

Surface complexes of phthalic acid at the hematite/water interface

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Abstract

The adsorption of *o*-phthalic acid at the hematite/water interface was investigated experimentally using batch adsorption experiments and attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectroscopy over a wide range of solution pH, surface loading, and ionic strength conditions. Molecular orbital calculations for several possible surface complexes were also performed to assign atomistic structures to the features observed in the ATR-FTIR spectra. The results of the batch adsorption experiments exhibit typical anionic characteristics with high adsorption at low pH and low adsorption at high pH. The adsorption of phthalic acid also exhibits a strong dependence on ionic strength, which suggests the presence of outer-sphere complexes. ATR-FTIR spectra provide evidence of three fully deprotonated phthalate surface complexes (an outer-sphere complex and two inner-sphere complexes) under variable chemical conditions. A fully deprotonated outer-sphere complex appears to dominate adsorption in the circumneutral pH region, while two fully deprotonated inner-sphere complexes that shift in relative importance with surface coverage increase in importance at low pH. Comparison of experimental and theoretical calculations suggests the two inner-sphere complexes are best described as a mononuclear bidentate (chelating) complex and a binuclear bidentate (bridging) complex. The mononuclear bidentate inner-sphere complex was favored at relatively low surface coverage. With increasing surface coverage, the relative contribution of the binuclear bidentate inner-sphere complex increased in importance.

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1. Introduction

The charging characteristics, solubility, and stability of metal (hydr)oxides in aquatic systems depend to a large extent upon interactions with naturally occurring organic acids [1]. Knowledge of these interactions is also needed to understand the mobility of contaminants, such as heavy metals and nonpolar organics, that may react with both metal oxides and organic acids [1–4]. Although the bulk of the organic acids as ligands in aquatic systems are associated with heterogeneous natural organic matter (NOM), numerous low-molecular-weight (LMW) acids (e.g., oxalic acid, citric acid, salicylic acid, and phthalic acid) are also present at significant concentrations [5]. The reactive nature of these LMW acids, like NOM, is dominated by carboxylic and phenolic functional groups [6–9]. These func-

tional groups react with the surface hydroxyl groups located on the metal oxide surfaces to form adsorbed surface complexes. The adsorption behavior in the system depends on the physical and chemical characteristics of the acid and oxide surface as well as an array of other factors, including, but not limited to, solution composition, pH, and time.

Historically, adsorption mechanisms for LMW acids have been evaluated based upon macroscopic observations (e.g., adsorption isotherms). While successful in describing the behavior observed, the results obtained from batch adsorption experiments fail to provide molecular-level understanding of the bonding mode and structure necessary to constrain surface complexation models suited for predictive simulations. Direct structural evidence can be gathered with in situ attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectroscopy, however, and many recent studies have applied this tool in an attempt to elucidate the structure of adsorbed LMW carboxylic acids [10–20]. Although the IR-active vibration frequencies associated with the LMW carboxylic acids are weakly

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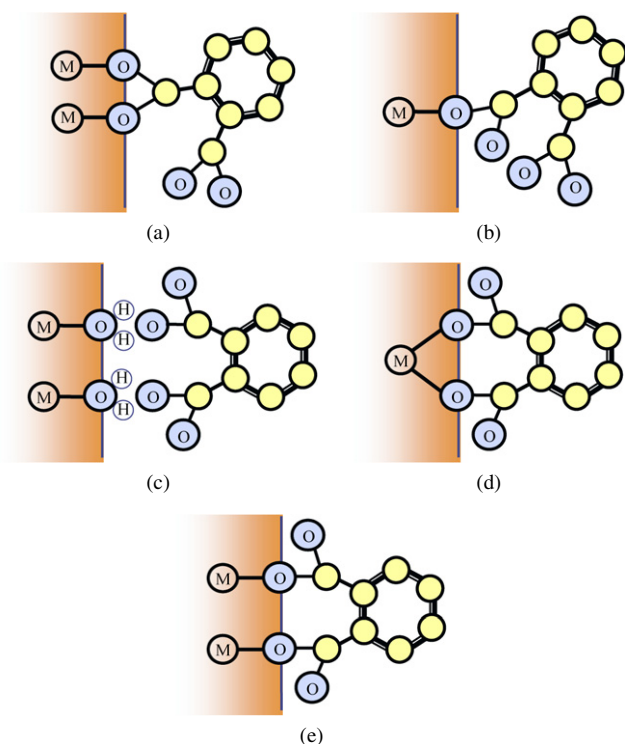


Fig. 1. Schematic of phthalate surface complex structures as proposed in previous studies: (a) binuclear (bridging) bidentate inner-sphere complex by a single carboxylate, BIN-BS [10]; (b) monodentate inner-sphere complex, MON [10]; (c) outer-sphere complex, OS [12,13]; (d) mononuclear (chelating) bidentate inner-sphere complex, MON-BB [12,13]; and (e) a binuclear (bridging) bidentate inner-sphere complex by both carboxylate groups, BIN-BB [14].

adsorbing, necessitating elevated acid concentrations [21], they are sensitive to changes in the structure, protonation state, and coordination environment of the target molecule and can be used to elucidate bonding mode and structure. In general, the adsorption of LMW carboxylic acids on metal (hydr)oxides is largely classified into two distinct modes: inner-sphere by strong direct bonding and outer-sphere by weak electrostatic attraction or hydrogen bonding.

Phthalic acid (benzene-1,2-dicarboxylic acid) is a simple LMW carboxylic acid that is ubiquitous in environmental systems, shares functional groups with NOM, and is known to interact with metal (hydr)oxides [7,22]. The adsorption of phthalic acid on metal (hydr)oxides has been extensively studied, and depending upon the system and methods applied, the mode of adsorption has been described as inner-sphere and/or outer-sphere. Tejedor-Tejedor et al. [10], for example, indicate that phthalic acid forms two inner-sphere complexes when adsorbed on goethite: a binuclear (bridging) bidentate complex, involving two oxygens of one carboxylate, each bound to one surface iron atom (BIN-BS, Fig. 1a), and a monodentate complex (MON, Fig. 1b). In contrast, Nordin et al. [12] and Persson et al. [13] suggest that two complexes are formed irrespective of the mineral type. They base this conclusion on results presented for three minerals (boehmite, aged γ - Al_2O_3 , and goethite) and provide evidence that the two complexes are an outer-sphere complex (OS, Fig. 1c) and an inner-sphere complex where both carboxylate groups form a mononuclear (chelating) bidentate

structure (MON-BB, Fig. 1d). On the other hand, Dobson and McQuillan [14] examined phthalate adsorbed onto four metal oxides (TiO_2 , ZrO_2 , Al_2O_3 , and Ta_2O_5) and indicate in each case that only one complex forms, a binuclear (bridging) bidentate complex where one oxygen from each carboxylate binds to one surface central atom (BIN-BB, Fig. 1e).

These discrepancies reflect not only the inherent system differences, but also the difficulties encountered in interpreting ATR-FTIR spectra. For example, due to the relative differences in electronegativities (e.g., $\text{Al}^{3+} = 1.47$, $\text{Fe}^{3+} = 1.64$) [23] or hydroxyl configurations (i.e., singly, doubly, and triply coordinated OH groups) [24], the bonding modes and structures of adsorbed complexes may depend upon the mineral type or prevalent crystallographic plane. Such differences may be subtle, however, and insufficient in magnitude to alter the coordination geometry to the extent that large shifts in IR vibrational frequencies can be observed. Under such a scenario, shifts in the position of the major IR-active vibrations upon adsorption may not be dramatic, and thus assignments based strictly on ATR-FTIR results may be inconclusive. Consequently, additional evidence in support of the assignment must be presented, perhaps by computational methods [25]. Such theoretical calculations can test a host of possible surface complexes and thus have been shown to be exceptionally useful in interpreting experimental IR spectra [26].

The objective of this study is to develop a molecular-level understanding of phthalic acid at the hematite/water interface. Hematite, which is abundant in weathered soils, was chosen as the model mineral. Hematite is also ubiquitous on Mars and molecular-level studies of interactions at the hematite interface may provide some insight into processes responsible for the formation of Martian soils [27]. In this paper, we present data from equilibrium batch adsorption experiments and ATR-FTIR spectroscopic measurements over a wide range of environmental conditions (i.e., pH, surface coverage). Spectroscopic results are also presented for aqueous free phthalic acid species and aqueous Fe(III)/Ca phthalate complexes. To facilitate spectral evaluation, we compared experimental results to vibrational frequencies calculated from a large suite of possible surface complexes using density functional theory [28] methods. Our results provide evidence for the existence of three fully deprotonated phthalate surface complexes on hematite (an outer-sphere complex and two bidentate inner-sphere complexes) and the relative importance of these complexes was shown to vary with chemical conditions.

2. Materials and methods

2.1. Materials

Deionized (Milli-Q Plus, Millipore) and boiled water was used for preparing all samples. All chemicals were analytical grade or better and were used without further purification. High-purity phthalic acid (benzene-1,2-dicarboxylic acid, 99.5%) was purchased from Alfa Aesar and used as received.

The hematite (α - Fe_2O_3) was prepared by adding sufficient ferric chloride salt (FeCl_3) to achieve 0.02 M total iron to

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