



Modeling metal ion-humic substances complexation in highly saline conditions



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ABSTRACT

Because highly saline groundwaters are found at potential repository sites for nuclear waste, geochemical models should predict the speciation of relevant radionuclides in brines, including their complexation with substances such as humic acids (HA). In this study, available experimental radionuclide-HA complexation data in high 1:1 background electrolyte solutions ($0.01 < m_{\text{NaCl/NO}_3/\text{ClO}_4} < 4$ molal, m) are reviewed. Discrepancies in the amplitude of ionic strength effects on radionuclide-HA complexation are observed, which might depend on the nature of the interacting radionuclide or on the origin of HA. However, significant differences in the experimental conditions and calculations applied to determine conditional metal ion-HA complexation constants hamper direct comparison between these datasets. To clarify whether metal ion-HA binding in saline solutions can be described, two sophisticated humic-ion binding models (Model VII and NICA-Donnan) are presently used. This is the first time that Model VII and NICA-Donnan are applied to predict metal ion-HA binding at high ionic strength ($I > 1$ m). The advantage of these models, compared to more simple ones (e.g., the polyelectrolyte or the charge neutralization models), is that both electrostatic and chemical contributions to the overall metal ion-HA binding are explicitly taken into account. Model VII and NICA-Donnan are shown to produce very similar results. Trends in conditional metal ion-HA binding constants and in the maximum metal ion uptake by HA (e.g., the loading capacity) with I agree with experiments. The present data evaluation suggests that most of the apparent discrepancies between various experimental datasets arise from differences in the experimental conditions. Both Model VII and NICA-Donnan predict that the specific ion interaction theory (SIT) parameters for metal ion-HA systems, which are required for high ionic strength with more simple models, vary with pH and metal loading. Overall, Model VII and NICA-Donnan are able to account for various mechanisms involved in metal ion-HA complexation, including the metal loading effects and cation competition, and might be helpful predictive tools for performance safety assessment up to highly saline conditions.

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1. Introduction

Humic substances (HS) such as humic (HA) and fulvic (FA) acids are ubiquitous in natural waters and form complexes with dissolved metal ions. They play a crucial role for metal ion mobility and bioavailability in the environment. HS exhibit extreme

complexity. The major HS cation-binding groups are the carboxylic and phenolic groups (Ritchie and Perdue, 2003), but less abundant softer Lewis bases (e.g., N- and S-containing groups) also contribute to cation-HS complexation (Tipping, 1998; Hesterberg et al., 2001). HS are macro-ions and electrostatic effects are relevant for their complexation properties. Moreover, several HS groups may bind a single cation, which either leads to a chelation effect (Martell and Hancock, 1996) or to the formation of a cation bridge between different organic molecules (e.g., Kunhi Mouvenchery et al., 2012). Hence, metal ions can form a large variety of complexes with HS,

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leading to apparent complexation constants that depend on pH, ionic strength and metal ion/HS concentration ratio (i.e., the metal loading) including the presence of competing cations like Ca and Mg. Substantial efforts have been made to determine thermodynamic metal ion-HS complexation constants and to develop predictive models for environmentally relevant conditions (e.g., Kim and Czerwinski, 1996; Benedetti et al., 1995; Tipping, 1998; Milne et al., 2001, 2003; Sasaki et al., 2008). Because of the complexity of HS, very different approaches have been proposed to describe the reaction between HS and metal ions.

The resulting metal ion-HS complexation models were developed for, and mainly applied to describe metal ion speciation under freshwater conditions, but were shown to be applicable for the more saline conditions that occur in estuaries and seawaters (e.g., Hiemstra and van Riemsdijk, 2006; Turner et al., 2008; Stockdale et al., 2011). Nonetheless, few studies have investigated metal ion-HS interactions under highly saline conditions, such as ionic strength (I) exceeding that of seawater (i.e., $I > 0.7\text{ m}$). The latter conditions are relevant with regard to the safety of nuclear waste disposal in rock salt formations or in specific clay formations. For example, deep waters in the Jurassic and lower Cretaceous clay rock formations in Northern Germany may contain salt concentrations as high as about 4 M (Mühlenweg et al., 1997). Sedimentary rocks currently investigated in Canada are in contact with brine solutions up to 6.5 M (Fritz and Frape, 1982). Although high ionic strength commonly leads to the coagulation of HS, this process has been shown to be incomplete in many cases and non-negligible amounts of dissolved HS were reported to persist (Wall and Choppin, 2003), which can react with dissolved metal ions.

Most of the radionuclide-HS complexation studies in saline solutions focused on HA. Because few data for FA exist, only HA binding properties at high ionic strength are discussed herein. Generally, at constant pH, the apparent radionuclide-HA complexation constants in monovalent background electrolyte solutions (e.g., NaCl or NaClO₄) decrease with increasing ionic strength from very dilute aqueous solutions up to 1 molal (mol kg⁻¹, hereafter denoted m). However, different binding behaviors are observed for $I > 1\text{ m}$. Specifically, UO₂²⁺- and Pu⁴⁺-HA complexation constants increase with increasing ionic strength (Labonne-Wall et al., 1999; Szabó et al., 2010), whereas Co²⁺-HA complexation does not vary substantially, and Ni²⁺-HA complexation slightly decreases (Kurk and Choppin, 2000) with increasing ionic strength. Although data from Czerwinski et al. (1996) and Wall et al. (2002) consistently show increasing Am³⁺/Cm³⁺-HA binding with increasing I , Czerwinski et al. (1996) observed minor variation in complexation constant values with I . This led them to propose an average value (with standard variation of ± 0.14 log units) for the entire range of I investigated, which contrasts with Wall et al. (2002) where much larger variations were reported (about 3 log units). Furthermore, for $1 \leq I \leq 3.5\text{ m}$, the maximum amount of radionuclide that is experimentally found to bind to HA (e.g., the so called loading capacity in the charge neutralization model) was shown to decrease with increasing I for trivalent actinides (Czerwinski et al., 1996), whereas it remained constant in the case of Pu(IV) (Szabó et al., 2010). All these discrepancies might be indicative of conformational changes in saline solutions, which would depend on the nature of the interacting radionuclide as well as on the origin of HA. However, significant differences exist in the experimental conditions and calculations applied to determine conditional metal ion-HA complexation constants between these different studies, which complicates data comparison. Some studies were conducted in non-complexing background electrolyte solutions (NaClO₄; Czerwinski et al., 1996; Szabó et al., 2010). High [Cl⁻] is environmentally relevant (as opposed to high [ClO₄⁻]), but metal ions can bind Cl⁻, which may affect the determination of

radionuclide-HA complexation constants. Complexation data for UO₂²⁺- and Am³⁺-HA binding from Labonne-Wall et al. (1999) and Wall et al. (2002) were obtained in acetate buffers under ambient (air) atmosphere. Like many ligands, acetate and carbonate form aqueous complexes with UO₂²⁺ and Am³⁺ and can compete with HA. Experiments were conducted at different radionuclide-to-HA concentration ratios, which might also affect HA charge and conformation. Finally, pH measurement is non-trivial in saline solutions. More specifically, “constant pH values” can refer to constant proton activity ($\text{pH} = -\log a_{\text{H}^+}$; Szabó et al., 2010), proton molality ($\text{pH}_m = -\log m_{\text{H}^+}$; Czerwinski et al., 1996; Labonne-Wall et al., 1999; Wall et al., 2002), or constant experimental values, as read on the pH-meter (pH_{exp} ; Kurk and Choppin, 2000; where the pH_{exp} - pH_m relationship is provided). Deviation between pH, pH_m and pH_{exp} as affected by I may also hamper comparison between different datasets.

Available radionuclide-HA complexation data have been analyzed using relatively simple models such as the Polyelectrolyte Model (PM; Torres and Choppin, 1984) or the Charge Neutralization Model (CNM; Kim and Czerwinski, 1996). These models can be conveniently included in the speciation codes used for performance safety assessment. Within these models, binding parameters may vary with pH and I . High salt levels require an appropriate treatment of activity coefficients for aqueous species in geochemical models, such as application of specific ion interaction theory (SIT; Ciavatta, 1980). Metal-HA complexation constants can also be extrapolated to $I = 0$ using SIT, when considering HA as a solute. However, due to HA complexity, SIT parameters are no more than adjustable parameters and their values have no clear physical significance according to the original authors (Czerwinski et al., 1996; Szabó et al., 2010). Given the differences in the experimental conditions between previous radionuclide-HA complexation studies and the different calculations applied for the determination of metal-HA complexation constants (e.g., with the CNM or the PM), it is difficult to evaluate how SIT parameters would evolve with changing metal ion concentrations and physico-chemical conditions.

More sophisticated models exist, such as the humic ion binding Model VII (Tipping et al., 2011), or its previous versions (Models V/VI: Tipping and Hurley, 1992; Tipping, 1998), and the NICA-Donnan model (Kinniburgh et al., 1996; Koopal et al., 2005). The description of HA properties relies on several assumptions, and the various models include a more or less detailed description of metal ion-HA interaction. In particular, the electrostatic and chemical contributions to the overall metal ion-HA binding are separated in the models. This is a major advantage for understanding metal ion-HA binding in saline solutions, because ionic strength is expected to more strongly affect electrostatic than chemical binding properties of HA. Unfortunately, as pointed out by Tipping (1998), the electrostatic approach included in Models V/VI/VII is unlikely to be applicable for $I > 1\text{ m}$. In contrast, NICA-Donnan equations seem to be applicable in highly saline conditions (up to 2 M), as shown for HA proton titration data (Benedetti et al., 1996), but, to our knowledge, it has never been tested for metal ion-HA complexation data.

In the following, we evaluate the applicability of Model VII and the NICA-Donnan model for saline aqueous solutions, focusing on the concomitant electrostatic approaches. The following analysis involves close inspection of the model equations in conjunction with comparisons of simulated and experimental HA proton titration and radionuclide complexation data. The mechanisms responsible for the effect of ionic strength on cation-HA complexation are also discussed within the context of the assumptions inherent to Model VII and NICA-Donnan. Finally, the impact of the physico-chemical conditions on the experimental determination of

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