

# ATR-FTIR investigation of the role of phenolic groups in the interaction of some NOM model compounds with aluminum hydroxide

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## Abstract

The role of phenolic groups in the interaction of natural organic matter (NOM) with metal hydroxides was investigated with ATR-FTIR spectroscopy and adsorption tests by employing a series of dihydroxybenzoic acids (DHBA) as the NOM surrogates and aluminum hydroxide as the adsorbent. All DHBA examined in this study were found to be adsorbed on aluminum hydroxide by forming inner-sphere complexes. Carboxylic groups governed the complexation of DHBA with aluminum hydroxide at low pH or in cases when the two hydroxyl groups were not adjacent to each other and neither of them was ortho to the carboxylic group. The involvement of the phenolic groups, ortho to another phenolic group or ortho to the carboxylic groups, in the complexation increased with increasing pH as the deprotonation of phenolic groups was easier at higher pH. The presence of phenolic groups increased the electron density of the carboxylic groups and facilitated the inner-sphere complexation of the carboxylic groups with metal hydroxide. The correlation between the  $pK_a$  values and the amount of organic acid adsorbed on the aluminum hydroxide revealed that the adsorption of DHBA at acidic pH was largely dependent on the surface chelate formation rather than on the electronic effect.

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## 1. Introduction

NOM adsorption on soil minerals in hydroxide forms has been extensively investigated (Davis, 1982; Benjamin et al., 1993; Ochs et al., 1994; Gu et al., 1995; Vermeer et al., 1998; Shen, 1999; Filius et al., 2003; Fu and Quan, 2006; Peng et al., 2006) as NOM adsorption can significantly alter the characteristics of the mineral surfaces in soils, thereby influencing the interactions between the mineral surfaces and organic/inorganic solutes in natural aquatic systems. As the carboxylic and phenolic groups in NOM molecules are considered to dominate NOM adsorption

behaviors, considerable efforts have been expended on the determination of the type of ligands involved in surface complexation between NOM and metal (hydr)oxide (Edwards et al., 1996). Kummert and Stumm (1980) observed that the general pattern for NOM adsorption onto metal (hydr)oxides was more consistent with that of organic acids binding to the surface through the carboxylic acid group than those binding through the phenolic group. An NMR investigation revealed that NOM adsorbing on oxide surfaces has a higher carboxylic acid content than does the fraction of NOM not adsorbing on oxides (Benjamin et al., 1993). However, Davis (1982) and Kim et al. (1989) argued that phenolic groups dominate the surface complex formation between NOM and the hydroxide surface, whereas carboxylic groups appear to be relatively unimportant. These contradictory findings require further

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verification of the role of phenolic groups in NOM adsorption on metal (hydr)oxides.

Some studies have been carried out to investigate the effect of phenolic groups on NOM adsorption by employing small organic acids bearing phenolic groups. Mitani et al. (1995) found that the adsorption of benzoic acid derivatives on chitosan beads was enhanced by the presence of additional phenolic groups. Evanko and Dzombak (1998) found that the adsorption of small organic acids on goethite was more influenced by the positions of phenolic groups than by the numbers of phenolic groups. Several studies have examined the adsorption of salicylic acid or *para*-hydroxybenzoic acid on metal (hydr)oxides and found that the phenolic group of salicylic acid complexed with metal (hydr)oxides but that of *para*-hydroxybenzoic acid did not (Kung and McBride, 1989; Yost et al., 1990; Tejedor-Tejedor et al., 1992; Biber and Stumm, 1994; Kubicki et al., 1997). However, none of these studies attempted to explore the effects of phenolic groups on the complexation with metal (hydr)oxide and the reasons for why organic acid adsorption can be enhanced in the presence of phenolic groups. Therefore, the adsorption of a series of dihydroxybenzoic acids (DHBAs) on metal (hydr)oxide was investigated with ATR-FTIR spectroscopy and adsorption tests to elucidate the role of phenolic groups in NOM adsorption.

## 2. Methods and materials

### 2.1. Preparation of organic acid solutions and aluminum hydroxide powders

Reagent-grade chemicals and double distilled de-ionized water were used to prepare all of the solutions used in this study. All chemicals used in this study were supplied from Sigma. The DHBAs, shown Fig. 1, were selected because their complexation with aluminum hydroxide enabled evaluation of the role of phenolic groups in their chelation properties. The ionic strength of all solutions in this study was maintained at 0.05 M with NaCl. The solution pH was adjusted with dropwise additions of NaOH or HCl as necessary.

Aluminum hydroxide was employed as the adsorbent in this study as it is one of the most abundant minerals in water environments (Hiemstra and Riemsdijk, 1996; Faust

and Aly, 1998). In addition, it has no discernible absorption in the mid-infrared range and does not interfere with ATR-FTIR spectroscopic investigations of DHBA adsorption. Amorphous aluminum hydroxide was prepared following the procedure described by Guan et al. (2005). In order to minimize any changes in the surface properties during the experiments, the aluminum hydroxide powders were allowed to age for more than one month before use (Laitti et al., 1996). The BET surface area of the prepared aluminum hydroxide powders was measured to be 49.56 m<sup>2</sup> g<sup>-1</sup> using a Surface Area and Pore Size Analyzer (Coulter SA 3100). The XRD analysis using a Powder X-ray Diffraction System (PW1830) showed that the aluminum hydroxide was amorphous. Electrophoretic mobility was used to determine the surface charge of aluminum hydroxide particles at various pH values and the point of zero charge (PZC) is the pH value at which the electrophoretic mobility is zero. The PZC of aluminum hydroxide particles was determined to be about pH 10.

### 2.2. ATR-FTIR spectra collection

The detailed procedure of collecting ATR-FTIR spectra was described by Guan et al. (in press). In brief, the spectra of the adsorbed species on the surfaces of aluminum hydroxide were collected after coating the ZnSe crystal with a thin layer of aluminum hydroxide powder following the method of Gong (2001) and subsequently filling the ATR cell with the DHBA solution. The spectra of adsorbed DHBAs were obtained by subtracting the spectra of aluminum hydroxide, water, and pure DHBA solutions at the same pH level and at the same ionic strength from the sample spectra (Biber and Stumm, 1994) with subtraction factors ranging from 0.98 to 1.02. The spectra of pure aluminum hydroxide in water were recorded at several pH levels between 5 and 9 without discernible changes.

The ATR-FTIR spectra of the DHBAs in solution were recorded at pH levels covering their pK<sub>a</sub> values so that the peak assignments could be made based on the species distribution in solution at different pH. The ATR-FTIR spectra of the DHBAs adsorbed on aluminum hydroxide were collected at three different pH levels, namely, pH 5, 7 and 9. At these pH levels, the dominant species in all DHBA solutions were dihydroxybenzoate according to the pK<sub>a</sub> values of different DHBAs. The concentration of DHBAs used for

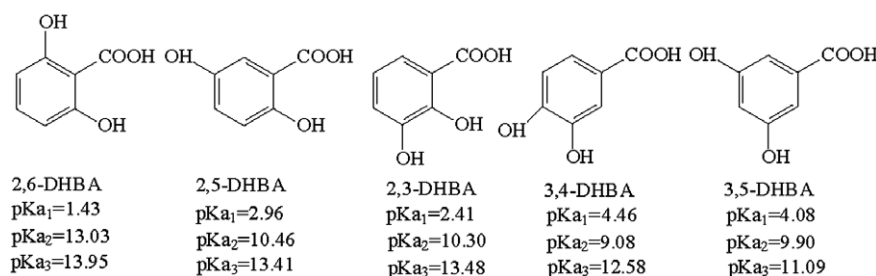


Fig. 1. Structure and pK<sub>a</sub> values of the dihydroxybenzoic acids employed in this study.

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