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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.

Keywords

Metal oxides; ATR-FTIR; PAH; Surface complexation; Interfacial structure

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).

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Supporting information

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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 interfacial 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, 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 $\text{Fe}(\text{NO}_3)_3$ (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 M Ω) 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 ($<2\ \mu\text{m}$) 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 $2\ \mu\text{m}$ size fraction was separated using centrifugation [14], freeze-dried and nitrogen BET surface area measured ($43.34\ \text{m}^2/\text{g}$) as described above.

2.3. Sorption studies

Batch techniques probed the sorption of 1H2NA (Aldrich, $\text{p}K_{\text{a}1}$ 2.7 (estimated by [15]), $\text{p}K_{\text{a}2}$ 11.8 (1:1 ethanol: H_2O) [16], estimated solubility $\sim 0.07\ \text{M}$, pH 4 [17]) and 2H3NA (TCI America, $\text{p}K_{\text{a}1}$ 2.9, $\text{p}K_{\text{a}2}$ 11.5 [18], estimated solubility $\sim 0.03\ \text{M}$, pH 4 [17]). Sorption of the two “HNA isomers” onto $5\ \text{g/L}$ goethite was investigated in triplicate as a function of: (i) time (0–144 h) at pH 4 (set with $0.001\ \text{M}$ Na acetate buffer) and an initial solution concentration of $50\ \mu\text{M}$; (ii) pH (pH 3–7; adjusted with NaOH/HCl) at $50\ \mu\text{M}$ initial solute concentration and 48 h equilibration time; (iii) solute concentration (0– $100\ \mu\text{M}$) at pH 4 ($0.001\ \text{M}$ Na acetate buffer) and 48 h equilibration time; (iv) ionic strength (0.001 – $0.1\ \text{M}$ set with the addition of NaCl) at pH 4 ($0.001\ \text{M}$ Na acetate buffer), initial solute concentration of $50\ \mu\text{M}$, and 48 h equilibration time; and (vi) competing anion (chloride, acetate, sulfate, and phosphate as Na salts) at ionic strength $I = 0.005\ \text{M}$ and pH 4, initial solute concentration of $50\ \mu\text{M}$, and 48 h equilibration time. For the ionic strength study, “2NA” (2-naphthoic acid, TCI America, $\text{p}K_{\text{a}}$ 4.02, and solubility $\sim 0.06\ \text{M}$, 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 $0.2\ \mu\text{m}$ polycarbonate membranes. Solute concentration in the filtrate was analyzed by HPLC (Agilent 1100 Series) using a mobile phase of 85% MeOH and 15% $0.01\ \text{M}$ phosphate buffer at pH 2.5, Zorbax SBC8 $4.2 \times 150\ \text{mm}$ 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 mass from solution phase is referred to as “percent sorbed” in the subsequent text.

Following HNA sorption and removal of the supernatant, $0.05\ \text{M}$ chloride, acetate, sulfate or phosphate at pH 4 was equilibrated with goethite for 48 h under conditions identical to those described for ionic strength study. The extent of desorption was ascertained from the resulting HNA concentration in aqueous solution.

2.4. Preparation of solution complexes

Na–HNA and Na–2NA complexes were prepared at $0.01\ \text{M}$ in both H_2O and D_2O . Monosodium salts of 2H3NA (TCI America) and 2NA (TCI America) were commercially available. Since Na–1H2NA was not commercially available, the acid form was slowly dissolved in H_2O or D_2O by titrating to pH ~ 5.5 with NaOH or NaOD. Fe–HNA solution

complexes were prepared in H₂O by slowly mixing equal volumes of 0.02 M Na–HNA solution and 0.06 M FeCl₃·6H₂O (J.T. Baker) at pH ~1.5 to achieve a final ratio of 3 Fe:1 HNA and to favor a 1:1 Fe–ligand complex without precipitation of the HNA, Fe, or the HNA–Fe complex. All work in D₂O was helium (He)-sparged and conducted under a He atmosphere. The HNA solutions produced a blue–violet solution with the formation of Fe–HNA complexes.

2.5. ATR-FTIR spectroscopy

The nature of the solute–surface interaction was probed with an N₂-purged Nexus 470 bench with DTGS detector (Thermo Nicolet) and a multibounce HATR flow cell accessory with a ZnSe 45° crystal (Pike Technologies, Inc.). The structure of the sorbed species was evaluated across pH/pD 4–6 and ionic strength 0.001–0.1 M NaCl at pH 4. pD experiments in D₂O were aimed at clarifying spectral regions complicated by H₂O bands and perturbing intramolecular H-bonding (IHB) in HNA [20].

IR spectra of solute molecules at the mineral–water interface are typically obtained by using metal oxide pastes containing the sorbed solute prepared by batch techniques (paste approach) or flow-through ATR-FTIR techniques. In the paste approach, the strong IR signal of water must be accounted for by subtracting out the hydration profile of a separate solute-free paste, often introducing spectral noise. Additionally, the paste approach may be difficult to adapt to compounds of low solubility such as the HNAs, since detectable surface coverage cannot be achieved by batch sorption techniques. Flow-through ATR-FTIR techniques, in which the ATR crystal is coated with a thin stable layer of metal oxide, placed in a flow-cell, and an influent of desired composition is input for a fixed period, have been valuable in the study of inorganic anions (e.g., [21]) and small organic anions (e.g., [10,22, 23]). Here, the IR bands of water are accounted for on the same solid sample onto which the solute is sorbed (see below). Additionally, a flow-through technique may allow for a greater surface coverage than equilibrium-based batch techniques, a particularly beneficial feature for the study of sparingly soluble compounds, such as HNAs. Other advantages of the technique include the small amount of solid required (e.g., 3–4 mg) and the detection of only surface accumulated solute, provided dissolved solute concentrations (influent) are kept below FTIR detection limit. Because of the direct advantages for investigating HNA surface complexes, the flow-through approach was utilized in this study.

Separate experiments were conducted as follows for each pH/pD and ionic strength tested. First, an initial background of the clean crystal was recorded and the crystal was removed from the bench. A slurry of 4 mg goethite in 1.5 mL H₂O or D₂O was dispersed by sonication, dried onto the crystal at 40 °C, gently rinsed with DI, and dried again. This method resulted in the most stable and consistent goethite coating. The flow-cell was assembled, returned to the bench, and a spectrum of the goethite (A) was recorded to ensure the oxide coating was completely dry and consistent with other experiments in the study. Solute-free solution at the desired pH/pD and ionic strength in either DI H₂O or D₂O was pumped through the cell for 20 min at 1 mL/min, after which a spectrum (B) was collected. Flow was then switched to a solution containing 50 µM solute in the same background matrix for 60 min at 1 mL/min and a final spectrum (C) was recorded. Spectrum B was subtracted from spectrum C by matching the hydration profiles to obtain the spectrum of the sorbed species. Optimum solute concentrations and the flow times noted above were determined from preliminary experiments that evaluated a range of equilibration times (20–120 min), flow rates (0.5–2.0), and influent solution concentrations (10–100 µM). Preliminary tests determined the FTIR detection limit for dissolved HNA to be 1 mM, ensuring that an influent HNA concentration of 50 µM was below the detection limit and that difference spectra only represented surface associated species. All experiments were repeated to confirm results.

Spectra of the solution complexes of Na–HNA, Na–2NA and Fe–HNA were collected in a goethite-free system using a 1.5 mL trough HATR cell (Pike Technologies) with similar components as for the flow-through cell. Spectra were collected in this order: clean dry crystal (background spectrum), solute-free solution, and solution of the desired HNA or 2NA complex. Spectra of the complexes were obtained by difference as described above and included 150 scans at 2 cm^{-1} resolution in all cases except for Fe complexes, which required 1000 scans.

2.6. Computational analyses

To aid in the assignment of spectral bands, infrared spectra were predicted using Jaguar v. 5.0 software with a Maestro v. 3.0 interface (Schrödinger Inc.). Geometry optimization and vibrational frequencies were computed using density function theory (DFT) approach with either B3LYP/6-311G^{++**} basis set for non-complexed monoanion or B3LYP/LACVP^{**} basis set for Fe-complexed compounds. Predicted wavenumbers were corrected by a factor of 0.9614 as is commonly recommended for B3LYP calculations [24].

3. Results and discussion

3.1. Batch studies

3.1.1. Kinetics—At 50 μM initial HNA concentration and a solution pH of 4, both isomers showed similar sorption trends between 0 and 144 h, reaching an apparent plateau at 48 h with sorbed concentrations of $8.25 \pm 0.03\text{ mmol/kg}$ and $8.14 \pm 0.02\text{ mmol/kg}$ (81–83% sorbed) for 1H2NA and 2H3NA, respectively (see Supporting information, Fig. S1). Based on these results, we selected 48 h sorption time for all other batch experiments.

3.1.2. pH edge—Between pH ~3 and 7, sorption trends were identical for both isomers with the greatest extents of sorption ($8.96\text{--}9.16\text{ mmol/kg}$) around pH 3.0–3.5, close to the $\text{p}K_{\text{a}1}$ of the HNAs (Fig. 2a). As pH increased above 3.5, sorption decreased but was still significant at pH ~7 ($2.19\text{--}3.33\text{ mmol/kg}$). The pH envelopes observed for the HNAs are typical of anions that interact with metal oxide surfaces through ligand exchange, including structurally related salicylate (*o*-hydroxybenzoate) [15,25–27]. Based on these findings, pH 4 was selected for all other batch studies.

3.1.3. Sorption isotherm—With increasing initial concentration from 0 to 100 μM at pH 4, sorption of both isomers increased with no evidence of an obvious sorption plateau (Fig. 2b). Both Langmuir and Freundlich equations could describe HNA isotherms. At initial concentrations of 10 μM and higher, 2H3NA sorbed to a significantly greater extent than 1H2NA. Sorption at much higher initial concentrations could not be evaluated due to the solubility limits of the HNAs, therefore the maximum HNA sorption capacity of goethite cannot be speculated or reliably predicted from Langmuir fit (data not shown). Similar results have been found for Langmuir fit of salicylate sorption on goethite and other oxides [5,27].

3.1.4. Ionic strength effects—Increasing ionic strength from 0.002 M to 0.101 M significantly reduced HNA isomer and 2NA sorption (Fig. 3a). However, even at 0.101 M ionic strength loss of HNA from solution remained significant: 51–56% sorbed. Similar trends were observed with 2NA, although the overall extents of sorption at a given ionic strength were generally 46–50% lower than those observed for the HNA isomers.

3.1.5. Multi-anion competition and desorption—Chloride, acetate, sulfate and phosphate, were included in competition studies with HNA isomer to further probe the nature of the HNA–goethite interaction because it is well established that the extent of

inorganic anion sorption increases as follows: chloride < acetate < sulfate < phosphate [28]. In recent research [29], the effects of anions such as these have been used to help discern the relative contributions of weak interactions, hydrophobic interactions, and ligand exchange for pentachlorophenol. At 50 μM initial HNA, pH 4, and ionic strength of $I = 0.005\text{ M}$ set with the competing anion, sorption of both isomers was decreased only slightly in the presence of chloride and acetate as compared to sorption without anion competition (e.g., comparable data from pH and ionic strength experiments, Figs. 2 and 3), but was significantly reduced by sulfate (0.73 mmol 1H2NA/kg and 0.69 mmol 2H3NA/kg; 7% sorbed) and completely inhibited by phosphate (Fig. 3b). Both phosphate and sulfate are considered to sorb onto goethite through an inner-sphere mechanism (e.g., ligand exchange) [21,30], although an outer-sphere interaction (e.g., specific and nonspecific electrostatic attraction) has also been observed for sulfate [21]. Notably, when sulfate or phosphate was present at equimolar concentration as the HNAs (50 μM) (data not shown), this same extent of competition was not observed possibly because the available goethite surface sites exceeded the combined solute concentrations.

In desorption studies conducted at pH 4, one extraction with 0.05 M solution of inorganic anion recovered sorbed HNA with varying efficiency depending on the identity of the anion: acetate (34–36%) < chloride (38–40%) << sulfate (80–82%) < phosphate (85–90%). The observed desorption, particularly that due to sulfate and phosphate competition, confirmed that HNA loss from solution was attributable to sorption.

3.1.6. Sorption mechanisms surmised from batch experiments—Observations including (i) pH edges typical of anions that sorb via ligand exchange, (ii) significant sorption at high ionic strengths, and (iii) strong competition with and desorption by sulfate and phosphate along with weak competition with and desorption by acetate and chloride, all pointed to HNA interaction with the goethite surface primarily via complexation to surficial Fe atoms (ligand exchange), with electrostatic interactions and hydrophobic interactions playing a smaller role. Nevertheless, the observed effect of ionic strength on HNA and 2NA sorption emphasized the role of electrostatics in the sorption process. Most importantly, the significantly greater sorption of the HNA isomers (which possessed both $-\text{COOH}$ and $-\text{OH}$ groups) over 2NA (which only possessed a $-\text{COOH}$ group), underscored the role of both the carboxylic and the phenolic groups in the formation of the surface complex, possibly via bidentate structure. The greater sorption of 2H3NA (than 1H2NA) at higher concentrations (Fig. 2b) could not be rationalized based on the batch studies alone.

3.2. ATR-FTIR studies

3.2.1. Peak assignments: HNA and 2NA solution spectra—Spectra of the aqueous solution of the sodium salt (“Na–HNA solution complexes” also referred to as monoanions) of 1H2NA, 2H3NA and 2NA in both H_2O and D_2O are shown in Fig. 4. Predicted frequencies from computational modeling correlated well with those observed for these solution species, with slopes of 1.00–1.02, intercepts of -27.3 to -32.2 , and r^2 of 0.996–0.999. Generally, the double rings of Na–HNA and Na–2NA along with the IHB in Na–HNA, which may form a pseudoaromatic moiety as indicated for salicylate [31], added to the spectral complexity when compared to related compounds, Na-benzoate and Na-salicylate, which have fewer peaks (Fig. 1) and less coupling of vibrational modes. HNA vibrational modes have been notated below with “ ν ” for stretching and “ δ ” for bending modes, and frequencies for dominant vibrational modes are listed in Table 1. Many of these modes are comparable to those of salicylate and other benzene derivatives [5,6], and a general description of the vibrational modes of benzene derivatives can be found in Refs. [32,33]. In all figures depicting FTIR spectra (Figs. 4–8), offset values were used for relative absorbance (y -axis) to aid spectral comparisons.

Phenolic and νCOO_s bands: Spectra of both HNA isomers indicated strong coupling between the COO^- and OH groups. In H_2O , $\delta\text{C}\phi\text{OH}$ (phenolic group bend) coupled with νCOO_s (carboxylate symmetric stretch) along with some ring vibration produced broad bands at $1311/1370\text{ cm}^{-1}$ for 1H2NA and $1315/1349/1373\text{ cm}^{-1}$ for 2H3NA (Fig. 4, Table 1). In H_2O , shoulders observed $\sim 1260\text{--}66\text{ cm}^{-1}$ for the HNA isomers may be from $\nu\text{C}\phi\text{O}$, the C–O stretch of the phenolic (OH) group. In D_2O , wherein the intramolecular deuterium bond (IDB) is weaker than the IHB, the coupling of the COO^- and OH(D) frequencies was diminished and revealed the $\nu\text{C}\phi\text{O}$ at 1266 and 1260 cm^{-1} for 1H2NA and 2H3NA, respectively. Furthermore, the peaks at 1311 cm^{-1} (1H2NA) and 1315 cm^{-1} (2H3NA) noted in H_2O were absent in D_2O and a broad peak/shoulder appeared in $1330\text{--}1336\text{ cm}^{-1}$ range in D_2O for both isomers. For 2NA, which has no phenolic group or IHB, νCOO_s was split at $1380/1359\text{ cm}^{-1}$ in H_2O and did not shift appreciably in D_2O .

νCOO_{as} bands: Computational results predicted νCOO_{as} (carboxylate antisymmetric stretch) to be strongly coupled with $\delta\text{C}\phi\text{OH}$ and ring vibrations: in H_2O , this band was found at $\sim 1582\text{ cm}^{-1}$ for 1H2NA and $1556\text{--}1582\text{ cm}^{-1}$ for 2H3NA (Table 1, Fig. 4). For 2NA which lacks the OH group, νCOO_{as} was observed at 1549 cm^{-1} . In D_2O , the coupling of the frequencies was diminished: the ring vibration and νCOO_{as} bands of the HNA isomers separated, the νCOO_{as} shifted to slightly lower wavenumbers (Table 1) confirming its assignment [5], and the ring vibration moved only slightly (1584 cm^{-1} for 1H2NA and 1579 cm^{-1} for 2H3NA). As expected, D_2O had comparatively little effect on the νCOO_{as} of 2NA, which shifted only slightly to 1556 cm^{-1} probably due to weakened solute–solvent interaction. For all compounds, the lack of a $\nu\text{C=O}$ band in the Na–2NA/HNA solution spectra, as well as in all other spectra discussed below, indicated delocalized charge over the carboxylic group, as previously observed for benzoate [8] salicylate [5,8], and indicated by our computational predictions.

Vibrations of the carbon skeleton: The spectral region below 1220 cm^{-1} was dominated by ring vibrations and in- and out-of-plane C–H bending, and ring vibration modes also dominated between $\sim 1400\text{--}1500\text{ cm}^{-1}$. As indicated above, ring vibrations coupled to other vibrations including νCOO_{as} and $\delta\text{C}\phi\text{OH}$ were also observed in the upper 1500's and lower 1600's cm^{-1} , e.g.: ~ 1582 (H_2O) and $1584/1627$ (D_2O) cm^{-1} for 1H2NA, 1582 and 1646 (H_2O) and $1579/1643/1608$ (D_2O) cm^{-1} for 2H3NA (Fig. 4). Similar but fewer ring vibrations were also observed in comparable regions of the 2NA spectra. As will be shown below, ring vibrations, particularly those in the 1400's cm^{-1} , were affected by intramolecular vibrational coupling (e.g., Fig. 1), metal complexation (Fig. 4), as well as by solvent characteristics including isotopic composition (i.e., D_2O vs. H_2O) (Fig. 4), pH and ionic strength (data not shown).

3.2.2. Fe–HNA solution spectra—HNA complexation with Fe apparently disrupted the IHB and consequently the coupling between functional group vibrations, eliminating $\delta\text{C}\phi\text{OH}$ and revealing $\nu\text{C}\phi\text{O}$ at $1261\text{--}1262\text{ cm}^{-1}$. Fe complexation shifted the νCOO_s to 1382 cm^{-1} for 1H2NA (Fig. 4). Corresponding bands in the Fe–2H3NA spectra were distinct from Na–2H3NA solution spectra with peaks/shoulders appearing at $1376/1346\text{ cm}^{-1}$. For both HNAs, Fe complexation produced many small peaks in the νCOO_{as} region across $\sim 1532\text{--}1565\text{ cm}^{-1}$ for 1H2NA and $\sim 1528\text{--}1577\text{ cm}^{-1}$ for 2H3NA. Attempts to predict vibrational modes of HNA–Fe complexes (data not shown) also yielded numerous peaks across this region that were attributable to stretching/bending of the ring, COO and $\text{C}\phi\text{O}$ groups and water coordinated to Fe; however, predicted frequencies did not pair well with experimental results. Because of the complication of this spectral region, it was not possible to make a firm assignment of the νCOO_{as} position in these spectra. However, the

peaks likely attributable to $\nu\text{COO}_{\text{as}}$ generally occurred at lower wavenumbers than the $\nu\text{COO}_{\text{as}}$ in the Na–HNA solution spectra.

3.2.3. Sorbed HNA spectra

HNA sorption spectra across pH/pD 4–6: The spectra of HNA sorbed onto goethite at pH or pD 4, 5 and 6 (Figs. 5–6) were generally similar to the Fe–HNA solution spectra. For both isomers, band intensities and resolution generally decreased as pH/pD increased (as evident in the noisy pD 6 spectra), possibly resulting from a decrease in sorption at higher pH/pD, an effect also observed for salicylate [11]. Most bands are preserved across pH and pD for both isomers, however pH 4 spectra contained additional bands.

At all pH/pD, both sets of frequencies associated with νCOO_{s} of 1H2NA moved to slightly lower wavenumbers ($1361\text{--}1367\text{ cm}^{-1}$) upon sorption (Table 1, Figs. 5–6). The νCOO_{s} could not be precisely located for 2H3NA because a broad peak (encompassing ring and νCOO_{s} modes) was noted in the $1340\text{--}1420\text{ cm}^{-1}$ range, with only the spectra at pH 4 exhibiting a notable shoulder at 1348 cm^{-1} . The $\nu\text{COO}_{\text{as}}$ spectral region for sorbed HNA, and particularly for 2H3NA, was often complicated by several broad or unresolved peaks making $\nu\text{COO}_{\text{as}}$ assignments difficult. This finding was similar to but less pronounced than that observed for Fe–HNA solution species. In some cases, distinct $\nu\text{COO}_{\text{as}}$ peaks could be discerned for some pH/pDs, for example: $\sim 1566\text{ cm}^{-1}$ (pH 4 and 5)/ 1533 and 1567 cm^{-1} (pD 4) for 1H2NA, and $1546\text{--}1551\text{ cm}^{-1}$ (pD 4–6) for 2H3NA. The coupled νCOO_{s} , $\delta\text{C}\phi\text{OH}$ and ring modes noted in Na–HNA spectra was replaced at most pH/pD's by the $\nu\text{C}\phi\text{O}$ at $\sim 1263\text{--}1265\text{ cm}^{-1}$ for 1H2NA and $\sim 1261\text{--}1266\text{ cm}^{-1}$ for 2H3NA in the sorbed HNA spectra. The $\nu\text{C}\phi\text{O}$ band positions for sorbed HNAs were generally unaffected by pH/pD and solvent denoting that the phenolic group was not H-bonded with the carboxylic group or with the bulk solvent. For 1H2NA, additional peaks were noted at 1303 cm^{-1} at pH 4 and 5, with corresponding peaks at 1307 cm^{-1} at pD 4 and 5.

At pH 4, spectra of both isomers were more complex than at other pH values, containing additional bands in the ring mode region (e.g., 1464 cm^{-1} for 1H2NA, and 1393 and 1463 cm^{-1} for 2H3NA), and at 1310 cm^{-1} for 2H3NA, a band attributed to the coupled νCOO_{s} + $\delta\text{C}\phi\text{OH}$ modes of the Na–HNA solution species. This latter assignment was corroborated by the absence of a 1310 cm^{-1} band in the corresponding D_2O spectrum, indicating that the band belonged to a protonated phenolic group.

Ionic strength effects on sorbed HNA spectra at pH 4: Across 0.001 to 0.01 M ionic strength at pH 4, carboxylate and phenolic bands did not shift greatly, with some exception in the $1500\text{--}1600\text{ cm}^{-1}$ region (Fig. 7). However, changing ionic strength did alter the shapes, proportions and resolution of several bands, particularly those attributed to ring vibrations (e.g., 1582 and $1464/1466\text{ cm}^{-1}$ for 1H2NA, and $1630\text{--}1635$ and $1451\text{--}1463\text{ cm}^{-1}$ for 2H3NA). These effects were not surprising, as differences in ionic strength alter the electronic environment surrounding the molecule thereby affecting spectral bands [20]. Additionally we also observed spectral band intensities for Na–HNA solution spectra change significantly across 0.001–0.1 M ionic strength (data not shown).

Sorbed 1H2NA on soil clay at pH 4: Generally, the spectra of 1H2NA sorbed onto goethite and the clay-sized fraction of the Fe-oxide-rich soil are markedly similar (Fig. 8), indicating that 1H2NA sorbed onto goethite in a similar fashion as onto the soil, in which goethite is likely a primary Fe oxide [34]. Interestingly, additional peaks were clear in the soil–clay fraction spectrum in the $\nu\text{COO}_{\text{as}}$ region at 1513 and 1547 cm^{-1} . While these peaks may have been due to 1H2NA sorbed to other soil minerals, identical experiments conducted on

hematite (J.T. Baker) and α -Al₂O₃ oxide (Alcoa) did not yield peaks at these positions (data not shown).

3.2.4. Proposed surface structures on goethite—Results from ATR-FTIR studies supported the batch results and provided specific information about the structure of the dominant surface complexes. The persistence of most bands at increased ionic strength indicated that surface bound HNA were unlikely to include species weakly held by long range electrostatic forces. In the sorbed HNA spectra, evidence for disruption of the IHB, the disappearance of δ C ϕ OH at most pH/D values, the absence of a C=O stretch, and the inability of D₂O to significantly alter peak positions for –COO and –CO(H/D) observed in H₂O solutions suggested (as detailed below) the deprotonation of both carboxylic and phenolic groups and their involvement with the surface. In Fe–HNA solution spectra and all HNA sorbed spectra (Figs. 1, 4-7), the appearance of ν C ϕ O was noted at ~1261–1265 cm^{–1}, as observed in the Na–HNA:D₂O spectra. Since the ν C ϕ O band positions for sorbed HNAs were generally unaffected by pH/pD or ionic strength, the appearance of ν C ϕ O may not point to phenolic (–OH) group participation in weak hydrogen bonding of commensurate strength to the IDB in Na–HNA:D₂O spectra. Instead, the presence and position of ν C ϕ O likely pointed to existence of surface complexes in which the phenolic group was not H-bonded with the carboxylic group or with the solvent. The ν C ϕ O occurred at frequencies above that expected for a phenolic group (C ϕ OH) not involved in hydrogen bonding but at approximately 10–12 cm^{–1} below that expected for a phenolate anion (C ϕ O[–]) or salicylate dianion (e.g., 1273) in aqueous (H₂O) solution [12,35]. This intermediate positioning of the ν C ϕ O would be expected if the phenolate group (C ϕ O[–]) were complexed to Fe. Thus, the presence of surface structures with the phenolate group complexed to Fe was inferred (Figs. 9a, 9b), as also noted by Yost and co-workers [5]. Further evidence that the phenolic group was deprotonated and surface associated was indicated by the loss of the δ C ϕ OH at most pH/D values. However, the more complex spectra at pH 4 for both isomers along with the peak at 1310 cm^{–1} for 2H3NA, a band attributed to the coupled ν COO_s + δ C ϕ OH modes of the Na–HNA solution species, pointed the possible presence of an additional Fe–HNA surface species that possessed a protonated phenolic group involved in an IHB or possibly H-bonding with the solvent or surface hydroxyl groups (Fig. 9c). If only the phenolic group were complexed with Fe, –COO bands would have been expected to shift to higher energies on release from the IHB. However, both ν COO_{as} and ν COO_s frequencies shifted lower energies (frequencies) on sorption to goethite and pointed to a weakened C–O bond as might occur if the –COO group complexed Fe. Possible surface structures depicted in Fig. 9 are similar to those previously postulated for salicylate sorbed onto metal oxides [5,6,11,27,36].

Typically, the charge delocalized COO[–] groups interact with Fe via one or both O groups. In previous research (e.g. [37]), comparison of $\Delta \nu$ COO values (the difference between ν COO_{as} and ν COO_s frequencies) in complexed (sorbed) and solution FTIR spectra has often been used to indicate mono- or bidentate complexation with respect to the –COO group. Generally for this comparison, greater $\Delta \nu$ COO in the complexed spectrum suggests involvement of one O due to increased asymmetry of the group, whereas a decrease in $\Delta \nu$ COO upon complexation suggests involvement of both O's in a mononuclear structure, and no change in $\Delta \nu$ COO suggests both O's are involved in a binuclear structure [38,39]. Originally, these guidelines were developed from examination of small carboxylates such as acetate. In our spectra, $\Delta \nu$ COO values (Table 1) could not be precisely determined because of the presence of numerous peaks across the 1500–1600 cm^{–1} region, which made precise ν COO_{as} assignment difficult. Typical $\Delta \nu$ COO values spanned 178–217 cm^{–1} (Na–2H3NA in H₂O), a wide range that did not vary consistently with sorption onto goethite. Additionally, $\Delta \nu$ COO was likely affected by changes in hydrogen bonding and by the possible presence of more than one surface structure. Based on the above and the rationale proposed by Yost and co-workers for salicylate [5], the use of $\Delta \nu$ COO in our research to

indicate the surface structure of the $-\text{COO}$ moiety seemed inapplicable. Also following the rationale proposed by Yost [5], we hypothesize a mononuclear monodentate surface structure with respect to the delocalized carboxylate group (Figs. 9a, 9b) because the phenolate oxygen and the two carboxylate oxygens cannot be geometrically configured to all bind surface iron atoms in tridentate mono-, bi- or tri-nuclear complexes.

The primary structure of HNA on the goethite surface involved both phenolate and carboxylate groups, was similar for both isomers and appeared to be a bidentate structure (Figs. 9a, 9b) as established for salicylate sorption to metal oxides [5,6]. Nevertheless, we could not differentiate between bidentate mononuclear (Fig. 9a) and bidentate binuclear (Fig. 9b) complexes based on our spectra for several possible reasons, including the likelihood that both types of complexes could be present. Additionally, frequencies of vibrational modes may differ due to the coordination of HNA to distinct surface sites (i.e., kink vs. edge sites) as well as the local chemical environment of each site (i.e., nature and identity of neighboring surface sites and complexes). Previous spectroscopic studies of salicylate complexation of Fe in solution and on goethite surface favored a mononuclear chelate, although the number of Fe ions involved in the complex could not be definitively determined [5,6].

Spectroscopic studies at lower pH may have revealed additional surface structures such as a monodentate complex (Fig. 9c), as primarily evidenced by additional peaks observed at pH 4 suggesting both the presence of an H-bonded and, possibly, a surface associated phenolic group. Earlier research on salicylate using polarized fluorescence spectroscopy demonstrated that up to five structures can be distinguished for salicylate sorbed onto an Al oxide, including monodentate complexes containing an IHB prevalent at low pH [36]. Additionally, salicylate sorption onto TiO_2 was best described by modeling with one monodentate and two bidentate species [27]. Thus, we could not exclude the possibility of a more weakly held species (so-called “outersphere”), which has been suggested for salicylate particularly at high surface coverages [12], however this type of interaction was not strongly supported by the batch results described above.

As with the batch studies, FTIR analysis did not provide direct insight into the greater extent of 2H3NA at high initial solute concentrations (Fig. 2b). Analysis of the two isomers using quantum chemical calculations (Spartan 06, Wavefunction, Inc., see Supporting information, Fig. S2) and visual evaluation of the postulated structures (Figs. 9a, 9b) indicated that the 1H2NA complexes were likely to be oriented with the naphthalene ring parallel to surface, whereas 2H3NA molecules were almost perpendicular to the surface. As such, the goethite surface can most likely accommodate a greater number of 2H3NA molecules, as compared with 1H2NA, resulting in a greater extent of sorption.

3.2.5. Proposed structures on iron oxide-rich soils—HNA complexation to the clay fraction of iron oxide-rich soils—HNA complexation to the clay fraction of iron oxide-rich soils via a bidentate structure involving both the phenolate and carboxylate groups was inferred from the similarity between the spectra of 1H2NA sorbed onto goethite and a soil clay fraction. The outstanding differences between the HNA–goethite and HNA–soil clay spectra were distinct peaks in the $\nu\text{COO}_{\text{as}}$ region, strongly suggesting that 1H2NA might be interacting with surfaces other than goethite, such as other Fe oxides, Al oxides or perhaps clay minerals. Biber and Stumm [6] showed that differences between FTIR spectra of sorbed salicylate were related to the metal involved in the complex (e.g., Fe vs. Al) and not to differences in oxide structure.

In contrast to soil clay fractions, sorption to intact soils cannot be easily analyzed via flow through FTIR techniques. Soil clay fractions, although not entirely representative of intact soils, typically dominate a soil's sorption capacity and are, therefore, valuable matrices for

analysis by FTIR. Thus our results also pointed to the promise for the application of FTIR techniques to environmental samples. Notably, the extremely low amount of organic matter in this soil and its relatively simple clay mineralogy compared to many other soils (see [40] for characterization of the whole soil) likely minimized spectral complexity.

3.3. Evaluation of the experimental approaches

The combination of traditional batch studies and ATR-FTIR spectroscopy using both solution spectra and a flow-through technique, along with a simple computational approach to predict vibrational frequencies helped propose interfacial structures of molecules with more complex IR spectra than salicylate. The coated crystal ATR-FTIR flow-through method appeared well-suited for studying compounds of low solubility, a characteristic that often limits the use of batch techniques and the paste approach. In addition, the solid coating on the crystal was stable throughout the experiment and contributed to the success of this approach. The efficacy of this method was enhanced through the use of both H₂O and D₂O, which proved vital not only to assign peaks and clarify spectral regions complicated by water absorption, but also to propose multiple sorbed species.

Despite its obvious advantages, the flow-through FTIR technique was not exempt from limitations encountered in the paste approach. For example, spectra often contained artifacts resulting from the processing of differential spectra along with noise and poor peak detection when sorption was low. Furthermore, spectra were influenced by solution pH, ionic strength, and background solution composition in general, making it difficult to compare qualities such as peak intensity and width for spectra collected under different experimental conditions. As such, caution was needed in interpreting the ATR-FTIR spectra and postulating structures of surface–solute complexes.

Clear delineation of surface–complex structure for compounds with coupled vibrational modes for key functional groups, particularly compounds with IHBs, was hindered by several factors. First, certain computational limitations were encountered with respect to vibrational predictions necessary to assign FTIR spectral bands for the HNAs, whose spectra were complicated in part by an IHB and for which there are few reported assignments in the literature. Predicted spectra of the HNA monoanion did not entirely match Na–HNA spectra particularly for bands most affected by Hbonding (e.g., νCOO_s). Additionally, computational modeling of Fe complexes provided reasonable Fe–HNA structures but the match between theoretical and experimental frequencies was much less precise than for Na–HNA. As such, assignment of spectral bands had to be made utilizing both vibrational predictions and literature based assignments for compounds of related structure (e.g., benzoate, phenol, phenolate, and salicylate). Second, the presence of IHB and coupled vibrational modes hindered the straightforward determination of surface structures from interpretations of differences between the spectra of the free solute (uncomplexed) and the complexed (sorbed) solute. For example, the phenolic group in sorbed HNA may be simply protonated, involved in an IHB, involved in H-bonding with the solvent, or involved in H-bonding with surface hydroxyl groups. Alternatively, the phenolic group may deprotonate to the form the phenolate ion and complex with surficial Fe ions. Differences in the appearance and positioning of the $\nu\text{C}\phi\text{O}$ in the free and complexed HNA spectra reveals changes in C–O bond strengths, but coupling of –OH and –COO[–] vibrational modes makes it difficult to isolate one or more of the five possible phenomena mentioned above. Furthermore, our knowledge of expected vibrational changes relative to a free solute involved in IHB is limited. Thus, the operative surface structure(s) may be inferred in relation to positioning of the $\nu\text{C}\phi\text{O}$ in compounds of related structure, such as phenolate and salicylate, but not determined with certainty. Likewise, $\Delta\nu\text{COO}$ values cannot be used to isolate the surface structure of the –COO complexation to Fe because the presence of an IHB between –COO[–] and –OH results in greater asymmetry and influences the vibrational

modes COO^- . As such, established guidelines with respect to the magnitude of $\Delta \nu_{\text{COO}}$ in free and complexed solutes (based on simple carboxylate structures) cannot be used to differentiate between monodentate–mononuclear, bidentate–mononuclear, or bridging bidentate complexes with respect to the carboxylate group. As such, FTIR studies can be used to propose a range of possible surface structures as done here and elsewhere (e.g., [6, 36]), while acknowledging the limitations with respect to differentiating spectra of similar surface species, e.g., mono- vs. binuclear complexes.

The above-mentioned limitations with respect to the use of FTIR for isolating surface species compels the continued use of batch techniques probing differences in sorption resulting from small differences in compound structure (e.g., 2NA vs. 1H2NA or 1H2NA vs. 2H3NA) and the effect of solute competition (e.g., sorption of HNA in the presence of phosphate or sulfate). In this work, we found that complimentary information from batch and FTIR techniques vital to mechanistic understanding of HNA sorption. For example, the greater extent of HNA sorption over 2NA in batch studies pointed to the role of the phenolic group, whereas the appearance and positioning of the $\nu_{\text{C-O}}$ pointed to likely surface structures. The batch results were particularly useful in this case because the lack of unique vibrational modes for $\nu_{\text{C-O}}$ complicated spectral interpretation. Also, batch studies were able to identify the greater sorption of 2H3NA at higher initial solute concentrations, a feature not easy to isolate in FTIR studies.

4. Summary

Investigation of the sorption of low-solubility compounds is becoming increasingly necessary. In the environmental sciences, concern is growing over the fate of compounds like large PAH degradation products, whose chemical properties may make them poor candidates for traditional batch studies that do not use cosolvents. Additionally, it is obvious that batch studies alone are insufficient to understand sorption phenomena and that spectroscopic studies, particularly those conducted in aqueous (or pseudo-natural) conditions, are vital for this information. To this end, we found that a combination of batch and flow-through FTIR studies was able to probe the sorption mechanisms of HNA isomers in goethite as well as a soil clay fraction. This combination of techniques should also prove valuable in studying even more complex molecules with IR-sensitive functional groups.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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

Fig. 2. HNA sorption onto 5 g/L goethite as a function of (a) pH (50 μ M initial HNA) and (b) initial HNA concentration at pH 4. Error bars represent standard deviations based on triplicate analyses.

Fig. 3.

Sorption of 50 μM 1H2NA, 2H3NA and 2NA ((a) only) onto 5 g/L goethite at pH 4 (a) as a function of ionic strength (NaCl) and (b) in the presence of competing anion at $I = 0.005$ M. Error bars represent standard deviations based on triplicate analyses.

Fig. 4. Spectra of 0.01 M HNA monoanion in H₂O and D₂O (pH ~6) and 0.01 M 1:1 Fe:HNA complex (pH ~1.5) for (a) 1H2NA and (b) 2H3NA, and (c) 0.01 M 2NA monoanion in H₂O and D₂O (pH ~6). Selected ring and -COO/-CO vibrations are indicated with solid and dashed lines, respectively.

Fig. 5. Spectra of 1H2NA sorbed onto goethite in (a) H_2O and (b) D_2O at pH/pD 4, 5 and 6.

Fig. 6. Spectra of 2H3NA sorbed onto goethite in (a) H₂O and (b) D₂O at pH/pD 4, 5 and 6.

Fig. 7. Spectra of (a) 1H2NA and (b) 2H3NA sorbed onto goethite at pH 4 and $I = 0.001, 0.01$, and 0.1 M.

Fig. 8. Spectra of 1H2NA sorbed onto goethite and the clay fraction of a Fe-oxide-rich soil at pH 4. Arrows indicate bands observed only for soil clay.

Fig. 9. Structures of proposed interactions of HNA with goethite surface: (a) bidentate mononuclear; (b) bidentate binuclear; (c) monodentate and bidentate through $-\text{COO}$, examples of possible additional structures at pH 4.

Table 1
Selected vibrational modes and corresponding wavenumbers for solution and sorbed species of 1H2NA and 2H3NA.

Vibrational modes ^a	Predicted monoanion		Solution species		Sorbed species	
			Monoanion in H ₂ O	Monoanion in D ₂ O	Fe:HNA solution complex	pH 4
1H2NA						
$\nu_{C=O}$			1266	1262	1264	1265
$\delta_{C=O}(H/D) + \nu_{Ring}^b + \nu_{COO_s}$	1293/1278		1311	1331 (ν_{Ring})	1294	1307
$\nu_{COO_s} + \nu_{Ring} + \delta_{C=O}(H/D)^c$	1373/1359		1370	1365	1382	1362
$\nu_{COO_{as}}^c$				1538–1548	1532–1565	1567/1533
$\nu_{Ring} + \delta_{C=O}(H/D) + \nu_{COO_{as}}$	1587 ^c		1582 ^c	1584	1582	1581
$\nu_{Ring} + \delta_{C=O}(H/D)$	1622		1629	1627		1617
$\Delta \nu_{COO}$	214–228		212	173–183	150–183	161–199
2H3NA						
$\nu_{C=O}$	1264		1260	1261	1261	1262
$\delta_{C=O}(H/D) + \nu_{Ring} + \nu_{COO_s}$	1295/1283		1315		1310	
$\nu_{COO_s} + \nu_{Ring} + \delta_{C=O}(H/D)^c$	1368/1354		1373/1349	1372	1376/1346	1376
$\nu_{COO_{as}}^c$				1543–1556	1528–1577	1546
$\nu_{Ring} + \delta_{C=O}(H/D) + \nu_{COO_{as}}$	1599 ^c		1556–1582	1579	1594	1576
$\nu_{Ring} + \delta_{C=O}(H/D)$	1634		1646	1643/1608	1646/1629	1639/1596
$\Delta \nu_{COO}$	231–245		178–217	171–184	152–231	158–218

^aFor a given mode, individual stretches or bends are listed in order of decreasing relative contribution.

^b“ ν_{Ring} ” refers to vibrations of the ring system.

^cBands used to compute $\Delta \nu_{COO}$.