



Formation of sandwich structure through ion adsorption at the mineral and humic interfaces: A combined experimental computational study



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HIGHLIGHTS

- Sandwich structure is prepared by ion adsorption at humic and mineral interfaces.
- Structure is unraveled by FT-IR spectroscopy and DFT calculations.
- Three potential formation routes are explored.
- Frequent conformational transitions for humic acids are detected.
- Role of metal ions during the sandwich structure formation is determined.

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ABSTRACT

Although ion adsorption at interfaces governs a variety of chemical processes, the underlying mechanisms remain controversial. We present a combination of dynamic light scattering, FT-IR spectroscopy and DFT calculations to probe the ion adsorption behaviors on montmorillonite and its mixture with humic acid (HA) as well as to unravel the composite structure and formation mechanism. Interaction structures of Ca^{2+} with HA, montmorillonite and their mixture are calculated, and computational frequencies show fine agreement with FT-IR results. The low ion affinities for HA explain that the aggregation kinetics of montmorillonite is significantly inhibited by forming composite with HA. Adsorption of Ca^{2+} on the mixture of HA and montmorillonite readily obtains sandwich-structured composite, where Ca^{2+} is situated at the midst and exhibits an essential stabilization effect. Furthermore, conformational transitions occur frequently for HA carboxylic groups during composite formation.

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Introduction

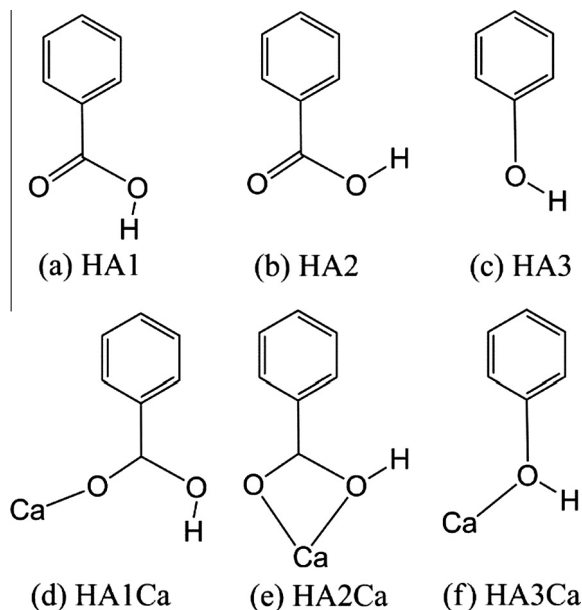
Ion adsorption at the interfaces is ubiquitous in nature and recently has emerged into one of the most debated topics in chemistry [1–3]. Organic matters and minerals constitute the principal material basis of the earth's soils, and both of them interact favourably with metal ions [4,5]. Metal ions, which are partially imported by human activities, are known to be an essential nutrition source for plants and animals, while some (e.g., Pb^{2+} and As^{3+}) are harmful and can result in environmental pollution [6]. To date, interactions of metal ions with organic matters and minerals have eluded a firm understanding. Humic acid (HA) that is based on phenol and benzoic acid motifs (Scheme 1) [7] is the major organic matters. The carboxylic and phenolic groups of HA were indicated to be crucial

for the complexation with metal ions [8–10]. Lishtvan et al. [11] demonstrated that the ion exchange capacity is dependent on the amount of carboxylic groups, and the close relevancy between carboxylic groups and metal ions was supported by FT-IR measurements [10–13]. As compared to HA, more attention has been invested on the interactions of metal ions with minerals [14–21]. Montmorillonite (Mont) carries obviously more negative charges than kaolinite and therefore corresponds to higher ion retention and adsorption capability [15–17]. Molecular dynamics simulations of kaolinite minerals showed that strongly adsorbed metal ions are situated above the hexagonal ring of siloxane surface [19].

Here, the composite formation through the aggregation of Mont–HA mixture in $\text{Ca}(\text{NO}_3)_2$ solutions was *in situ* observed by the multi-angle dynamic light scattering (DLS) technique. Then FT-IR spectroscopy and DFT calculations were used to comprehend the structural and energetic aspects of Ca^{2+} adsorption onto HA, Mont and their mixture, and the experimental and computational frequencies were compared with each other. On such basis,

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Scheme 1. Computational models for humic acid (HA) and their interactions with Ca^{2+} .

potential routes and reaction energies of the composite formation as well as role of metal ions played during the composite formation were unravelled.

Methodologies

The detailed experimental and computational methodologies were given in the supporting information. Samples of Mont and its mixture with HA were each sonicated for 2 min, and $\text{Ca}(\text{NO}_3)_2$ solutions of different concentrations were respectively added. The BI-200SM multi-angle laser light scattering instrument (Brookhaven Instruments Corporation, New York, USA) with the BI-9000AT auto-correlator was used to *in situ* monitor the hydrodynamic diameter growths of Mont and its mixture with HA. The laser device was polarized vertically with a wavelength of 532 nm. The hydrodynamic diameters were recorded every 30 s at a scattering angle of 90° (298 ± 1 K). After pretreatments, FT-IR spectroscopic measurements (Perkin Elmer Co., USA) were recorded for samples of HA as well as HA and Mont–HA adsorbed with Ca^{2+} , over the $4000\text{--}400\text{ cm}^{-1}$ range at 4 cm^{-1} resolution.

In agreement with our previous works of aluminosilicates [22,23], cluster models of Mont were partitioned into high-level (in ball and stick) and low-level (in stick) regions, which were simulated by B3LYP/6-31 + G(d,p) and B3LYP/3-21G methods, respectively. B3LYP/6-31 + G(d,p) were also used for adsorbents on Mont as well as HA models, Ca^{2+} interactions with HA.

Results and discussion

As indicated in Fig. S3, the hydrodynamic diameters of Mont and Mont–HA mixture (4.0 wt% HA) in $\text{Ca}(\text{NO}_3)_2$ solutions grow gradually with the increase of experimental time. At a given concentration c_0 , the hydrodynamic diameters of Mont–HA mixture are smaller than those of Mont, and this becomes more conspicuous at higher concentrations; e.g., Mont and Mont–HA mixture in 3.0 mmol/L $\text{Ca}(\text{NO}_3)_2$ solutions have diameters of 7977.7 and 1794.7 nm ($t = 15$ min), respectively. As compared to Mont, HA and other organic matters are rather structurally flexible and consist of abundant carboxylic groups that are ideal targets to accommodate metal ions [8–10]; despite that, the ion adsorption affinities on HA are substantially lower than those on Mont, as verified by the latter DFT calculations. This further causes the significant retardation to the aggregation processes.

The TAA rate, the total average aggregation rate from $t = 0$ to an arbitrary time t ($t > 0$), can be expressed as [24],

$$\text{TAA} = \frac{1}{t} \int_0^t v(t, c_0) dt \quad (1)$$

where $v(t, c_0)$ (nm/min) is the instantaneous aggregation rate at time t .

As indicated in Fig. 1, the TAA rates of Mont and Mont–HA mixture in $\text{Ca}(\text{NO}_3)_2$ solutions increase pronouncedly at the low concentration ranges while almost stay at the plateau at the high concentration ranges. In each case, the TAA rates can be presented by two linear functions, and intersection of these two lines corresponds to CCC (critical coagulation concentration). The CCCs for Mont and Mont–HA mixture are equal to 2.4 and 12.1 mmol/L, respectively. Hence, the composite formation through the aggregation of Mont–HA mixture in $\text{Ca}(\text{NO}_3)_2$ solutions retards substantially the aggregation kinetics as compared to that of Mont, which is consistent with the hydrodynamic diameter results discussed above. Below we will focus on unravelling the composite structure as well as its formation mechanism.

FT-IR spectra of HA as well as HA and Mont–HA mixture in $\text{Ca}(\text{NO}_3)_2$ solutions are given in Fig. 2. According to the literatures [25,26], in the case of bare HA, the absorption peak (ν) at 1716 cm^{-1} is assigned to the stretching vibrations of carboxylic

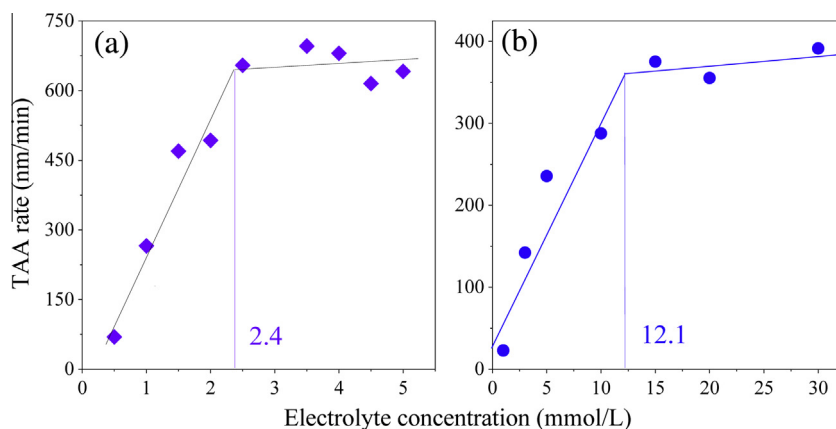


Fig. 1. The TAA rates for (a) Mont and (b) Mont–HA mixture as function of $\text{Ca}(\text{NO}_3)_2$ concentrations.

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