



Hydroxynaphthoic acid isomer sorption onto goethite

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ABSTRACT

This study used batch and attenuated total reflectance–Fourier-transform infrared (ATR-FTIR) flow-through techniques, along with computational chemistry, to probe the sorption of hydroxynaphthoic acid (HNA) isomers at the goethite–water interface. The HNA isomers employed in this study, 1-hydroxy-2-naphthoic acid and 2-hydroxy-3-naphthoic acid, possessed an intramolecular hydrogen bond (IHB) between their carboxyl and hydroxyl groups, which resulted in coupled vibrational modes. Complimentary information from batch and ATR-FTIR studies suggested surface complexation via a bidentate structure, involving both the carboxylate and phenolate groups, as the dominant mode of sorption. A secondary HNA surface species noted only at pH 4 appeared to sorb via the carboxylate group, with the phenolic group involved in IHB or H-bonded to the solvent or surface hydroxyl groups. Despite the lack of unique vibrational modes for the key functional groups our experimental approach was successful in proposing interfacial structures, while acknowledging the limitations with respect to differentiating mono- vs. binuclear complexes. Finally, the spectral similarity of HNA sorbed onto goethite and onto the clay fraction of an iron oxide-rich soil suggested analogous solute interaction in pure phase minerals and soils.

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1. Introduction

Our perception of how organic compounds sorb to mineral surfaces influences many areas of scientific investigation including environmental contaminant fate, the dynamics of natural organic matter (NOM), the development of surfactants, and the control of metals corrosion. With regard to contaminant fate and NOM dynamics in particular, much of our knowledge of sorption–desorption phenomena emanates from the analysis of traditional batch experiments. These techniques remain indispensable experimental approaches because they rely on well-established methodology and can often be adapted to test a variety of solids, solutes, and environmental variables. However, batch studies cannot yield substantive information on sorption mechanisms or surface structures and their applicability is commonly limited by the chemical characteristics of the solute of interest (e.g., solubility, detectability).

To gain a much-needed deeper molecular understanding of interfacial processes, research increasingly employs techniques such as Fourier-transform infrared (FTIR), Raman, and fluorescence spectroscopy [1]. Computational chemistry is also being used to describe likely mechanisms of interaction, to predict spectroscopic peaks of sorbed compounds, and to visualize the solute–solid in-

terfacial structure (e.g., [2–4]). Using a broad-spectrum approach that combines the above techniques with batch studies has the potential to offset the limitations of any one technique. Indeed, this approach has recently been effectively applied to the investigation of sorption of the antibiotic ofloxacin to silicon and aluminum oxides [3]. In this case, molecular modeling and FTIR techniques allowed the authors to propose likely mechanisms of sorbate–oxide interactions and to interpret trends in batch experiments, findings which provide insight into the environmental fate of ofloxacin.

Extensive previous spectroscopic research on salicylic acid, structurally related to hydroxynaphthoic acids (the subject of this study), indicated that sorption onto goethite [5,6] and other metal oxide surfaces [2,7–11] occurs primarily through ligand exchange involving both carboxylic and phenolic groups and at least one surficial metal center. In addition, studies point to a weaker interaction that may also occur at high surface coverage and/or low pH [12]. Some of the above-mentioned salicylic acid studies included computational approaches, in addition to FTIR (e.g., [2,11]), that not only helped to propose probable sorbed structures but also helped with the assignment of IR bands.

In aqueous solution, surprisingly more complex FTIR spectra result from seemingly small changes in compound structure, as is the case for compounds structurally related to benzoic acid (Fig. 1). In particular, the addition of a phenolic group *ortho* to the carboxylic group introduces an intramolecular hydrogen bond (IHB) that obscures the distinct vibrational modes of these groups. Thus,

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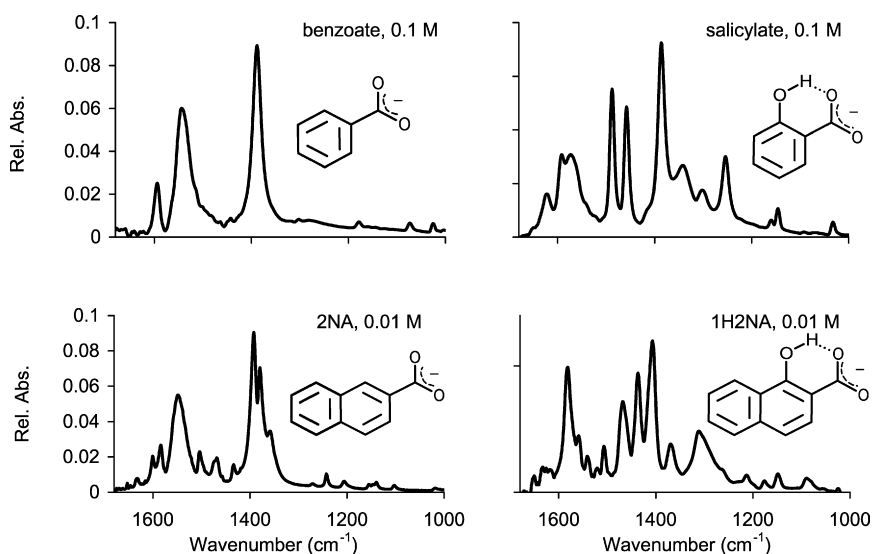


Fig. 1. IR spectra of benzoate, salicylate, 2-naphthoic acid (2NA), and 1-hydroxy-2-naphthoic acid (1H2NA) in H₂O.

the coupling of vibrational modes results in FTIR spectra lacking unique IR bands for key functional groups [5,6] and precludes the clear delineation of sorption mechanisms for all but the simplest ionogenic organic compounds, despite the fact that many substances of research interest (e.g., NOM, pesticides, drugs, and personal care products) often have complex structures.

This research is focused on the sorption two hydroxynaphthoic acid isomers (1-hydroxy-2-naphthoic acid: “1H2NA” and 2-hydroxy-3-naphthoic acid: “2H3NA”; chemical structures shown in Fig. 2) onto goethite (FeOOH) and related surfaces. 1H2NA and 2H3NA are degradation products of the ubiquitous contaminants phenanthrene and anthracene, respectively. In addition, these hydroxynaphthoic acids possess more “complex” IR spectra than the structurally related, well-studied salicylic acid (Fig. 1). The objective of this study was to evaluate the combined use of batch, ATR-FTIR flow-through techniques, and computational chemistry for probing the sorption of 1H2NA and 2H3NA at the goethite–water interface. In addition, analogous solute interactions were probed in the clay fraction of an iron oxide-rich soil.

2. Materials and methods

2.1. Goethite synthesis

Goethite was prepared according to Schwertmann and Cornell [13] by mixing 1 M Fe(NO₃)₃ (J.T. Baker) with 5 M KOH (Mallinkrodt) in a 1:1.8 ratio, diluting the slurry 7.1 times with deionized water, and incubating at 60 °C for 60 h. The precipitated goethite was repeatedly washed and centrifuged with deionized (DI) water (18 MΩ) until electrical conductivity of the supernatant reached a stable minimum. Goethite was freeze-dried, multi-point nitrogen BET surface area was measured (26.71 m²/g, Gemini 2360), morphology characterized with transmission electron microscopy (Philips 301) (1–3 μm), and mineralogy confirmed through ATR-FTIR (details below) and X-ray diffraction (Phillips Electronic Instruments XRC-3000).

2.2. Soil clay preparation

The clay-sized (<2 μm) fraction of an Fe-oxide rich, low organic matter soil (series: Georgeville; order: Ultisol; Duke Forest, Durham, NC) was prepared by first sonicating whole soil in DI water. The 2 μm size fraction was separated using centrifugation [14],

freeze-dried and nitrogen BET surface area measured (43.34 m²/g) as described above.

2.3. Sorption studies

Batch techniques probed the sorption of 1H2NA (Aldrich, pK_{a1} 2.7 (estimated by [15]), pK_{a2} 11.8 (1:1 ethanol:H₂O) [16], estimated solubility ~0.07 M, pH 4 [17]) and 2H3NA (TCI America, pK_{a1} 2.9, pK_{a2} 11.5 [18], estimated solubility ~0.03 M, pH 4 [17]). Sorption of the two “HNA isomers” onto 5 g/L goethite was investigated in triplicate as a function of: (i) time (0–144 h) at pH 4 (set with 0.001 M Na acetate buffer) and an initial solution concentration of 50 μM; (ii) pH (pH 3–7; adjusted with NaOH/HCl) at 50 μM initial solute concentration and 48 h equilibration time; (iii) solute concentration (0–100 μM) at pH 4 (0.001 M Na acetate buffer) and 48 h equilibration time; (iv) ionic strength (0.001–0.1 M set with the addition of NaCl) at pH 4 (0.001 M Na acetate buffer), initial solute concentration of 50 μM, and 48 h equilibration time; and (vi) competing anion (chloride, acetate, sulfate, and phosphate as Na salts) at ionic strength *I* = 0.005 M and pH 4, initial solute concentration of 50 μM, and 48 h equilibration time. For the ionic strength study, “2NA” (2-naphthoic acid, TCI America, pK_a 4.02, and solubility ~0.06 M, pH 4 [17,19]) was also included. All experiments in this study were conducted in DI water unless otherwise noted, and all glassware was acid-washed prior to use. Experiments were conducted in triplicate at room temperature in the dark in amber glass vials with Teflon-lined caps and an end-over-end shaker was used for equilibration of the reactors.

In all cases, goethite was pre-equilibrated overnight in the background matrix prior to addition of HNA, 2NA, or competing anion. Following the addition of the solute(s) and equilibration for the predetermined time, the final pH was measured and the slurry centrifuged and filtered through 0.2 μm polycarbonate membranes. Solute concentration in the filtrate was analyzed by HPLC (Agilent 1100 Series) using a mobile phase of 85% MeOH and 15% 0.01 M phosphate buffer at pH 2.5, Zorbax SBC8 4.2 × 150 mm column, with UV detection at 252 nm (1H2NA), 237 nm (2H3NA), and 230 nm (2NA). Goethite-free blanks prepared in the same manner served as the measure of initial concentration. Extent of sorption was calculated as difference between the initial and final solute concentrations normalized to mass of solid in the reactor. Evidence from desorption studies (details below) confirmed that the measured solute loss from solution using the above protocol represented loss by sorption alone. Therefore, percent loss of compound

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