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► **To cite this version:**

Pascal E. Reiller. Modelling Metal-Humic Substances/Surface Systems: Reasons for Success, Failure and Possible Routes for Peace of Mind. Mineralogical Magazine, 2012, 76 (7), pp.2643-2658. 10.1180/minmag.2012.076.7.02 . cea-00766089

HAL Id: cea-00766089

<https://cea.hal.science/cea-00766089>

Submitted on 12 Sep 2019

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Modelling Metal–Humic Substances/Surface Systems: Reasons for Success, Failure and Possible Routes for Peace of Mind

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Mineralogical Magazine 76 (7), 2643-2658.

<http://doi.org/10.1180/minmag.2012.076.7.02>

ABSTRACT

Iron oxides and oxy-hydroxides are commonly of considerable importance in the sorption of ions onto rocks, soils and sediments. They can be the controlling sorption phase even if they are present in relatively small quantities. In common with other oxides and clay minerals, the sorption pH-edge of metals is directly linked to their hydrolysis: the higher the residual charge on the metal ion, the lower the pH-edge. Modelling of this process has been successfully carried out using different microscopic or macroscopic definitions of the interface (e.g. surface complexation or ion exchange models that may or may not include mineralogical descriptions). The influence of organics on the sorption of many metals is significant. This organic material includes simple organic molecules and more complex exopolymeric substances (e.g., humic substances) produced by the decay of natural organic matter. Sorption of these organics materials to mineral surfaces has also been the subject of a large body of work. The various types of organics do not share the same affinities for minerals in general, and for iron oxides and oxy-hydroxides in particular. In those cases in which successful models of the component binary systems (i.e., metal/surface, metal/organic, organic/surface) have been developed, the formation of mixed surface complexes, the evolution of the surface itself, the addition order in laboratory systems, and the evolution of natural organic matter fractions during sorption, have often precluded a satisfying description of the metal/surface/organic ternary system over a sufficiently wide ranges of parameter values (i.e. pH, ionic strength, concentration of humic substances). This manuscript describes the reasons for some successes and failures in the modelling of the ternary systems. Promising recent advances and possible methods of providing more complete description of these intricate systems are also discussed.

1. INTRODUCTION

Natural organic matter (NOM) exerts a significant influence on the sorption of metals onto minerals surfaces in soils and sediments. Its influence on the migration behaviour of radionuclides has been recognized in many studies. Examples include the migration of plutonium in soils following the nuclear detonation at Nagasaki (Mahara and Miyahara, 1984; Mahara *et al.*, 1988; Mahara and Kudo, 1995; Fujikawa *et al.*, 1999) and the Chernobyl accident (Matsunaga *et al.*, 2004); the migration of actinide-group elements in soils at Oak Ridge National Laboratory (McCarthy *et al.*, 1998a,b); and the interaction of radionuclides with mining debris (wood and oil) at the Nevada Test Site (Zhao *et al.*, 2011). Natural organic matter is released by the decay of biological material through complex mechanisms. Although these have been studied for a many years, aspects of the composition and structure of NOM remains as puzzles for scientists. Achard (1786) proposed alkaline-extracted humic substances (HS) as simple and useful analogues for NOM more than two centuries ago. Modern definitions of humic substances are still linked to his extraction methods (Stevenson, 1982; MacCarthy, 2001b). The organic molecules produced during the diagenesis of biological material are so complex that HS are still not fully characterized (MacCarthy, 2001a,b). Briefly, HS are composed of humine, which is insoluble in all pH conditions; humic acid (HA), which is insoluble in acidic pH conditions; and fulvic acid (FA), which is soluble in all pH conditions and is retained on polyacrylic resins (XAD-8) (Stevenson, 1982; Aiken *et al.*, 1985; Ghabbour and Davies, 2001).

The use of HS in studies of the complexation and sorption properties of NOM has generated a large body of work. Although HS remains poorly characterized, some general features have emerged. From a structural point of view, Wershaw (1986, 1989, 1993, 1999) proposed that NOM was made up of aggregates of small molecules. As part of NOM, HS also contain aggregates of small molecules (Aiken and Malcolm, 1987; Chin *et al.*, 1994; Plancque *et al.*, 2001; Kujawinski *et al.*, 2002b; These *et al.*, 2004) and organic nanometre-scale entities (Bouby *et al.*, 2002; Baalousha and Lead, 2007; d'Orlyé and Reiller, 2012) with a fractal organization (Österberg *et al.*, 1995; Senesi *et al.*, 1997; Rice *et al.*, 1999), which can clump together to form larger aggregates (Pinheiro *et al.*, 1996; Manning and Bennett, 2000; d'Orlyé and Reiller, 2012). The 'micelle-like' or 'membrane-like' paradigm proposed by Wershaw (1986, 1993, 1999, 2000) may initially appear too organized to reflect the inherent heterogeneity of NOM or HS, but the recognition of a degree of organisation in NOM aggregates undoubtedly stems from Wershaw's work. Analyses by mass spectroscopy (Plancque *et al.*, 2001; Kujawinski *et al.*, 2002a; These *et al.*, 2004) and nuclear magnetic resonance (NMR) techniques (Kim *et al.*, 2003; Simpson *et al.*, 2003) have shown the extensive heterogeneity of NOM, and this is also corroborated by recent sequential extraction protocols using high performance size exclusion chromatography (HP-SEC) coupled to mass spectroscopy and NMR (Nebbioso and Piccolo, 2011, 2012).

Figure 1 shows a schematic representation of a humic acid aggregate. Following Nachttegaal (2003), carboxylic acid groups and other hydrophilic and fatty acids are located on the outside of the aggregates, whereas aromatic and hydrophobic groups occupy the centres. The compositions of NOM and HS are dominated by carbon, oxygen and hydrogen, with minor sulfur and nitrogen; their strong reactivity towards metal ions and minerals is mainly driven by carboxylate and phenolate functional groups, which imply a weak selectivity and comparable interaction for analogous cations (van Dijk, 1971; Reiller and Buckau, 2012). Although relatively large molecular masses have been reported for HS (mainly based on HP-SEC studies using globular proteins), the terms polymer or polyelectrolyte seem inadequate to describe them as no repetitive structure, or well-defined building blocks, have been identified. Observations of sorbed HS by atomic force microscopy (AFM) have revealed that they occur as small entities that aggregate and disaggregate with changes in pH and ionic strength (Maurice and Namjesnik-Dejanovic, 1999; Plaschke *et al.*, 1999), rather than as the coiled or elongated structure that are typical of polymers (Ogoshi and Chujo, 2005). The distribution of charges and the binding strengths of the alkaline and alkaline-earth metals are also very different between polymers and humic acids (van den Hoop *et al.* (1990). A reversible disruption of the structure under the influence of acids has been clearly demonstrated (Piccolo *et al.*, 2000, 2001). Nevertheless, the ionic strength dependence of HA sorption, and to a minor extent of FA sorption, has some commonalities with polyelectrolytes (Blaakmeer *et al.*, 1990; Böhmer *et al.*, 1990).

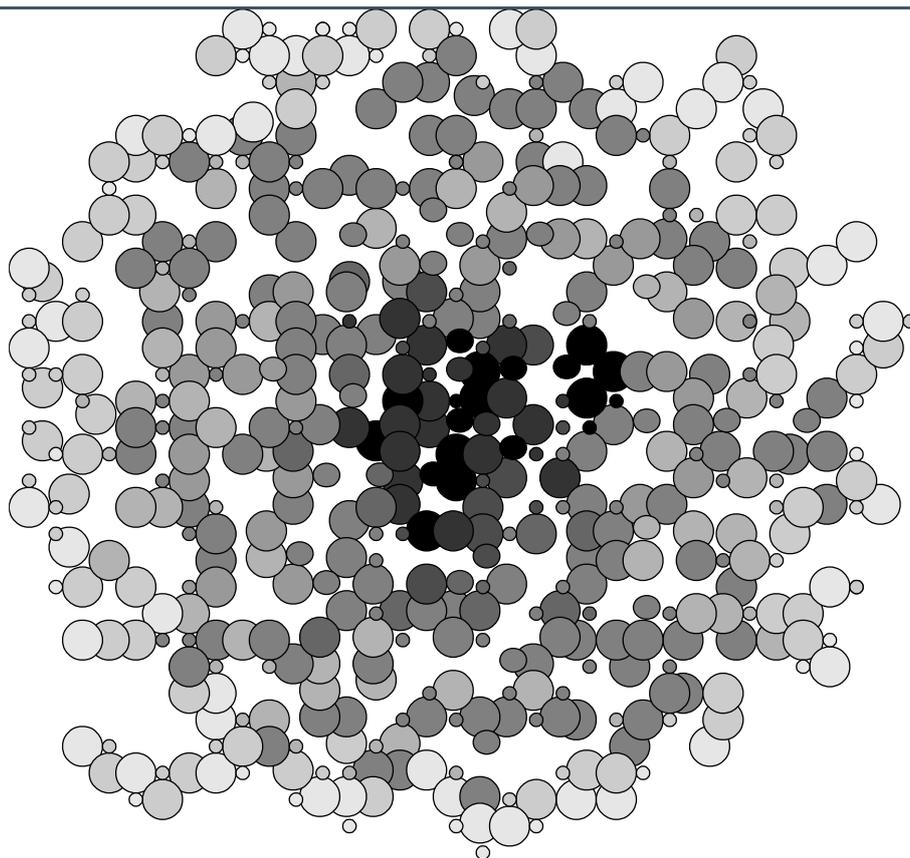


Figure 1. A schematic representation of a heterogeneous humic acid aggregate composed of different entities of different sizes. The entities can be viewed as molecules or aggregates of molecules. The grey shades represent the differences in hydrophobicity, with darker entities being more hydrophobic.

A simple approach in modelling a complex system is to test the linear additivity of its different binary components (Zachara *et al.*, 1994; Vermeer *et al.*, 1999). In this case these systems are: (1) the metal/HS complexation system (which also includes systems in which metals are complexed by inorganic ligands, i.e. OH^- , CO_3^{2-} , PO_4^{3-} ...); (2) the HS/surface sorption system; and (3) the metal/surface sorption system. The assumption of linear additivity requires these systems to be acting simultaneously and independently, without deviation due to modifications of one of the constituents or the formation of a ternary surface complex. It is worthwhile noting that in some successful models of ternary systems (e.g. Zachara *et al.*, 1994; Heidmann *et al.*, 2005), the linear additivity of the binary systems does not always represent the behaviour of ternary systems on a sufficiently large parametric domain (e.g. pH, ionic strength, metal concentration; Robertson and Leckie, 1994; Vermeer *et al.*, 1999). Indeed, Tipping *et al.* (1983) came to the conclusion that there is a need to account for “the creation of extra uptake sites of relatively high affinity” when surface and HS interact to explain their results. Following Lavoisier (1789, chapter XIII), these sites cannot be created from nothing (*creation ex nihilo*), but are more probably produced (*creation ex materia*) by the sorption process (Janot *et al.*, 2011; Janot, 2011) and conformational rearrangement (Amal *et al.*, 1992; Au *et al.*, 1999).

In this paper binary metal/HS and HS/surface systems are reviewed, and different ternary metal/HS/surface systems are described. The focus is primarily on radionuclides, but also includes illustrative examples of other metal ions. The reasons that prevent the linear additivity of binary system from properly described ternary systems are identified, and techniques that have the potential to produce more realistic models of the ternary systems are described.

2. BINARY SYSTEMS

2.1. The metal/HS binary system

The interaction of HS with metal ions follows the Irving and Williams (1948) series (Schnitzer and Skinner, 1966, 1967; Kerndorff and Schnitzer, 1980): alkali-metal interactions are weak (van den Hoop *et al.*, 1990; d'Orlyé and Reiller, 2012) and the strongest interaction is with M^{4+} elements (Reiller, 2005; Reiller *et al.*, 2008). The interaction is weakly selective between analogous metals (*vide supra*). For the lanthanides (Ln) and actinides (An), the strength of interaction increases from M(V), NpO_2^+ (Kim and Sekine, 1991; Seibert *et al.*, 2001); to M(III) and M(VI), Eu^{3+} , Sm^{3+} , Am^{3+} , Cm^{3+} , UO_2^{2+} (Czerwinski *et al.*, 1994, 1996; Sonke, 2006; Pourret *et al.*, 2007; Sachs *et al.*, 2007; Marang *et al.*, 2008; Reiller *et al.*, 2011a); to M(IV), Th^{4+} , U^{4+} , Np^{4+} , Pu^{4+} (Nash and Choppin, 1980; Reiller *et al.*, 2003; Reiller, 2005; Reiller *et al.*, 2008; Beneš, 2009; Szabó *et al.*, 2010; Stockdale *et al.*, 2011). Modelling of the metal/HS binary systems is possible using semi-empirical techniques (Hummel, 1997; Tipping, 2002; Reiller and Buckau, in press). Due to the intrinsic heterogeneity of the systems, the strict application of thermodynamics is often awkward. In particular, it is difficult to produce thermodynamic models. In particular, it is difficult to unequivocally define a standard state for a mixture of molecules in which the composition and possible interactions between the components are unknown. Extra-thermodynamic assumptions are therefore made (e.g. varying operational constants with physico-chemical parameters such as pH and ionic strength), that hide the variation of an extensive parameter [e.g. number of available sites (Reiller and Buckau, 2012)]. These models allow satisfactory operational description of the experimental results as long as the defined 'HS object' is not modified during the reaction (e.g. by complexation or sorption). However, due to the possible modification of HS during complexation reactions (Caceci and Billon, 1990; Plaschke *et al.*, 2002; Christl and Kretzschmar, 2007), semi-empirical complexation models must be applied with great care.

In some cases, modifications are not important. Reiller *et al.* (2011b) showed that both the Eu(III)-HS complexation strength and complex symmetry were comparable for different HP-SEC fractions of HA. In contrast, Claret *et al.* (2008) clearly showed that both the Eu(III)-HS complexation strength and complex symmetry were greatly modified for fractions of HA that have undergone sorption onto α - Al_2O_3 . This leads to questions about the modifications during sorption in the HS/surface binary system.

2.2. The HS/surface system

There is a large body of work which describes the sorption properties of HS using simple models including small organic molecules, polymers or polyelectrolytes, however, these simple representations do not adequately represent the sorption behaviour of HS. Due to the relative abundance of carboxylate functional group, the sorption of HS reaches a maximum around the pK of carboxylic acids, and it decreases with increasing pH (Tipping, 1981a, 1981b; Gu *et al.*, 1994; Ochs *et al.*, 1994; Vermeer *et al.*, 1998; Reiller *et al.*, 2002; Claret *et al.*, 2008). In this respect it follows the behaviour of weak acids in general (Blesa *et al.*, 1984; Dzombak and Morel, 1990; Marmier and Fromage, 2000) and of simple carboxylic organic acids in particular (Davis and Leckie, 1978; Gu *et al.*, 1995; Evanko and Dzombak, 1998; Borah *et al.*, 2011). The importance of catechol functional groups on the sorption behaviour of HS should not, however, be underestimated (Borah *et al.*, 2011; Gu *et al.*, 1995).

Although the structure of HS is not strictly polymeric, the sorption behaviour of HS on minerals has commonalities with polyelectrolytes, particularly with respect to the influence of ionic strength. At low concentration [i.e. $C < 10^{-3}$ mol/L (Szekeres *et al.*, 1998)], when simple organic acids are undergoing competition with the background electrolyte, i.e., when a decrease of sorption when the ionic strength increases (Schulthess and McCarthy, 1990; Mesuere and Fish, 1992; Ali and Dzombak, 1996), the sorption of HS, and particularly HA, increases with ionic strength (Murphy *et al.*, 1994; Schlautman and Morgan, 1994; Au *et al.*, 1999; Reiller *et al.*, 2002; Weng *et al.*, 2006; Janot *et al.*, 2012). The influence of lateral hydrophobic interactions between the humic entities is also important (Ochs *et al.*, 1994; Nachttegaal, 2003). Fulvic acids, which form aggregates of lesser dimension than those of HA, show intermediate behaviour as no, or only weak, influence of ionic strength has been demonstrated (Schlautman and Morgan, 1994; Filius *et al.*, 2000; Reiller *et al.*, 2002). This can be linked to the particulate nature of HA and the decrease in the Debye lengths of both the surface and HS aggregates (a charge screening effect).

The combination of these specific and non-specific (aggregation, lateral interactions) properties that influence the sorption of HS onto surfaces produces a subtle balance between surface complex formation and electrostatic forces that depends on three factors: (1) the pH of the solution, which controls the ionization and surface charge of the HS aggregates and surface, respectively; (2) the ionic strength, which controls the surface potential and of the conformation of HS aggregates; and (3) the free energy of the specific adsorption of the HS aggregates. As long as the surface charges are opposite ($\text{pH} < \text{pH}_{\text{pzc}}$, HS are negative and the surface is positive), the first two factors encourage sorption. The last factor implies an extension of this sorption domain, and explains why sorption is not nil at the point of zero charge of the mineral surface and why it extends up to more basic pH values, even if the electrostatic contribution is not favourable. This influence of the specific interaction is observed, for instance for sorption of borate or silicate onto iron oxides

(Blesa *et al.*, 1984; Marmier and Fromage, 2000), for various benzoic acids (Davis and Leckie, 1978; Gu *et al.*, 1995; Evanko and Dzombak, 1998), for polyelectrolytes (Chibowski and Wisniewska, 2002) and for humic substances (*vide supra*). As the sorption of HS is driven by interactions of carboxylate and to a lesser extent phenolate groups with hydroxylated surface sites (Gu *et al.*, 1995; Yoon *et al.*, 2004), but also by non-specific interactions, modelling is not trivial.

Humic substances/surface binary systems have been extensively modelled. The largest proportion is surface complexation models that suggest ligand exchange on hydroxylated sites (e.g. Filius *et al.*, 2000) based on spectroscopic evidence (Gu *et al.*, 1995; Wershaw *et al.*, 1995). In these studies, the HA were mostly defined as indistinct mixtures of entities that undergo surface complexation, although some authors have attempted to account for their complexity and heterogeneity. Humic substances can be conceptualized as particules that are chemically fixed to a surface by one or more of their functional groups. The remainder of the particle is weakly bound by lateral hydrophobic interactions. According to Ochs *et al.* (1994) the lateral interaction produces a membrane-like structure similar to that described by Wershaw (1986). In this model, the number of mineral surface sites is overcompensated by sorbed humic sites (Vermeer, 1996; Au *et al.*, 1999; Reiller *et al.*, 2002). Such surface particles have been observed in atomic force microscopy (Maurice and Namjesnik-Dejanovic, 1999; Namjesnik-Dejanovic and Maurice, 2000).

As NOM and HS are heterogeneous mixtures, sorptive fractionation occurs, and this depends on the nature of both the organic extract and the mineral surface (Davis and Gloor, 1981; Gu *et al.*, 1994; Kaiser and Zech, 1997; Meier *et al.*, 1999; Namjesnik-Dejanovic *et al.*, 2000; Hur and Schlautman, 2003, 2004a, 2004b; Reiller *et al.*, 2006; Claret *et al.*, 2008; Pitois *et al.*, 2008; Janot *et al.*, 2012), and on equilibration time (Gu *et al.*, 1994; van de Weerd *et al.*, 1999). This has been characterized by techniques including SEC, UV-Visible, time-resolved luminescence spectroscopy, and asymmetric flow-field flow fractionation, for different ternary systems. As a result of the reduction in the dielectric constant of water at the surface of a mineral (Booth, 1951), one can also assume that the more hydrophilic entities have a low affinity for the surface, leading to an over representation of hydrophobic entities, and a higher molecular mass fraction on minerals. This has been observed experimentally (Gu *et al.*, 1995; van de Weerd *et al.*, 1999). The evolution of sorption with time is also of interest. Rapidly sorbed low molecular mass fractions (Ochs *et al.*, 1994; Avena and Koopal, 1999), are replaced by higher molecular mass fractions (Gu *et al.*, 1994; van de Weerd *et al.*, 1999; Pitois *et al.*, 2008) following slow kinetics (Ochs *et al.*, 1994; Avena and Koopal, 1998; Vermeer and Koopal, 1998) that are function of the NOM to mineral surface mass ratio (van de Weerd *et al.*, 1999). In the case of metal oxides, exchange reactions between fractions of different molecular mass and hydrophobicity proceed more rapidly in the aromatic and low molecular mass fractions (Avena and Koopal, 1999; Pitois *et al.*, 2008). The origin of the slow kinetics step can be viewed as slow exchange between non-sorbed hydrophobic humic entities and those that are already sorbed (Kaiser and Guggenberger, 2000). These mechanisms are thought to

be the cause of the modification of humic fraction during transport in sediment column experiments (Johnson *et al.*, 2002).

An important outcome of this sorptive fractionation is that the 'HS object', as defined in a model, contains material that can fractionate and therefore the properties of the HS can evolve. The differences reported by Claret *et al.* (2008) between their original Eu(III)-HA complex and Eu(III) complexed by HA fractionated onto α -Al₂O₃, result from these fractionation phenomena. In this case, the interaction between the fractionated HA and Eu(III) is less significant than that between the original HA and Eu(III). By contrast, Heidmann *et al.* (2005) showed that the Cu(II)-FA interaction after fractionation onto kaolinite was more significant than that before fractionation. This is reminiscent of the 'creation of sites' in Tipping *et al.* (1983) for the Cu(II)/HA/goethite system.

Different strategies can be used to model this apparent increase of affinity. Weng *et al.* (2007) proposed an adaptation of the metal/HA binary system free energy during sorption. A strong hypothesis is that the free energy change associated with humic substance aggregates at equilibrium has the same chemical potential, including electrostatic effects, sorbed to the surface and remaining in solution. In other words, the defined 'humic object' is the same in solution and at the surface but its free energy is changed due to sorption. It has been shown, however, that there are changes in the composition of HA due to sorptive fractionation (*vide supra*). A schematic view of the sorptive fractionation process is proposed in Figure 2; the humic acid aggregate leaves the more hydrophobic fraction onto the surface as the lower molecular mass and hydrophilic fractions are released in the bulk.

The quantification of functionality after sorptive fractionation was proposed by Janot *et al.* (2010, 2011) for a HA by spectrophotometric titration. In the framework of the non-ideal competitive adsorption-Donnan (NICA-Donnan) model (Kinniburgh *et al.*, 1999), it was shown that a substantial proportion of the more acidic functionality (those with the lower $\log_{10}\tilde{K}_H$ in the framework of the NICA-Donnan model) remained in suspension, and that this has an influence on the metal-HS_{sorbed} and metal-HS_{free} complexes, and on the metal/HS/surface ternary system. This quantification relies on the operational relationship between the optical properties of humic substances and the potentiometric titration. This operational relationship is less elegant and thermodynamically consistent than the proposition of Weng *et al.* (2007), but it accounts for the observed modification of functionality and composition of the 'HA objects' during sorption. It should be noted that this relationship still needs to be determined for each HS.

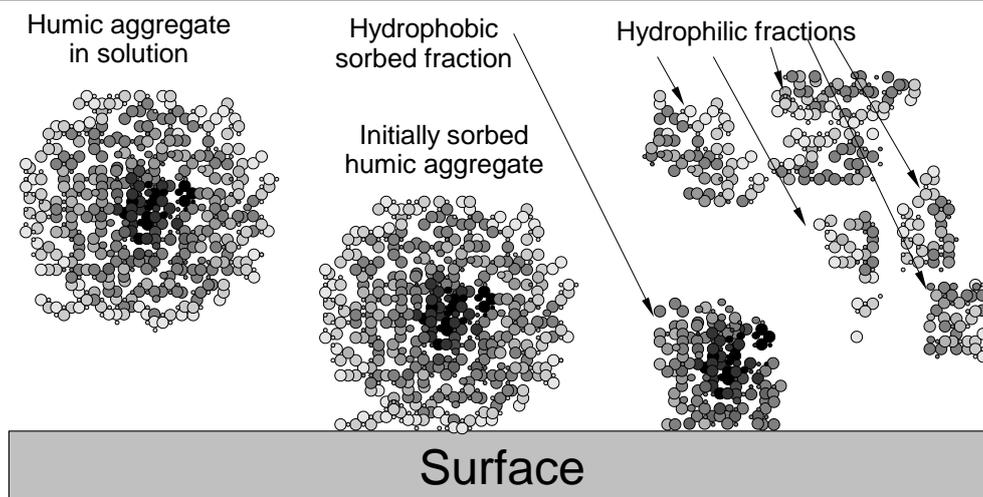


Figure 2. A schematic representation of sorptive fractionation of the NOM aggregate (see Figure 1) onto mineral surfaces.

2.3. The metal/surface system

The binary metal/surface system has been widely described in the literature and only the basic properties that are necessary to understand ternary systems will be discussed.

The sorption pH-edge of metals on minerals is closely related to their first hydrolysis constant (Bradbury and Baeyens, 2005a, 2005b, 2009). As shown schematically in Figure 3, at trace concentrations sorption commonly occurs at pH 8-10 for AnO_2^+ (Turner *et al.*, 1998); at pH 5-7 for Ln/An^{3+} (Fairhurst *et al.*, 1995; Rabung *et al.*, 2000, 2005; Tan *et al.*, 2008; Janot *et al.*, 2011); at pH 3-5 for UO_2^{2+} (Waite *et al.*, 1994; Lenhart and Honeyman, 1999); and at pH 2-3 for An^{4+} (Murphy *et al.*, 1999; Takahashi *et al.*, 1999; Reiller *et al.*, 2002, 2005; Romanchuk *et al.*, 2011). The modelling was mainly done through surface-complexation models of various kinds (Hiemstra *et al.*, 1989a, 1989b; Davis and Kent, 1990; Dzombak and Morel, 1990), with ion-exchange models (Alliot *et al.*, 2005a, 2005b, 2006; Motellier *et al.*, 2003; Tertre *et al.*, 2010), and also with mixed ion-exchange/non-electrostatic surface-complexation strategies (Bradbury and Baeyens, 2002, 2005a; Bradbury *et al.*, 2005; Bradbury and Baeyens, 2009).

The influence of ionic strength depends on the nature of the minerals. For well-defined oxides there are mostly no influences on the sorption of metals (Zachara *et al.*, 1994; Reiller *et al.*, 2002; Janot, 2011). For clays, however, an ionic strength influence is clearly evident (Zachara *et al.*, 1994; Bradbury and Baeyens, 2002).

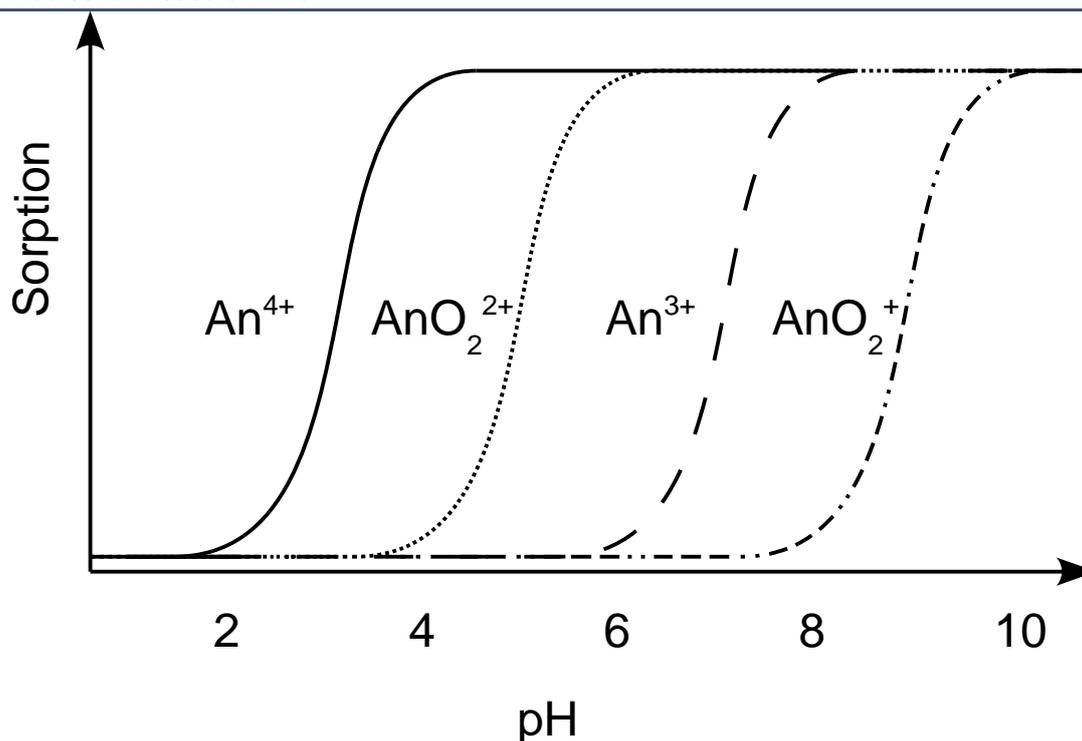


Figure 3. A schematic comparison of actinides pH-edge at trace concentration for An(V) (AnO_2^+), An^{3+} , An(VI) (AnO_2^{2+}), and An^{4+} .

3. THE TERNARY METAL/HS/SURFACE SYSTEMS

3.1. Influence of sorptive fractionation of HS

In ternary systems, in which metal cations, minerals and NOM coexist, there are complicated interactions among the three components; these interactions can be competitive or synergistic. The sorption of metals in these ternary systems generally increases before the mineral sorption edge compared to the metal/surface binary system, due the sorption of metal-HS complexes, and then decreases after the pH-edge due to desorption of HS. The metal sorption eventually decreases at more alkaline pH values. This general pattern is found for all metals and, in particular, for all the redox states of radionuclides (Figure 4) [e.g. Ln/An(III) (Fairhurst *et al.*, 1995; Tan *et al.*, 2008; Janot *et al.*, 2011), U(VI) (Payne *et al.*, 1996; Zeh *et al.*, 1997; Lenhart and Honeyman, 1999; Krepelova *et al.*, 2006), and An(IV) (Takahashi *et al.*, 1999; Reiller *et al.*, 2002, 2005)].

The results of the modelling strategies depend on the nature of the mineral phases. For clay minerals, linear additive models are relatively successful (Dalang *et al.*, 1984; Zachara *et al.*, 1994; Heidmann *et al.*, 2005). For oxides, linear additive binary models do not always produce reliable and adequate description of ternary systems across wide ranges of pH, ionic strength, metal and HS activities (Robertson and Leckie, 1994; Robertson, 1996; Vermeer *et al.*, 1999; Christl and Kretzschmar, 2001). Tipping *et al.* (1983) proposed that the reactivity of sorbed HA was modified during sorption and that 'extra uptake sites' with higher reactivity were created on the surface, or more probably,

were exposed during sorptive fractionation. Binary linear additivity under-predicts metal sorption in the ternary systems above the sorption pH-edge (Vermeer *et al.*, 1999; Christl and Kretzschmar, 2001). This may be related to the formation of ternary surface complexes, as is observed in many simple organic molecules (Schindler, 1990, and references therein; Alliot *et al.*, 2005a, 2005b, 2006).

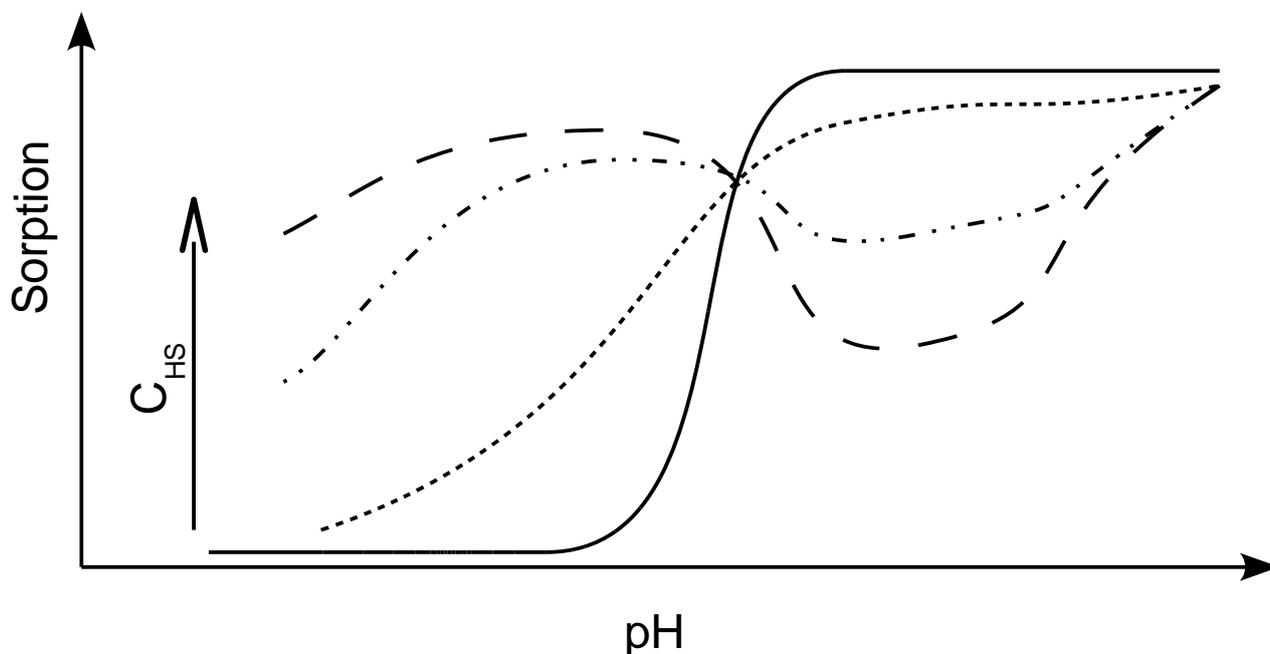


Figure 4. A schematic representation of the variation in metal sorption onto mineral surfaces with increasing concentration of humic substances (C_{HS}). The dotted, dashed-dot-dot, and dashed line represent an increasing concentration of humic substances.

In well-defined oxides minerals an increase of ionic strength leads to an increase in metal sorption, which can in turn be related to an increase in HS sorption – e.g. Co(II)/HA/gibbsite system (Zachara *et al.*, 1994) and Eu(III)/HA/alumina system (Janot, 2011). As there is a clear effect of ionic strength on metal sorption in the case of some clays – e.g. Co(II)/HA/clay (Zachara *et al.*, 1994) –, it is not easy to discriminate between the different effects of ionic strength on both metal and HS.

Another factor is the influence of metal/HS complexation on the sorption of HS onto minerals. This has been shown for some systems [e.g. the Pb(II)/FA system (Heidmann *et al.*, 2005) and the Eu(III)/HA (Janot, 2011)], but is not common to all systems [e.g. the Cu(II)/FA system (Heidmann *et al.*, 2005)]. Heidmann *et al.* (2005) noted that the difference between Cu(II)/FA and Pb(II)/FA systems was linked to the H^+/M^{2+} molar exchange ratios [i.e., ~ 1 for Pb^{2+} , and ~ 1.5 for Cu^{2+} , respectively (Christl *et al.*, 2001)]. The authors linked the differences in the ternary system evolution to the possible metal-induced aggregation of their FA following the decrease in negative charge induced by metal complexation. The molar H^+/M^{n+} ratios requires that 1 mole of complexed M^{2+} leads

to the release of 1 mole of H^+ for Pb^{2+} , and 0.67 mole for Cu^{2+} , respectively (Christl *et al.*, 2001; Heidmann *et al.*, 2005). Hence, the reduction in negative charge due to complexation is greater for Pb^{2+} than Cu^{2+} . In the case of Eu^{3+} , Marang *et al.* (2006, 2008) and Janot *et al.* (2010, 2011) obtained H^+/Eu^{3+} molar exchange ratios of ~ 1.3 , and 1.6, respectively, which are comparable to those in the H^+/Cu^{2+} system, but with a higher metal charge. The reduction in negative charge is thus more important for Eu^{3+} than for Cu^{2+} , and is corroborates the proposition of Heidmann *et al.* (2005). Interestingly, the study of Heidmann *et al.* (2005) was on kaolinite whereas Janot *et al.* (2010, 2011) experimented on $\alpha-Al_2O_3$.

Another influential parameter is HA functionality modification during sorption. To examine this, it is important to compare the proposition of Tipping *et al.* (1983) for the creation of extra uptake HA sites upon sorption with the results obtained by Janot *et al.* (2010, 2012) and Janot (2011). It is clear in Janot *et al.* (2012) that after the HA sorption experiment onto $\alpha-Al_2O_3$ the H^+ affinity for non-sorbed HA is lower than for the original HA. Therefore, higher H^+ affinity sites are present in the sorbed fraction. Applying the same reasoning on $Eu(III)/HA/\alpha-Al_2O_3$ system, Janot *et al.* (2012) proposed that the sorbed-HA complex would have a higher affinity for Eu^{3+} than the original HA. Therefore, the higher than anticipated degree of sorption in ternary system is not due to the 'creation of extra sorption sites', but to their accessibility following sorptive fractionation.

3.2. The particular case of tetravalent metals

A further complication is present with (IV) redox states, which produce tetravalent cations (M^{4+}), in systems in which the sequence of addition is important (Figure 5). Although an effect which depends on the addition sequence has been reported for some metals with (III) redox states, it is not long lived in $Cm(III)$ (Wang *et al.*, 2004). The sequence of addition is of particular importance for $An(IV)$ (notably Th, U, Np, Pu) undergoing strong complexation reaction with HA (*vide ante*) as the corresponding $An(III, V, VI)$ may be oxidised or reduced to $An(IV)$ in the presence of HS [e.g. $Np(V)$ (Zeh *et al.*, 1999; Artinger *et al.*, 2000) or $Pu(III, V, VI)$ (Nash *et al.*, 1981; Sanchez *et al.*, 1985; André and Choppin, 2000; Marquardt *et al.*, 2004; Dardenne *et al.*, 2009)]. It has been shown (Figure 5) that if HS is sorbed onto a mineral surface, and $M(IV)$ is added afterwards, the classical pattern of sorption hindrance after the sorption pH-edge is observed (Takahashi *et al.*, 1999; Reiller *et al.*, 2002, 2005; Bouby *et al.*, 2011). However, if $M(IV)$ is sorbed on a mineral surface before the addition of HS (Figure 5) $M(IV)$ sorption is much less hindered (Takahashi *et al.*, 1999; Reiller *et al.*, 2002, 2005). A relatively weak dependence on equilibration time has also been demonstrated (Reiller *et al.*, 2005). The reasons behind this addition order effect are not yet clear. It is possible that the incorporation of M^{4+} into the mineral structure, or into a surface precipitate, would impede its removal by HA. Alternatively, the response of tetravalent metal to the fractionation of HS may induce a very high affinity of M^{4+} for surface-bound HA.

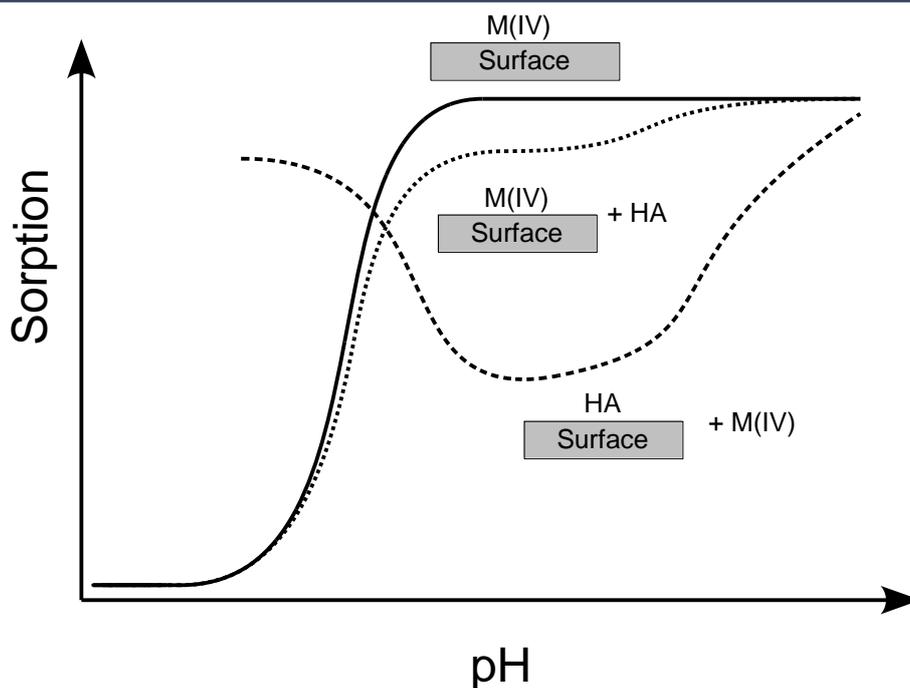


Figure 5. The effect of the addition order on M^{4+} sorption onto minerals in the ternary systems $M(IV)/HA/surface$: the solid line represents the M^{4+} pH-isotherm, dashed line represents the case where HA is equilibrated with the surface before the addition of $M(IV)$, and dotted line represents the case where $M(IV)$ is equilibrated with the surface before the addition of HA.

4. CONCLUSIONS AND PERSPECTIVES

The modelling of the ternary metal/HA/surface systems, at the laboratory scale or in the field, is not simple. The modelling of ternary systems using binary linear additivity meets with only partial success. This is due to the difficulty in defining an unambiguous standard state for aggregates of humic substances. Humic substances can form ternary complexes with metals and surfaces. The definition of ternary complexes in the case of HS is not straightforward (*vide ante*) but evidence exists for additional organic ligands that interact with metal/HA systems (Dierckx *et al.*, 1994; Glaus *et al.*, 1995; Morgenstern *et al.*, 2000; Reiller and Buckau, 2012), and that metal/HA/oxide systems behave differently than the constituting binary systems (Tan *et al.*, 2008; Janot *et al.*, 2011). There is now strong evidence that a sorptive fractionation modifies the functionality of HS aggregates and hence that the ternary surface-bound and the bulk humic phases differ from those of the binary metal/HS and HS/surface systems.

Possible ways of overcoming the change in functionality following sorptive fractionation include estimating the change in free energy from the deviation between the linear additivity and the ternary system, or directly quantifying the modification through titration. Both strategies have their advantages and drawbacks: in the former, no modification of functionality is imposed when clear experimental evidence exists for it; in the latter, the

functionality modifications rely on an operational function that is not based on a theoretical understanding of the sorptive fractionation.

The need to better understand ternary metal–NOM–surface systems and to improve the accuracy and reliability of the modelling remains. More information about the molecular phenomena that produce sorptive fractionation and change the distribution of functionality is required. Important questions about ternary systems include (1) what are the main driving forces of sorptive fractionation? (2) Is sorptive fractionation driven by a change in conformation of the NOM aggregates due to polarity change between the bulk and the surface? (3) Is sorptive fractionation driven by the sorbed NOM fraction, which shows a higher affinity for the metal, which in turn induces a change in the composition of the NOM aggregates and finally a change in conformation of NOM aggregates? (4) Is sorptive fractionation controlled by kinetics? (5) What first-order phenomena are needed to model a particular metal–HS–mineral system? Answers to all of these questions are required to provide a satisfactory model of a ternary system, especially if more than an operational view is required. As long as these questions limit our understanding of the ternary metal–NOM–surface system, however, we will be unable to produce satisfactory models.

5. ACKNOWLEDGMENT

This review has been possible through the financing of the different work in CEA (CEA/DDIN/MRISQ and CEA/DDIN/RSTB). The reviewers and editors are acknowledged for kind polishing of the Frenglish, and for useful comments and suggestions.

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