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Treatment of temperature dependence of interfacial speciation by speciation codes and temperature congruence of oxide surface charge

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ABSTRACT

In several published articles dealing with the temperature dependence of surface charging of and solute adsorption at mineral/water interfaces that involve surface complexation modelling via the purely diffuse layer model or the triple layer model, speciation codes were employed that do not allow specification of temperature in the input and therefore no explicit temperature variation. Omitting temperature variation should cause errors in the calculations. A priori it is expected that the temperature dependence of the dielectric constant of water, changes in volume (and thus molar concentration), and the appearance of absolute temperature in the electrostatic term of surface complexation models cannot be simply neglected. Calculations involving the models without temperature correction and with temperature correction, however, show that in the case of surface charging, no noticeable difference arises between calculations including or omitting the temperature corrections. In the present work we show that this arises from compensation of the respective temperature dependencies of the different variables. Our considerations and calculations explain why previous omission of temperature dependence has gone unnoticed. We also discuss temperature congruence of surface charging, i.e. master curves that do not depend on temperature, when the charge is normalized with respect to the point of zero charge at the respective temperatures. We conclude that temperature congruence is probably not a general phenomenon. Consequently, the validity of assuming temperature congruence has to be verified. We suggest a simple way to do so.

1. Introduction

Temperature dependence of reactions at mineral water interfaces has been of significant interest over the last decades (Brady, 1992; Machesky et al., 1998, 2001, 2015; Rozalen et al., 2009). Beyond the purely experimental studies, surface complexation modelling has often been involved in the interpretation of the results in the above cited references. Traditional surface speciation codes have been typically restricted to 298.15 K, such as a particularly popular one of the MINEQL family namely the parameter fitting code FITEQL. The code has been extensively used in the past and is currently replaced by codes like PhreeqC or VisualMinteq coupled to shell optimizers.

Estes et al. (2013) have used FITEQL to do calculations on temperature dependent data in the Eu-hematite system. The model for the Eu-uptake has to involve an acid-base model for the bare hematite, encompassing the temperature range studied. While the authors do not present any calculation for the charging of their hematite at temperatures different from 25 °C (or room temperature), they do apply FITEQL4 calculations to the uptake of Eu at variable temperature applying a purely diffuse layer model (DLM). Others had previously applied surface complexation modelling (Tertre et al., 2006b) with a DLM, again without specification on how the temperature within FITEQL3 (Herbelin and Westall, 1996) was handled. The DLM requires at least one additional parameter input beyond the classical FITEQL input parameters. Yet, other groups have used FITEQL for temperature dependence employing the constant capacitance model (Angove et al., 1999; Finck et al., 2007, 2008) or the extended constant capacitance model (Angove et al., 2006). These two models avoid the diffuse layer term and the variation of the capacitance with temperature is self-consistently handling the required temperature dependence that otherwise would have to be accounted for in the source code. The triple layer model includes both capacitance regulated terms and a diffuse layer. This might make a priori estimates difficult as to whether it is important to fully consider the temperature dependence of the variables. It could simply depend on parameter values, like the value of the capacitance or electrolyte binding constants.

Room temperature corresponds more or less to the temperature at which the major parts of the experimental data that pertain to surface complexation studies were and still are collected. The small difference

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to standard temperature is typically disregarded. Some of the studies that involve modelling over a range of temperature have applied the constant capacitance approach using these classical codes (Angove et al., 2006; Halter, 1999), while in other case separate codes have been written that allow the use of more complex models and explicit temperature corrections (Machesky et al., 2001). As mentioned above, it seems that codes that do not allow such explicit temperature corrections have been previously used to model temperature dependent data. Using the simple constant capacitance model (CCM) it is possible within the classical codes to express the temperature dependence by correcting concentrations (i.e. accounting for example for the change in volume in the solute and solid concentrations) and by including the values for the capacitance at a given temperature in the appropriate way. This is required due to the occurrence of the absolute temperature T in the electrostatic term, P = exp(-zFψ/[RT]), where z represents (transfer of) charge, ψ is a surface potential, while F and R have their usual meanings. For the constant capacitance model within FITEQL, the following equations are relevant in that context:

$$P = \exp(-zF\psi/[RT^{\circ}]) \tag{1}$$

$$\sigma = C\psi \tag{2}$$

In equation (1) T° is the absolute temperature as specified in the source code of FITEQL. In equation (2), σ is the surface charge density, C is the capacitance. Inserting eq. (2) in eq. (1) yields

$$P = \exp(-zF\sigma/[CRT^{\circ}]) \tag{3}$$

As pointed out, in standard FITEQL, T° = 298.15 K, is defined in the source code. There is no way to change the value in the input file. The source code would need to be modified to change the entry for T°, or to add an additional input variable to occur in input files. The capacitance specified in the input (denoted as C) is in general expected to vary with temperature. Since the only occurrence of temperature in the electrostatic part of the CCM is via equation (3), the appropriate change of the entry for the capacitance, simultaneously allows involving the variation of the capacitance value with temperature and the variation of the temperature itself. This can be done by adjusting the input capacitance according to

$$C = C_T(T/T^{\circ}) \tag{4}$$

Where T denotes the actual temperature and C_T the respective capacitance value.

The situation becomes more complex for other electrostatic models. For instance if FITEQL is used for temperature dependent data within a diffuse layer model, calculations will neglect the temperature dependence that is inherent to the diffuse layer charge potential relationship, i.e. the Gouy-Chapman equation, as implemented in FITEQL, and as discussed in more detail later. It implies various appearances of temperature dependence. The multi-layer approaches like basic Stern, triple layer or three planes models involve both capacitances, which could be treated as described above for the constant capacitance model, and the Gouy-Chapman model, which requires for the correct treatment the implementation of the temperature dependencies in the source code.

As a consequence only the CCM can be used with standard FITEQL to obtain correct results for data at temperatures different from 298.15 K. Room temperature calculations have traditionally been carried out with the temperature being set to 298.15 K and this is not expected to cause significant problems.

For the examples discussed in this work, the surface complexation modelling parts have completely ignored the temperature dependence of the electrostatic factor and other parameters that change with temperature. This concerns purely diffuse layer (Estes et al., 2013; Tertre et al., 2006b) and triple layer (Ward and Brady, 1998) models. To a large extent this stems from the non-availability of fitting routines for surface complexation modelling that allow variation of temperature, which has changed with the advent of PhreeqC or VisualMinteq. To what extent these codes have the direct link to temperature variation of all the involved parameters needs to be checked by the respective users of the codes.

In the next sections we illustrate the relevance of temperature from various points of view. Fig. 1 shows how the electrostatic term, i.e. P in equation (1), changes with temperature for z = 1 for three different values of ψ according to equation (1). For potentials around 100 mV, P changes by about half a log unit between 0 and 100 °C, while between 25 and 75 °C the change is still a quarter of log unit. The effect increases with increasing the number of charges transferred to the interface and with an increase in the surface potential. Within the diffuse layer model, at low salt levels Dzombak and Morel obtained model inherent potentials up to 200 mV (Dzombak and Morel, 1990). This simple view clearly suggests some effect if temperature dependence was simply ignored in parameter estimation and calculations are redone with a code that involves temperature dependence. However, the actual difference will also depend on how the potential changes with temperature, which in turn depends on how the charge densities change. Therefore, the overall effect cannot be simply evaluated from the results in Fig. 1. To relate the magnitude of the expected effect to solution chemistry, we compare the "activity coefficients" for the surface species, i.e. P, to that of an aqueous solution species. Therefore, Fig. 1 also includes the variation of the proton activity coefficient (logarithmic scale) as a function of temperature for two salt levels of monovalent electrolyte. Clearly the effect of temperature on solute activity coefficients is very small compared to the variation of the electrostatic factor (in the range of salt levels tested here).

Overall, at low potentials, i.e. close to the point of zero charge, the variation of the electrostatic term is comparable to that of the activity coefficient of the proton at 100 mM, whereas at 100 mV the variation is about half a log unit for the electrostatic factor, i.e. not negligible at all. Since the above calculations cannot consider potential changes of the surface potential of a given sample with temperature, a comprehensive evaluation of the extent of the temperature effects on model parameters requires the full model calculations.

As pointed out above, several examples in the literature can be found where the temperature dependencies in the electrostatics have been entirely omitted. Calculations in those cases were done with FITEQL to fit surface complexation parameters to experimental data

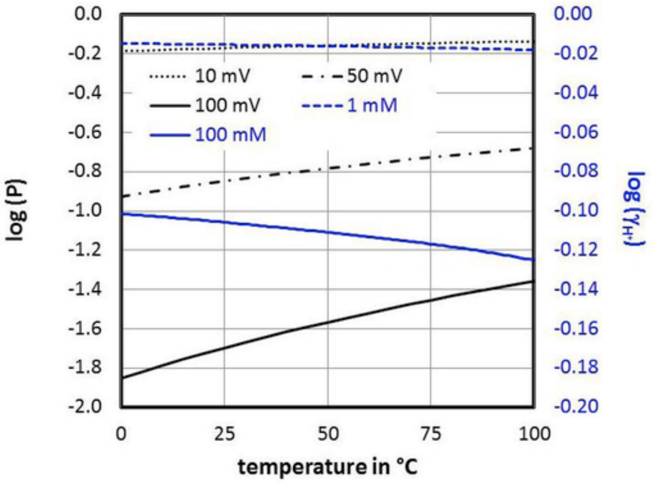

Fig. 1. Variation of the electrostatic term (here as log (P), left axis, black) and the activity coefficient of the proton (log (γ_H+), right axis, blue) with temperature for three distinct surface potentials and two salt levels (monovalent electrolytes), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

obtained at different temperatures. Those studies will be used for calculations in the present work what follows.

In the study by Tertre et al. the temperature dependence within a diffuse layer model study has been entirely neglected (Tertre et al., 2006b) when they used FITEQL to obtain model parameters. Curiously in companion papers (Tertre et al., 2005, 2006a) Tertre et al. use a speciation code, that is more general than FITEQL, and probably includes temperature variation in a self-consistent way. According to what is (or is not) written in the papers, no peculiarities in model results were observed, when switching from one code to another.

A more recent diffuse layer model investigation by Estes et al. (2013) also involves FITEQL to model variable temperature data. Moreover, it includes an interesting approach to handling the temperature dependence of oxide charging in aqueous solutions. It relies on the measurement of the endpoint of a mass titration and subsequent variations of temperature to obtain the variation of the point of zero charge (pzc) with temperature. The treatment involves the assumption of temperature congruence, which means that correct scaling of (titrable) surface charge density vs. pH curves yields one master curve for data collected at different temperatures. With this assumption, based on a single potentiometric titration curve and assuming equal enthalpies for reactions of the two protonation steps, it becomes possible to obtain the expected charging behavior of a mineral within a diffuse layer model (DLM) over a wide range of temperatures. The beauty of the approach is in its simplicity and the limited experimental effort.

We will also (though in less detail) address the TLM application by Ward and Brady, that again involves FITEQL application to temperature dependence (Ward and Brady, 1998). Details of these calculations can be found in the SI.

We will discuss the three above articles to understand why omission of the temperature dependence in the application of FITEQL has not caused any suspicion and has apparently gone unnoticed so far. We also discuss temperature congruence, where our considerations are restricted to temperatures ranging from 0 to 100 °C.

1.1. *Treatment of temperature in interfacial speciation*

Temperature has various effects on parameters and variables in surface complexation models. By parameters we denote intrinsic stability constants and capacitance values (where applicable), which in principle will change with temperature. The temperature variation is typically obtained by fitting parameters to experimental data sets obtained at different temperatures. This concerns in the present case the model ingredients for which the temperature dependence is known or needs to be known/determined. For aqueous speciation, the stability constants for the formation of all relevant aqueous species needs to be known at the temperature of interest. Furthermore, the activity coefficients of all these species are required. Only in cases where stability constants have been determined on concentration scales for the temperature and ionic medium of interest, such data can be directly used. Concerning the properties of water, the density of water is required when molal scales are used in mass law equations and mole valances to recalculate the volume specific input to the Gouy-Chapman equation. In the latter the static dielectric constant of water is needed. Input of the correct values of the latter two in the calculations can be via temperature functions within the source code by specifying the temperature of interest or via input options in the input files.

From the description of the procedures in the three above referenced papers, which have used FITEQL to evaluate parameters at variable temperature, the temperature dependence of these variables must have at least partially been omitted.

To illustrate how difficult it is to deduce what exactly has been done in published surface complexation modelling, we address some points from the paper by Estes et al. (2013) that may be of importance:

- In the surface complexation modelling part, Estes et al. (2013) describe the following changes they made to FITEQL4 (Herbelin and Westall, 1999): (i) inclusion of a database link, (ii) improvement of code stability, and (iii) improvement of the activity correction options. For self-consistent calculations within the DLM as a function of temperature it is necessary to involve the temperature dependent static dielectric constant of water. This may have been done via the database link. The precise nature of the database link is not described though.
- Most obvious, the exponential term in the DLM includes the temperature as well. Higher temperature leads to smaller absolute values of the argument of the exponential function (eq. (1), with the outcome shown in Fig. 1).
- The precise procedure in using FITEQL is not specified by Estes et al. (2013). FITEQL works on molar basis. This can be easily transferred to molal, which is the preferable unit when variations in temperature are involved. The DLM involves the Gouy-Chapman equation. Its implementation requires the ionic strength to be used in molar units. This introduces in the temperature dependent case the interference of water density as a function of temperature as described elsewhere (Machesky et al., 1998). Obviously the correct treatment has to be consistent with the experimental procedures. Thus heating a solution prepared on the molar scale will result in a new molarity at the new temperature. If calculations are done on the molal concentration scale, recalculation of molar concentrations of NaCl, and also for the solid concentration (in g/L) as a function of temperature are required. In standard FITEQL this also leads to a change in surface site concentration.

From the available information in the above referenced work (Estes et al., 2013; Tertre et al., 2006c; Ward and Brady, 1998) it has to be assumed that the above points have not been included in the acid base or solute uptake modelling, respectively. As pointed out, FITEQL does not allow a separate entry of the temperature. Temperature is specified in the source code, as is (implicitly) the value of the dielectric constant of water.

The present authors have adjusted FITEQL2 to handle these issues self-consistently through the input file for all the popular electrostatic models. Effects of water density changes have to be corrected for by the user as well as activity coefficients. This version has been used for the calculations shown later and is available for free on request. The code has been previously used for temperature dependent surface complexation calculations by Kersten and Vlasova (2009a, b).

In the next sections we discuss in detail the two examples, where the DLM was used with FITEQL at variable temperature, but no distinct temperature corrections were done. An initial remark could be made on the choice of the model. Estes et al. (2013) and Tertre et al. (2006b) used a 2-pK DLM approach. No (significant) temperature dependence of ΔpK_a is apparent in their published parameters. Moreover, while it is often argued that the one-site 2-pK DLM is the simplest model, 1-pK models are even simpler. Combination of the 1-pK model with the point of zero charge data would eliminate the assumption about the equal enthalpies of the reactions and allow application of the known value directly. The choice of the electrostatic model would need to be considered: The diffuse layer model is probably not a good choice since it produces irregular shapes of the charging curves in combination with the 1-pK approach (Lutzenkirchen, 1998). If one is not willing to accept this, one might choose the constant capacitance model, and in this case the capacitance would be a fitting parameter with unknown temperature dependence.

Variations of salt levels complicate things further. A Stern model with and without electrolyte binding requires temperature dependence of the capacitance value. Involving electrolyte binding requires the temperature dependence of the binding constants. Overall and as will be seen later, a DLM is probably the best option when significant effort in experimentation is to be avoided. If one is willing to accept acid-base models that do not precisely describe surface charge data, the 1-pK option might be preferable. In the following sections we first discuss the paper by Estes et al. (2013) in some detail with a focus on the point of zero charge and temperature congruence, and we show that the omission of temperature dependence in the model calculations has remarkably little effect on the outcome of calculations. In the subsequent section we discuss in some detail the paper by Tertre et al. (2006b) to understand the compensating effects that must be at work in relation to experimental data.

1.1.1. Discussion of the paper by Estes et al

The major parameter in the 2-pK DLM (and in generic 1-pK models) is the point of zero charge. This requires a discussion about the difference of the various experimental data reported by Estes et al. for the points of zero charge at 25 °C (7.36 from mass titration, 7.34 from ΔT titration, 7.5 fromsurface titration), with respect to the value obtained at 7.2 (from fitting). Mass titration probably yields the most reliable value among the four. The end point of the mass titration is often used to fix the zero level in the full pH-titration (Fig. 3 in the paper by Estes et al.). We had difficulties in applying this, because in the above referenced figure, unfortunately, it is not clear whether the y-axis is total proton concentration (TOTH) or net adsorbed proton concentration (H^+_{ads}). Both are on relative scales when initially abstracted from raw titration data, and the reported values are above a certain unknown level of TOTH or H^+_{ads}.An absolute level has to be defined by independent data from mass titrations or electrokinetics.

FITEQL allows estimating model parameters from both kinds of experimental data (i.e. TOTH and H^+_{ads}). With the available information no conclusions can be drawn about the y-axis in the above referenced Figure. Based on the published model parameters, calculations of total proton and adsorbed proton concentration were carried out. This is discussed in some detail in SI (in particular with respect to Figure SI1, where we compare the two scales). The numerical values would suggest that Fig. 3 in the paper by Estes et al. does show proton uptake. However, we also suspect a misprint in the units (nmol/L). The value of 800 nmol/L at pH 3.5 would mean a concentration of 8×10^{-7} M, which appears unrealistically low both for total and adsorbed proton concentration.

Turning back to the effect of temperature, based on the results in Fig. 2, it appears that in the present case, the concerns raised above are all minor or somehow compensating effects. Our calculations yield no major changes, when neglecting the effect of temperature on solution dielectric constant and water density, the omission of temperature variation in the exponential term, and keeping the molar concentrations (affecting electrolyte and surface site concentration), and the activity coefficients, as if they were at 25 °C (Fig. 2). As pointed out above, this is a priori somewhat surprising given the effect in the electrostatic factor at higher surface potentials (Fig. 1).

In the following we discuss the fact that the procedure to obtain the charging properties at variable temperature results in complete temperature congruence, an issue that has been discussed before (Fokkink et al., 1989). Fig. 3 shows that the charging curves from Fig. 2 coincide for all temperatures, if they are scaled to the respective points of zero charge at each temperature. The parameters for 80 °C were obtained from a published report (http://www.osti.gov/scitech/servlets/purl/1253947).

The thermodynamic treatment by Estes et al. (2013) results in $\Delta pK_a \approx 1.9$, insensitive to temperature, which explains why the charging curves are uniform. The crucial point is whether temperature congruence is real. If it is, one might wonder up to which temperatures it can be assumed. The experimental data by Fokking et al. show temperature congruence between 5 and 60 °C for hematite (Fokkink et al., 1989). The same authors found temperature congruence for rutile.

The more extensive study on rutile by Machesky and co-workers analyzed temperature dependent charging of rutile over a much broader

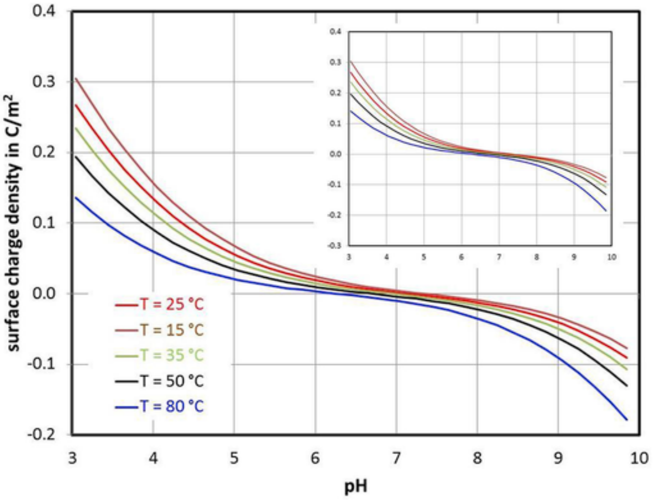

Fig. 2. Surface charge density calculations with parameters given by Estes et al. in 0.01 M medium for the indicated temperatures. The figure shows the calculations including additional corrections for changes in water density and dielectric constant in the Gouy-Chapman equation with temperature. Concentrations were corrected using the water density values from the value at the molar scale at the 25 °C value, and surface site concentrations and activity coefficients were also corrected to the respective temperatures. The inset shows the same calculations that do not include these corrections.

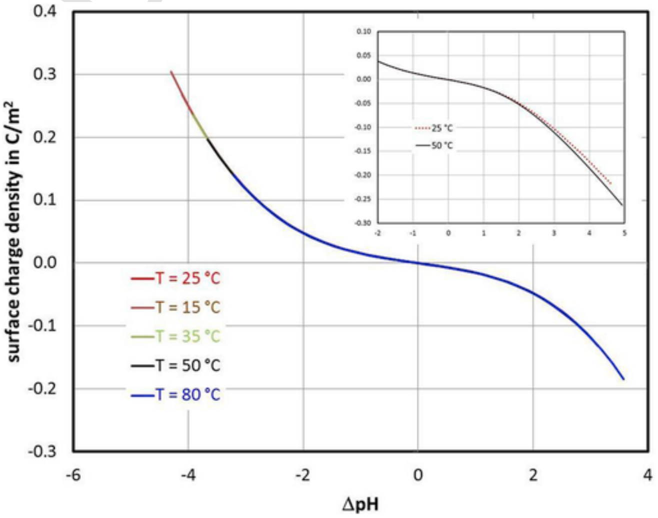

Fig. 3. Calculated surface charge densities for hematite scaled to the respective points of zero charge at different temperatures (corresponding to the inset in Fig. 2). The inset shows similar calculations for rutile, which exhibit deviations from temperature congruence already at 50 °C in 0.01 M medium.

temperature range (Machesky et al., 1998) from which a revised version of the MUSIC model emerged (Machesky et al., 2001). The experimental data sets for this system do not show full temperature congruence, see Fig. 6 in Machesky et al. (1998). Yet the differences in the scaled charging curves for 0.03 m NaCl remain small in the temperature range below 100 °C (i.e. between 25 and 50 °C, respectively). Significant temperature incongruence does occur for the higher temperatures. In conclusion, the question remains whether temperature congruence should be accepted as a valid assumption for the temperature range in which for example Estes et al. performed their Eu uptake experiments, i.e. for which they used the acid-base model. The unscaled modelling results for 10 mM NaCl that we obtained based on parameters from Machesky et al. (2001) for rutile show the same patterns as those reported by Estes et al. (see Figure SI2 for this comparison): a shift of the curves to lower pH with increasing temperature (Fig. 2). The inset to Fig. 3, however, shows that strict temperature congruence within the rutile model does not occur but that the deviation is small. In the multi-layer model that is used by Machesky et al. the departure from temperature congruence is caused by the stronger increase in the anion binding constant relative to the cation binding constant with increasing temperature, which causes higher charging on the negative side of the points of zero charge with increasing temperature, while on the positive side temperature congruence prevails. In subsequent work, Machesky et al. (2015) have pointed out that the temperature incongruence for the negative surface is due to the closer approach of the cations in the "inert" electrolyte with increasing temperature. Such changes in surface speciation have been rarely studied spectroscopically, but have resulted from modelling for selenate on goethite for example (Kersten and Vlasova, 2013). While this might be studied experimentally for example by ATR-FTIR with appropriate cells, in our lab we plan to use laser spectroscopy in the future to investigate such effects for Eu and Cm adsorption on mineral surfaces.

While temperature congruence based on the available data is certainly not sustainable above 100 °C, for temperatures below 100 °C the situation is more ambiguous. Thus by comparing the data for rutile from Machesky et al. and to another data set (Fokkink et al., 1989) temperature congruence for a given mineral cannot be generalized, since it is observed the latter case, but not in the former. Reasons for this can be the nature of the samples or differences in the "inert" electrolyte used. Therefore, it is in principle necessary to experimentally prove or disprove temperature congruence prior to applying the approach by Estes et al. described earlier. This approach will save time and effort and remains applicable if temperature congruence occurs, since it avoids the measurement of charging data as a function of salt levels and other variables.

The simplified modelling approaches discussed above (i.e. combination of the 1-pK generic model with DLM or CCM) cannot account for the ion specific effects that occur in the rutile system studied by Machesky et al. (1998, 2001) in combination with an asymmetric charging curve. Instead data that involve the absence of temperature congruence will require a Basic Stern model at least. It is also believed that the procedure by Estes et al. remains an alternative within a diffuse layer model that is not applied to systems that require accurate charging values (like migration calculations that do not involve transport of protons). In such (buffered) systems the DLM is merely used to account for the variation of the conditional adsorption constant for a solute.

A simple improvement of the method by Estes et al. might involve measurement of the isoelectric point to constrain the pristine point of zero charge at the reference temperature. Another probably necessary (but still simple) set of measurements that would reveal potential asymmetry in the counter-ion adsorption could be either electrokinetic measurements as a function of salt content around the IEP at a given temperature, or an electrolyte titration at 25 °C, i.e. addition of the electrolyte to the sample at the mass-titration endpoint. Yet another option would be a ΔT titration at a higher electrolyte concentration. Ideally, symmetry of the charging curve is obtained with respect to the pristine point of zero charge at 25 °C, and the points of zero charge from mass titration do not shift with electrolyte addition at the different temperatures.

Overall, the omissions in the calculations and the unverified assumptions that were discussed concerning the paper by Estes et al. will not have huge effects in the surface complexation modelling. As already mentioned the model could be further simplified by using a 1-pK version. This would imply an additional compromise concerning the electrostatic factors that are already inaccurate for a 2-pK DLM.

1.1.2. Discussion of the paper by Tertre et al

In the study discussed in this section, temperature dependence within surface complexation modelling was also not included (standard FITEQL was used). The underlying experimental work deals with the charging of kaolinite and montmorillonite in NaCl systems at 25 and 60 °C (Tertre et al., 2006b). Experimentally, no noticeable effect of temperature in charging was observed except for the data in 0.5 M NaCl for montmorillonite. These conditions were picked in the present work to evaluate why comprehensive temperature correction has so little influence on the calculated charges (as has become clear from the previous case). The parameters from Tables 3 and 4 in Tertre et al. were taken for the model calculations assuming the use of molar concentrations. Fig. 4 shows the results of the calculations involving the respective constants at the respective temperatures, i.e. at 25 °C (Fig. 4A) and at 60 °C with and without complete temperature correction (Fig. 4B).

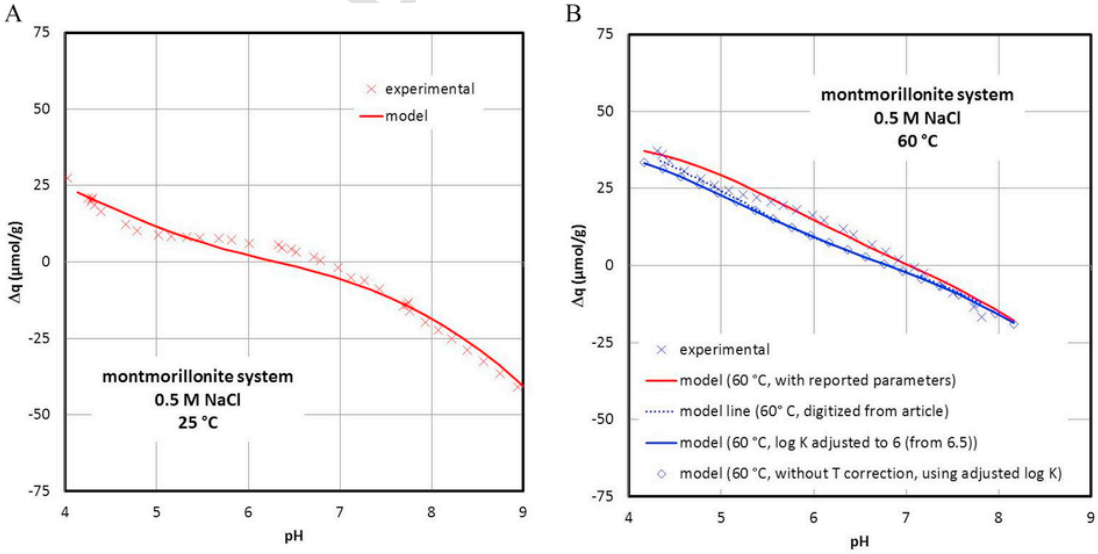

Fig. 4. A: Surface charge obtained from potentiometric acid-base titration as reported by Tertre et al. for montmorillonite in 0.5 M NaCl at 25 °C (Tertre et al., 2006b) and model calculation using the parameters by Tertre et al.**B**: Surface charge obtained from potentiometric acid-base titration as reported by Tertre et al. for montmorillonite in 0.5 M NaCl at 60 °C (Tertre et al., 2006b) and model calculation using the parameters reported by Tertre et al. (red line) without any temperature corrections. The dashed blue line corresponds to the model digitized from the original paper. The blue full line corresponds to a model calculation with a corrected value for the log K as described in the text without temperature corrections and the diamonds correspond to the latter calculations but including temperature corrections. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Although our simulations in Fig. 4A for 25 °C reproduce the model calculations in the original paper fairly well, additional effort was required to reproduce the original model results at 60 °C. The red line in Fig. 4B shows the results with original parameters and full temperature corrections. While the simulation fits the experimental data reasonably well, it deviates from the original modelling results (blue dashed line as digitized from the corresponding figure in the original article).

Whereas the text of the original article states "A change of nearly one log unit is found only in the case of the protonation constant for the aluminol site on montmorillonite.", the difference in Table 3 of that paper is 1.4 log units. With difference of 0.9 log units, the full blue line in Fig. 4B agrees fairly well with the original model. The remaining calculations were done with the adjusted constant. Slight differences in activity coefficients in the two sets of calculation are not relevant for the following discussion (see Fig. 1). Fig. 4B clearly, therefore, corroborates that full temperature correction does not result in significantly different results compared to omission of the temperature dependencies, even if small numerical differences are discernible.

To analyze in detail the occurrence of the temperature influence in the electrostatic term, we discuss the Gouy-Chapman equation for monovalent ions

$$\sigma = -\sqrt{8000\varepsilon\varepsilon_o IRT}\,\sinh(\frac{F\Psi}{2RT}) \tag{5}$$

σ is the surface charge density, ε the dielectric constant of water (relative permittivity), which depends on temperature, I is the ionic strength, and Ψ is the surface potential. The other symbols have the usual meaning. Rearranging this equation, the surface potential becomes

$$\Psi = \frac{2RT}{F} arc\ \sinh(-\sigma/\sqrt{8000\varepsilon\varepsilon_o IRT}) \tag{6}$$

The electrostatic term P can be calculated as

$$\begin{aligned} P &= \exp(-\frac{F\Psi}{RT}) \\ &= \exp(-2arc\ \sinh(-\sigma/\sqrt{8000\varepsilon\varepsilon_o IRT})) \end{aligned} \tag{7}$$

Thus T in the exponential term effectively disappears and the remaining T dependence under the square root involves the product ε × T and I (in molar units). While in most textbooks ε in the Gouy-Chapman equation is the dielectric constant of pure water, recent work by Ohshima suggests the use of the static dielectric constant of the medium. This introduces a dependence on the concentration and composition of the bulk electrolyte concentration (Ohshima, 2006, 2012). Increasing the NaCl concentration has been reported to decrease the static dielectric constant (Hasted et al., 1948) relative to pure water. This aspect is discussed in reference to Figure SI3.

Assuming for the time being that the relevant issue is the square root of the product of the dielectric constant of water and the absolute temperature, in Fig. 5 the dielectric constant is plotted vs. temperature (black line, left axis), while on the right axis (blue line) the square root of the product of temperature and dielectric constant of water is plotted. It can be seen that the temperature dependent term changes by less than a factor of 1.04 between 298.15 K and 358.15 K. This explains the absence of observable deviations in the surface complexation modelling involving the purely diffuse layer model in this temperature range, since the change in molar ionic strength is comparatively small as well. Heating of a 0.5 M NaCl solution prepared at 20 °C has an ionic strength of 0.488 M at 60 °C according to calculations using a Pitzer database. This would increase the error from about 4% to about 5%.

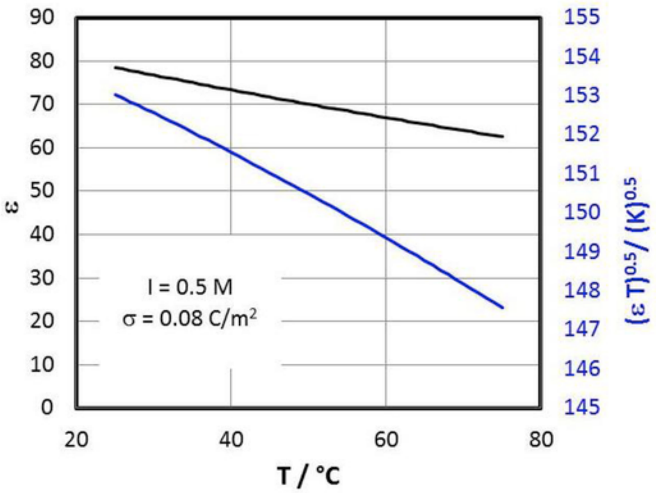

Fig. 5. Change of the dielectric constant of pure water with temperature (black line, left axis) and change of the square root of the product of absolute temperature and dielectric constant of water with temperature (blue line, right axis). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

In agreement with this minor change, small numerical differences in surface charge do occur but remain invisible on Fig. 4B. Additional calculations show that the error in neglecting the temperature is about 5% at 75 °C for the conditions in the respective Figures. For lower salt content at which the purely diffuse layer model is more appropriate (0.5 mM) the estimated error in the exponential term is a bit above ten percent at 99 °C.

While ignoring the full temperature calculation has a minor effect on the calculated surface charge density, the surface potential is affected as shown in Fig. 6. Unlike for surface charge densities, differences for the two cases at 60 °C (with and without full correction) are clearly discernible for the surface potential for the two temperatures studied by Tertre et al.

The difference arises because the charge potential relationship is affected by temperature. While the charge does not change visibly, Fig. 7 indicates that at identical charge densities higher temperatures will result in higher absolute potentials. So ignoring the temperature dependence leads to lower absolute potentials for a given surface charge density. The two overlapping lines prove that identical charge potential relationships are used, if the temperature is kept constant.

The compensating effect can be further evaluated by plotting the quotient of potential and absolute temperature (Fig. 8). This quotient represents the temperature dependent part of the argument of the exponential in the electrostatic term (Eq. (1)). The lower potential is di-

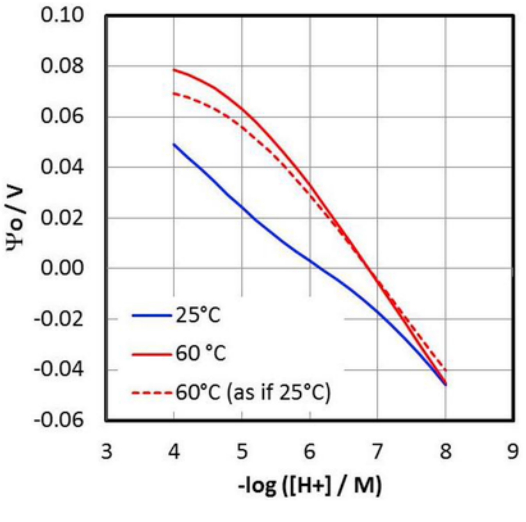

Fig. 6. Surface potential as a function of pH (here given as – log ([H$^+$]/M) as calculated with the parameters used in Fig. 4.

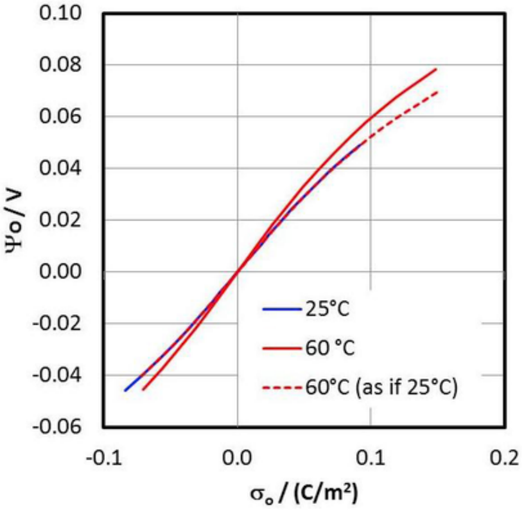

Fig. 7. Surface potential vs surface charge density in the purely diffuse layer model at 25 and 60 °C. The entry "60 °C (as if 25 °C)" corresponds to the case where no temperature correction has been applied (i.e. temperature was kept at 25 °C but the log K values for 60 °C were used).

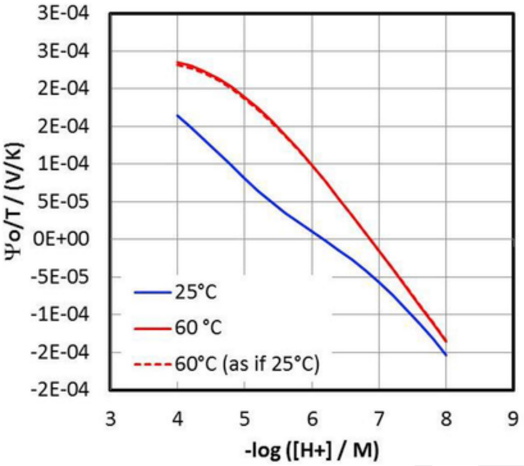

Fig. 8. Temperature depending part within the electrostatic term (Eq. (3)) as a function of pH, more precisely – log ([H$^+$]/M), for the three cases discussed.

vided by a lower temperature which in this example leads to nearly complete compensation.

For other electrostatic models the compensating effect that we found for the DLM will not necessarily occur. It has been mentioned that constant capacitance type models allow self-consistent treatment with any code, since variations can directly be introduced by the capacitance value(s). Models involving both a capacitance and a diffuse layer (like the basic Stern or the triple layer/plane models) are expected to be more involved. In SI (Figures SI4-SI9) this is shown for the triple layer model (TLM) involving parameters from a separate study (Ward and Brady, 1998). In essence, the temperature dependence can be seen to be governed by the effect in the inner layer, i.e. by changes in the capacitance. The diffuse layer part is suppressed by the inner layer. Calculations similar to those discussed in the previous section again show the absence of an effect when omitting temperature dependence in the surface charge density calculations.

2. Conclusions

We have discussed the omission of temperature dependence within surface complexation modelling in three published studies. Examples for such omissions, two within a diffuse layer model and one in a triple layer model application, have apparently gone unnoticed. We show that compensating effects within the diffuse layer model finally cause indiscernible differences in calculations of titrable surface charge. Differences do appear in surface potential calculations.

We furthermore discussed the applicability of a very elegant approach to obtain temperature dependence of surface protonation constants within a diffuse layer model. The approach inherently assumes temperature congruence of surface charge (meaning that scaled surface charge densities with respect to the point of zero charge at each temperature coincide). We conclude that in order to be applicable, temperature congruence of surface charge densities should be proven experimentally, since temperature congruence is not a generalizable property.

In conclusion a number of code inherent and model inherent parameters will depend on temperature. Temperature itself appears in the electrostatic terms of surface complexation models For the constant capacitance models standard 25 °C calculations can simulate other temperatures correctly by adjusting the capacitance value. This involves the potential change of the capacitance with temperature and the change of temperature itself. Models involving the diffuse layer require a temperature dependent dielectric constant entry. This can be done by either specifying the value in an input file or by implementing a temperature function for the dielectric constant, which allows its correct calculation from a specified temperature. Finally, correct treatment of concentration scales is required, involving the use of volume specific units for the ionic strength of the 1:1 electrolytes in the Gouy-Chapman equation even if molal units are used for the mass law and mole balance equations. The stability constants for the formation of all species have to correspond to the temperature of interest.

Clearly, the user has to make sure that the code he is using has all the required options correctly implemented. This is not the case for standard FITEQL. In other common speciation codes, the user will need to inquire to what extent the details are correctly implemented. Home-made or adjusted codes like the one used by Machesky et al. (2001) or the modified version of FITEQL used in the present work control these issues, but may be inconvenient to use or not accessible.

Finally, it has to be pointed out that the compensatory factors observed in the present work for temperatures below 100 °C need by no means apply to other conditions and users should not rely on the results presented here, but explicitly correct for temperature variation. The same holds in principle for temperature congruence of charging curves which may be a useful concept below 100 °C but is simply not valid for other conditions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2018.12.023.

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