

Proton transfer processes in polar regions of humic substances initiated by aqueous aluminum cation bridges: A computational study

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ABSTRACT

An overview of the variety of processes induced by the aluminum cation interacting with carboxyl and carboxylate groups is given by means of quantum chemical density functional theory (DFT) calculations. Different hydration states of Al^{3+} ranging from the hexaquo complex down to the unhydrated cation and direct/indirect bonding with the polar groups are considered. The calculations reflect the amphoteric character of the hydrated aluminum complex showing in most cases its acidic character via proton transfer from the water molecules of the hydration shell to the carboxylate group, but in some cases also deprotonation of the carboxyl group. Several additional processes are observed such as interconversion of bidentate and monodentate bonding by the carboxyl/carboxylate groups and strong hydrogen bonding between proton transfer partners. Comparison with analogous previous investigations on cation bridges induced by calcium and sodium shows the pronounced activity of the triply charged aluminum cation. The importance of the strong polarizing and bridging power of the aluminum cation for soil organic matter with low exchange capacities and a low concentration of charged groups is discussed.

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1. Introduction

Humic substances (HS) play a critical role in speciation, transport and deposition of a diversity of plant nutrients and contaminants ranging from metal ions to lipophilic compounds (Livens, 1991; Piccolo et al., 1999). They show the ability of forming complexes with various functional groups in soils, which is a significant factor affecting the retention and mobility of pollutants in soils and waters, deciding, therefore, its fate in the environment (Pandey et al., 2000). Additionally, these complexation processes are important in stabilizing the structures of humic substances against biotic and abiotic degradation (Domazetis and James, 2006; Wrobel et al., 2003). The current approach to the structure of HS is based on the concept that relatively small amphiphilic compounds come together in a supramolecular association basically stabilized by non-bonded interactions such as hydrogen bonds, Coulombic, van der Waals and π - π interactions (Piccolo, 2001, 2002; Piccolo and Conte, 1999; Wershaw, 1999).

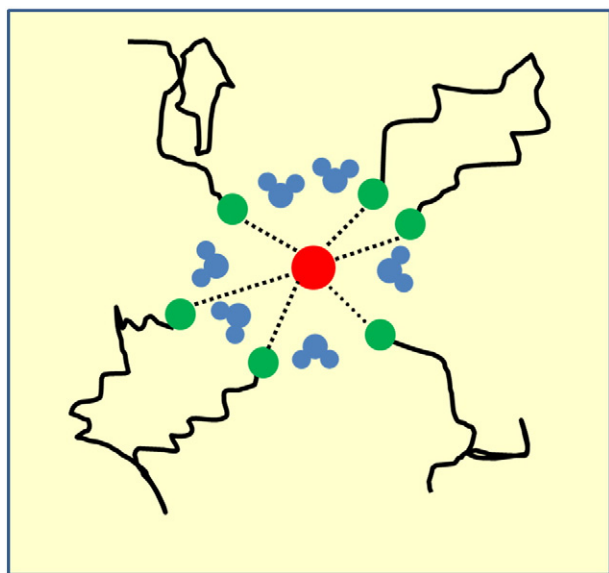
Cation bridges (Arnarson and Keil, 2000; Feng et al., 2005; Piccolo et al., 1999) and water molecular bridges (WaMB) (Aquino et al., 2011a, 2011b; Schaumann and Bertmer, 2008) constitute an important interaction type, cross-linking otherwise disconnected groupings

containing negative charges or polar functionalities within the organic polymer. Especially the presence of multivalent cations, such as Ca^{2+} and Al^{3+} , is known to largely enhance adsorption through cation bridges (Nebbioso and Piccolo, 2009). Besides the influence these cations exert on the global structure and rigidity of HS, especially the aluminum cation calls for attention considering also its toxicity inhibiting the growth of plants (Bollard, 1983; Kinraide and Parker, 1990; Parker and Bertsch, 1992). Additionally, it has been found that the presence of organic material reduces the aluminum toxicity substantially (Hue et al., 1986) by formation of complexes, which do not penetrate the cell walls of plants so easily as free aluminum.

Theoretical modeling of the interaction of HS with cations and hydrogen bonds can provide useful insight into the structural manifold of the different complexes and tautomeric structures. The structural complexity of the HS is well known (MacCarthy, 2001; Schulten, 1995) and, therefore, concrete global modeling is difficult (Schulten and Schnitzer, 1995) and computationally very demanding. Due to the supramolecular structure of the HS local interactions become important, especially for the strong interactions involving cations. Thus, the concept followed in this work consists of the quantum chemical investigation of local model complexes to be described in the following, which allow the simulation of particular atomistic situations that may occur in real soil processes. A schematic representation of such a local interaction between a central cation and surrounding polar groups and water molecules is presented in Scheme 1. Containing degradation

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Scheme 1. Bridging cation interacting with polar HS groups and water molecules.

products of lignin, cellulose, waxes, etc., the most prominent metal binding sites are carboxylate and phenolate groups (Kinniburgh et al., 1999; Ritchie and Perdue, 2003). In this work we concentrate on the carboxylate group, which is an excellent prototype for polar groups present in HS. Its high abundance in HS has been documented, e.g., for the Suwannee River humic substance which has strong acid character ($pK_a \sim 3$) and contains about 9.6 mol kg^{-1} of carboxyl carbon (Baalousha et al., 2006).

The hydration of Al^{3+} , especially its first and second solvation shells, has been studied extensively by means of experimental (Fiat and Connick, 1968; Ohtaki and Radnai, 1993; Waluyo et al., 2011) and theoretical (Bylaska et al., 2007; Hofer et al., 2008) investigations. From ^{17}O NMR (Fiat and Connick, 1968), X-ray measurements (Waluyo et al., 2011) and molecular dynamics (Bylaska et al., 2007; Hofer et al., 2008) an inner shell coordination number of 6 has been found indicating a tightly bound inner solvation shell. The second hydration shell is more flexible and a concrete structure cannot be established unambiguously (Bylaska et al., 2007; Hofer et al., 2008; Ohtaki and Radnai, 1993). Pentameric aluminum complexes were studied in recent work (Saukkoriipi and Laasonen, 2010) by means of Car-Parrinello molecular dynamics (CPMD) and systematic comparison of different density functionals showing, for example, similar good performance of the PBE and B3LYP functionals in molecular DFT calculations. The aluminum hexaaquo complex is known to be a weak Brønsted acid comparable in strength to the acetic acid and its deprotonation products have amphoteric character (Koubek, 1998). It should be noted that with the deprotonation also a dehydration of the inner solvation shell is connected (Ikeda et al., 2006).

The interaction of aqueous Al^{3+} with carboxylic/carboxylate groups has been studied by means of different quantum chemical methods (Aquino et al., 2000, 2001; Kubicki et al., 1999; Tunega et al., 2000). These studies include mono- as well as polyfunctional acids investigating mono to polydentate complexes. In Kubicki et al. (1999) the importance of monodentate and protonated bidentate complexes is discussed. The calculations presented in Tunega et al. (2000) show that the monodentate structure is only slightly preferred. These calculations also demonstrate that explicit inclusion of a first hydration shell and using additionally a continuum model provides a good description of these molecular complexes.

The goal of this work is to investigate the role of aluminum cation bridges based on the afore-mentioned approach of local interactions based on the molecular situation envisaged in Scheme 1. As polar moieties carboxyl/carboxylate groups were chosen. Following previous work

on the effect of WaMB connecting polar groups in HS (Aquino et al., 2009, 2011a, 2011b) and to take into account the limited flexibility of these carboxyl groups attached to a nonpolar environment, they were connected to aliphatic chains forming fatty acids, which were anchored at the far end terminal methyl group. This construction is used as a means to simulate the local restriction of the mobility of molecular segments. The bridging function (Scheme 1) is realized by sandwiching the Al^{3+} by two fatty acid chains as indicated in Scheme 2. This scheme also displays the two basic interaction types (direct and indirect) between the central cation and the carboxyl/carboxylate groups. This model, especially the fixed distance between the fatty acids, allows the study of the water mediation in this interaction. Moreover, proton transfer processes can be investigated reflecting the amphoteric character of the aqueous Al^{3+} complex. Comparison will be made to previous work (Aquino et al., 2011c) where the bridging capacity of Ca^{2+} and Na^{+} was investigated.

Another important aspect of this work is the relation to heat-induced restructuring processes in soil organic matter performed in differential scanning calorimetry (DSC) measurements (Schaumann and Leboeuf, 2005), which could lead to aluminum complexes with reduced water content that will change their properties considerably. Corresponding chemical effects can be quite different under such situations since Al^{3+} will act now as a strong Lewis acid. This property has already been shown to be quite influential in previous investigations on mineral surface models used as catalyst for forming peptide bonds (Aquino et al., 2004). In addition to the focus on different cationic species and their comparison, the influence of pH is investigated as well by considering different protonation states of the carboxyl groups.

The computer simulations reported in this work require extended calculations on large molecular clusters including chemical bonding and a large variety of nonbonded interactions ranging from strong Coulomb forces to weak hydrogen bonds. Quantum chemical approaches are clearly to be preferred in such cases in order to model these interactions in full generality. To accommodate the resulting large computational cost, an efficient DFT approach is used consisting of the combination of the nonhybrid PBE functional (Perdew et al., 1996) and the resolution of identity (RI) approach (Hättig, 2003) to speed up the computation through efficient calculation of the two-electron integrals.

2. Computational details

The structural model for a local HS environment is shown in Scheme 2. It has been used before in our previous investigation on cation bridges involving Na^{+} and Ca^{2+} (Aquino et al., 2011c) and consists of two fatty acids containing 11 carbon atoms each, with the carboxyl/carboxylate groups representing polar regions in which cation bridges can be formed. The relative positions of the two terminal $-\text{CH}_3$ groups at the other end of the chains were kept fixed at a distance of $\sim 15 \text{ \AA}$ in all calculations mimicking a limited rigidity of the HS backbone. The water content directly involved in the cation bridges was regulated by the number of water molecules inserted/depleted, which varies from 1 to 6 considering the aluminum-hexaaquo complex as a reference. Environmental effects were taken into account at the level of a polarizable continuum solvation model (Klamt and Schuurmann, 1993) by embedding the complexes into a polar continuum surrounding with a relative dielectric constant of water ($\epsilon_r = 78.4$). A nonpolar environment was modeled on the basis of the isolated systems.

Two kinds of complexes were investigated. In the first type, named “direct” (Scheme 2a), complexes were constructed by placing the bare Al^{3+} ion directly linked to the deprotonated carboxyl groups of each chain. This procedure generated a structural type $[(\text{COO}^-)_2\text{Al}^{3+}]$. For simplicity, only the reactive center will be specified throughout the paper. Concerning the complete structure see Scheme 2. Starting from it, a series of hydrated direct complexes was generated by adding in sequence up to six water molecules without breaking the direct $\text{Al}^{3+}/\text{COO}^-$ linkages. In a similar way the aluminum cation has been inserted between the fatty acids where only one carboxyl group was

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