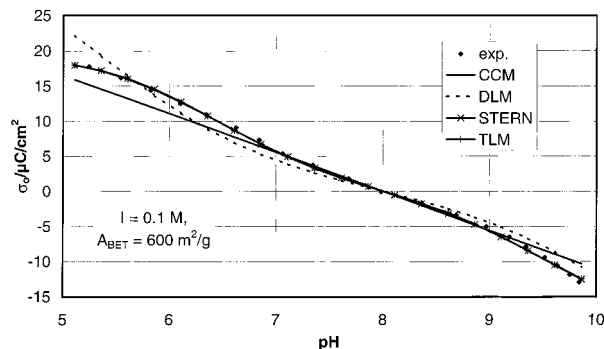


FIGURE 2. Graphical comparison of the ability of four different 1-pK models to describe the basic charging behavior of HFO. Experimental data from Cox and Gosh (12).

the model seems acceptable when based on the value of WSOS/DF, Figure 1 shows that the model curve yields a significant deviation from the experimental data and the other models with respect to the shape(!) of the calculated curve. The best fit curve for the 1-pK DLM has the same shape in Figure 2, where modeling results for HFO are shown. This latter figure reflects the difference in SOS/DF values for the different models. It is apparent that the 1-pK CCM is clearly inferior to the BSM and TLM approaches.

From the whole of the goodness of fit parameters, it can be summarized that the DLM versions always give the worst fit to the experimental data both for the 1-pK and 2-pK approaches.

Furthermore, it is apparent that the 1-pK BSM and the 2-pK CCM approaches are most successful in describing the experimental data.

It is probably not necessary to apply a 1-pK TLM combination, since in all cases the 1-pK BSM gives a slightly better description with fewer adjustable parameters. Additional calculations have shown that for the outer capacitance values different from 0.2 F/m² the 1-pK TLM fit to the data can be slightly improved.

If data for one value of ionic strength are to be described it is interesting that the 2-pK CCM gives an even better fit to the experimental data than the 1-pK BSM in three of seven cases. Note that the overall number of adjustable parameters is equal in these two cases. However, in the case where an objective weighting of the experimental data is possible in the optimization procedure, the 1-pK BSM is performing better. Since this is the most meaningful example, it could be argued that the 1-pK BSM is the appropriate model in terms of goodness of fit. In the application of the 2-pK CCM to the anatase data (17) and the rutile data (16), a minimum of WSOS/DF as a function of the capacitance value could not be obtained. In such cases the author has chosen to select the parameters at the minimum of ΔpK_a for modeling

purposes. Note that for a 1-pK model in a similar situation such an arbitrary constraint would be more difficult to define. The observation that no minimum exists with the consequence of some arbitrary choice of parameter values has two aspects: (1) Parameters with a lower value of WSOS/DF than those reported in Tables 1 and 3 exist. (2) A well-defined parameter set does not exist.

The second point will be a major disadvantage for models where such situations occur. If some model version cannot yield a unique parameter set, this model can be rejected, since either no parameters are obtained at all or the parameters would have limited physicochemical significance if the model was considered to be reasonable. In the case of the CCM, the situation might be different if site concentration is assumed to be known as is sometimes done (11). In such a case, site concentration is not an adjustable parameter, and the parameter estimation procedure is different from the one applied in the present paper. However, in such cases the low values of site densities are not generally accepted. Thus the MUSIC model (20) relies on crystallographic estimations of site densities and does not predict any saturation in proton adsorption.

From the present results the 1-pK BSM should have the best future perspective. To come to this conclusion, the present paper focuses on the quality of the different models in terms of goodness of fit and the ability to obtain a unique (meaningful) parameter set. Koopal (21) comes to a similar conclusion with respect to the 1-pK BSM approach based on different considerations, which have to do with a closer relation to a more realistic modeling approach, namely the MUSIC model (20). Borkovec (22) has provided a sound basis for both the 1-pK and 2-pK models from statistical mechanics and indicates that in most cases the 1-pK approach is sufficient and to be preferred because of the decreased number of adjustable parameters. Both the 1-pK and the 2-pK models can be interpreted as special cases of the MUSIC model (20). In particular, the 1-pK model with its fractional charges comes from the calculation of formal charge using the Pauling principle, and eq 3 was initially proposed for singly coordinated surface hydroxyls (θ) of certain solids. Equation 2 appears for the case of silica in the MUSIC model. Since no protonation of silica occurs, this results in a special case of a "1-pK approach with a 2-pK formalism". Due to this, the special case of silica has not been discussed here in terms of goodness of fit. It has been found though that the DLM is, in the case of silica, a model that is able to give good fits to surface charge data (17), i.e., the gap between the DLM and the CCM is relatively small.

At this point it seems necessary to discuss the situations in which the simple surface complexation models as those applied in this paper will be reasonable. The MUSIC model requires a detailed characterization of samples, e.g., in terms of contributions of different crystal planes. For well-defined sorbents this is possible, although the role of imperfections is most probably something that has yet to be addressed. For environmentally important sorbents, the necessary characterization is almost impossible. Therefore, surface complexation modeling will rather be based on the simple approaches discussed here. However, in such cases it cannot be expected that a mechanistically correct description will be achieved. The 1-pK approach is closer to the more complex model though (21).

Two further points in favor of the 1-pK approach can be stressed: knowledge of the temperature dependence of PPZCs would be sufficient to describe temperature-dependent charging in terms of eq 3, whereas the 2-pK model would require optimization of two additional parameters (eqs 1 and 2) at each temperature. Temperature dependence is, of course, of utmost importance environmentally. Since most laboratory studies are done at 298 K, some extrapolation of

those results is necessary; with fewer measurements and less data treatment, such extrapolation will be greatly facilitated. Note that capacitances and maybe even site densities will remain as unknowns for the respective models. There are theories available to predict PPZCs for certain solids, e.g., ref 23; electrolyte binding constants, ΔpK_a , and capacitances can, in principle, also be predicted by a similar approach (24, 25). The present use of this approach with a 2-pK TLM is somewhat difficult to understand for several reasons: With a 1-pK approach, ΔpK_a need not be predicted at all. Undesirable discrepancies between the same parameters for identical systems have been obtained (25), which is a direct consequence in difference of the underlying experimental data and suggests that a choice in the available data has to be made or that the variability of data has to be accepted and must be interpreted by more complex models. A self-consistent approach that could help avoid such problems might be as follows: (1) Predict PPZCs (23). (2) Select surface charge data that are in agreement with those predicted PPZCs; only with this restriction can it be ensured that the theory is applicable to a certain solid. (3) Optimize electrolyte binding constants and capacitance values with a 1-pK BSM using predicted PPZCs with eq 3 and some estimate for site densities (25) or optimized site densities. (4) Use these values for calibration, and predict parameters for systems for which no data are available.

Such a use of PPZC prediction is not expected to be correct in all cases because, again based on more complex models (20), it is apparent that different crystal planes may have different PPZCs and that the contribution of the individual crystal planes will determine the overall PPZC of a certain sample. Therefore, Sverjensky's prediction of PPZCs is not a safe one; such predictions should only be used in cases where more complex models cannot be used or where accurate measurements are not possible.

From most of the above considerations there are strong arguments for the 1-pK approach especially in combination with the BSM. Concerning the modeling results presented in the present paper, however, the present author would like to stress at this point that his results are in agreement with the chosen experimental data and optimization procedure. With other data and/or data treatment, it must at present be stated that general conclusions are impossible. A final point worth noting in this context is that the quality of the different models is not the same when they are applied to different data for one sorbent (Tables 1 and 2 for anatase, Tables 4 and 5 for HFO). Both these points indicate that more work on comparing models is necessary.

In the Introduction, objectivity was claimed to be one requirement in comparisons of models to achieve. It turns out, though, that this is not as easy as the numbers in Tables 1–7 might indicate. Thus, the footnotes indicate several points which might be interpreted as bias. One of them is the use of the minimum of ΔpK_a as an additional constraint in the case 2-pK CCM and might create problems when compared to the treatment of the 2-pK BSM and TLM approaches. The situation leading to the use of this constraint is that there is no minimum of (W)SOS/DF as a function of C. However, the fitting routine converges, which is not the case for the 2-pK BSM and TLM versions. Instead of the minimum ΔpK_a we might also accept the lowest value of (W)SOS/DF that can be achieved. This, however, would not be satisfactory either. A more rigorous treatment would then be to reject the CCM. The present author does not wish to exclude that a similar situation may occur with other models, hence this disadvantage might be more common than it appears from the present results. Another bias might be the choice of the ionic medium. The restriction to 0.1 M might be interpreted as being in favor of the CCM, which in cases of high ionic strength is expected to be appropriate. However,

according to the author's own experience the CCM is also quite successful in lower ionic strength (17).

Finally the reader might wonder why the actual parameters corresponding to the best fit situations are not given. This is due to the fact that in surface complexation modeling quite often parameters (especially the acid–base parameters of a sorbent) are taken from (sometimes several) different previous determinations by other authors and with different sorbent samples, which are (maybe only) nominally identical. In many of those cases no comparison of the resulting model with experimental data is done. Thus the basic underlying model can at least be suspected to be inadequate with respect to the actual properties of the sorbent, which in turn may lead in some cases to incorrect predictions (17). The present author believes that the acid–base properties of a sorbent should be determined for any surface complexation modeling study if possible. It can be stated that the best fit parameters obtained in this study are all within the range of what is physically reasonable.

Hopefully, when it comes to judging models by some goodness of fit parameter, the importance of objective weighting of experimental data is also made obvious in the present paper.

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