



## ATR-FTIR and XPS study on the structure of complexes formed upon the adsorption of simple organic acids on aluminum hydroxide

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### Abstract

Information on the binding of organic ligands to metal (hydr)oxide surfaces is useful for understanding the adsorption behaviour of natural organic matter on metal (hydr)oxide. In this study, benzoate and salicylate were employed as the model organic ligands and aluminum hydroxide as the metal hydroxide. The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra revealed that the ligands benzoate and salicylate do coordinate directly with the surface of hydrous aluminum hydroxide, thereby forming inner-sphere surface complexes. It is concluded that when the initial pH is acidic or neutral, monodentate and bridging complexes are to be formed between benzoate and aluminum hydroxide while bridging complexes predominate when the initial pH is alkalic. Monodentate and bridging complexes can be formed at pH 5 while precipitate and bridging complexes are formed at pH 7 when salicylate anions are adsorbed on aluminum hydroxide. The X-ray photoelectron (XP) spectra demonstrated the variation of C 1s binding energy in the salicylate and phenolic groups before and after adsorption. It implied that the benzoate ligands are adsorbed through the complexation between carboxylate moieties and the aluminum hydroxide surface, while both carboxylate group and phenolic group are involved in the complexation reaction when salicylate is adsorbed onto aluminum hydroxide. The information offered by the XPS confirmed the findings obtained with ATR-FTIR.

**Key words:** adsorption; aluminum hydroxide; benzoic acid; complexation; natural organic matter; salicylic acid

### Introduction

Natural organic matter (NOM), ubiquitously present in soil, sediment and water, has a profound influence on water chemistry due to its protolyzing and complexing characteristics (Allard *et al.*, 1991). NOM, especially humic acids and organic acids of low molecular weight (LMW), forms strong complexes with aluminum, iron, and some heavy metals (e.g. Pb). However, the structure of the complexes formed between NOM and aluminum hydroxide has not been clearly elucidated, which affects the adsorption behaviour of NOM on mineral surfaces.

Although NOM is an extremely complex and diverse group of organic matter without well-defined structures, the nature of the major functional groups of NOM has been well characterized, such as carboxyl, hydroxyl, phenolic, alcohol, carbonyl and methoxyl etc., among which carboxyl and phenolic are the most important functional groups responsible for the adsorption of NOM on metal oxide (Snoeyink and Jenkins, 1980). Research with simple organic acids can provide valuable insight into the adsorption mechanism of NOM in systems containing mineral surfaces (Evanko and Dzombak, 1998; Ali and Dzombak, 1996). Two simple organic acids, including

benzoic acid and salicylic acid, with carboxyl and phenolic functional groups were employed to investigate the structure of the complexes formed between NOM and aluminum hydroxide. Aluminum hydroxide is chosen since it is an important soil component. For example, bayerite, gibbsite and boehmite contain a large portion of aluminum hydroxide (Hiemstra and Riemsdijk, 1996).

The *in-situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) method developed by Tejedor-Tejedor and Anderson (1986) was adopted in this study. To provide further evidence for the complexation of organic acid and metal oxide, we obtained the X-ray photoelectron (XP) spectra of organic acid in pure solid state as well as in the adsorbed state on aluminum hydroxide. XPS measurements from the C 1s region of the spectrum can provide a complementary measure of the surface condition and its electronic properties (Han *et al.*, 2000).

### 1 Methods

#### 1.1 Aluminum hydroxide preparation

The aluminum hydroxide was prepared following the procedure described by Guan *et al.* (2005). In brief, the pH of a 0.167 mol/L AlCl<sub>3</sub> solution was adjusted to 6±0.1 and

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maintained at this pH level by adding sodium hydroxide. After the pH level of this suspension became stable without any further addition of alkali, it was stirred at room temperature for another 48 h. The suspension was then filtered, re-suspended and centrifuged and the supernatant was decanted. The aluminum hydroxide obtained was freeze-dried and stored at room temperature. The BET surface area of the aluminum hydroxide powders prepared in our study was measured to be 49.56 m<sup>2</sup>/g 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. The surface charge of aluminum hydroxide suspension decreased with increasing pH and its point of zero charge (PZC) was found to be pH 10.

### 1.2 Adsorbate employed in this study

Sodium benzoate and sodium salicylate were employed in this study as the model organic acids. They were greater than 99% pure and received no further purification after got from the Sigma Company.

### 1.3 FTIR tests

A single-beam Fourier transform infrared spectrophotometer, equipped with a cooled deuterated tri-glycine sulfate (DTGS) detector (Peltier), was utilized for the ATR-FTIR analysis. The ATR cell is equipped with a trapezoidal ZnSe crystal (45° angle of incidence) as the internal reflection element. Sixteen scans with a resolution of 2 cm<sup>-1</sup> were averaged to obtain each spectrum. This study focused on a part of the mid-infrared region, 1000–1800 cm<sup>-1</sup>. The ATR spectra of organic acid solution were recorded after filling the ATR cell with organic acid solution. The spectra of adsorbed species on the surfaces of aluminum hydroxide were obtained after coating the ZnSe crystal with a thin layer of the aluminum hydroxide power following Gong (2001), and then filling the ATR cell with the organic acid solution. Each ATR spectrum was recorded with the blank ATR cell as the background. The spectra of adsorbed organic acid were obtained by subtracting the spectra of aluminum hydroxide, water and pure organic acid solution from the sample spectra (Biber and Stumm, 1994; Guan *et al.*, 2006). The ATR sample cell was cleaned after measurement by washing with double-distilled deionized water and ethanol, until no significant bands due to impurities appeared in the spectrum of the blank ATR cell.

In all cases, the concentrations of the organic acid solutions used in this study were fixed at 0.1 mol/L. The pH was adjusted with NaOH or HCl solution prior to each test. To examine the adsorption of the organic acid on aluminum hydroxide as a function of pH, a pH range of 5 to 9 was selected to reflect the “real world” conditions. The pH dependent adsorbed organic acid spectra were collected after 4-h adsorption since the preliminary real time *in situ* ATR-FTIR test study on the adsorption of the organic acid on aluminum hydroxide demonstrated that the peaks of the adsorbed organic acid did not shift much and no new peaks appeared in 24 h.

### 1.4 XPS tests

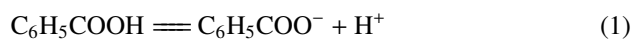
To provide further evidence for the chemisorption of organic acid on aluminum hydroxide, we obtained the X-ray photoelectron spectra of organic acid in pure solid state as well as in the adsorbed state on aluminum hydroxide. The solid samples of adsorbed organic acid on aluminum hydroxide were obtained by conducting adsorption tests. The adsorption experiments were conducted as follows. 30 ml aluminum hydroxide suspension was mixed with 10 ml organic acid solution to set the initial concentration of organic acid at 60 mg/L as TOC and aluminum hydroxide at 1.25 g/L. Sodium chloride (0.05 mol/L) was used as the background electrolyte. After mixing for 24 h, the solution was filtrated with a 0.45-μm membrane filter made of cellulose acetate (MFS). Hereafter, the solids retained on the filter paper were freeze-dried before they were subject to the XPS analysis. The XP spectra were collected by using a PHI5600 photoelectron spectrometer (Physical Electronics) with an Al K<sub>α</sub> X-ray source (1486.71 eV of photons) to determine the elements such as C and O atoms present. The vacuum in the sample analysis chamber during measurements was 1.33×10<sup>-6</sup> Pa. The energy scale of the spectra was calibrated relative to the C 1s binding energy (*E*<sub>b</sub>=285.0 eV) of the hydrocarbon layer at the sample surface.

## 2 Results and discussion

### 2.1 ATR-FTIR analysis

The FTIR spectra of the benzoic acid and salicylic acid solutions at different pH levels are illustrated in Figs.1a and 2a, respectively. The peak assignment for the infrared spectra of the solutions is mainly based on the distribution of the species in the organic acid solution at different pH and the available peak assignment data in the literature (Nakamoto, 1997; Socrates, 2001; Yost *et al.*, 1990; Biber and Stumm, 1994; Varsányi and Sözke, 1969).

The spectral changes of benzoic acid are interpreted in terms of acid-base equilibrium:



which has a p*K*<sub>a</sub> value of 4.12 (Martell and Smith, 1974). The ATR-FTIR spectrum at pH 3 should correspond to the benzoic acid, the one at pH 4 to a mixture of benzoate ions and benzoic acid, and the one at pH 7 to the benzoate anions. The decrease in the intensity of the bands at 1601, 1542 and 1389 cm<sup>-1</sup> when the pH drops from 7 to 4 and the disappearance of these three peaks at pH 3 strongly suggest that these bands are attributable to vibration of the carboxylate moieties. The doublet at 1601–1598 cm<sup>-1</sup> and 1543–1541 cm<sup>-1</sup> corresponds to the asymmetric stretching vibration of COO<sup>-</sup> group and the peak at 1389 cm<sup>-1</sup> can be assigned to the symmetric stretching vibration of the carboxylate moieties. The disappearance of the peaks at 1700, 1319 and 1279 cm<sup>-1</sup>, when the pH increases from 4 to 7, implies that these bands are caused by the vibrations of the COOH group. The peak at 1700 cm<sup>-1</sup> is assigned to the asymmetric vibration of C=O (*v*<sub>as</sub> (C=O)) while the

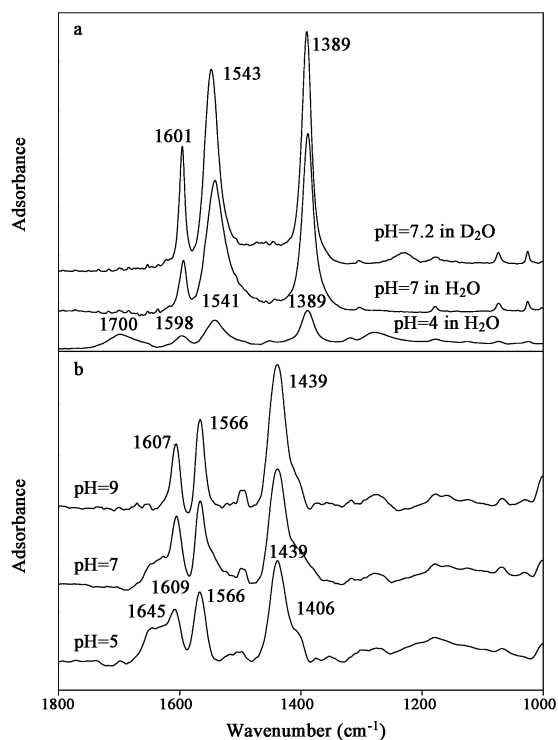


Fig. 1 ATR-FTIR spectra of dissolved sodium benzoate at different pH levels (a) and benzoate adsorbed on aluminium hydroxide at different pH (b).

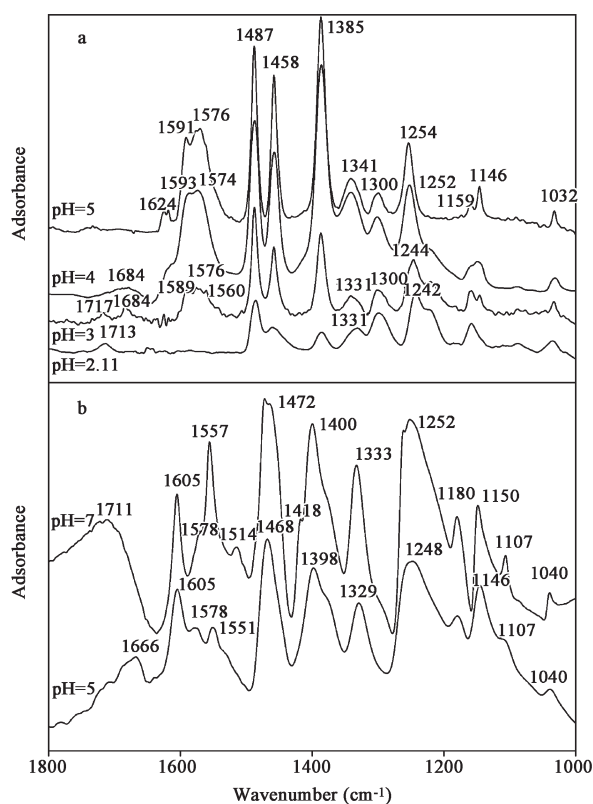


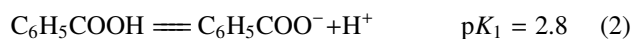
Fig. 2 ATR-FTIR spectra of dissolved sodium salicylate at different pH levels (a) and salicylate adsorbed on aluminium hydroxide at different pH (b).

peak at approximately 1319 cm<sup>-1</sup> is assigned to the C–OH bending vibration, possibly coupled with the deformation vibration of the O–H group at 1279 cm<sup>-1</sup>.

Table 1 ATR-FTIR peak assignments for salicylic acid

| Peak position (cm <sup>-1</sup> ) | Peak assignments                           |
|-----------------------------------|--|
| 1713–1717                         | $\nu_{\text{as}}$ (COOH)                   |
| 1624                              | $\nu_{\text{as}}$ (COO <sup>-</sup> )      |
| 1589–1591                         | C–C ring stretch ( $\nu$ )8a               |
| 1576                              | $\nu_{\text{as}}$ (COO <sup>-</sup> )      |
| 1487                              | C–C ring stretch ( $\nu$ )19b              |
| 1458                              | C–C ring stretch ( $\nu$ )19a              |
| 1385                              | $\nu_{\text{as}}$ (COO <sup>-</sup> )      |
| 1331–1341                         | Bending mode of the phenolic (Ph–OH) group |
| 1300                              | Bending vibration of the carboxylic C–OH   |
| 1242–1254                         | Stretching vibration of (Ph–OH)            |

In this study, aqueous solutions containing salicylic acid were investigated from pH 2 to pH 5. According to the acid-base equilibrium of salicylic acid:



The fully protonated salicylic acid predominates in the solution at pH below 2.8 and the singly protonated salicylate anions are predominant at pH ranging from 2.8 to 5. The peak assignment for salicylic acid solutions is summarized in Table 1. The asymmetric vibration of COO<sup>-</sup> in salicylate appears at higher frequency than that in benzoate and is attributable to the inner hydrogen bonding in salicylate, which shortens the C=O bond. With increasing pH both the peak corresponding to the bending vibration of Ph–OH group became narrower and that belonging to the stretching vibration of C–O bond in the phenolic group shifted to higher frequency by 10 cm<sup>-1</sup>, which can be ascribed to the stronger hydrogen bonding at higher pH for salicylate. According to Yost *et al.* (1990), the peaks at 1589–1591, 1487 and 1458 cm<sup>-1</sup> are associated with the vibration of the benzene ring and their intensities increase at higher pH. It is proposed that dissociation of the carboxylic group affect electron density and its distribution on the benzene ring, which in turn affect the vibration of the benzene ring and lead to the enhancement of intensity.

Fig. 1b demonstrates the ATR-FTIR spectra of adsorbed benzoate on aluminum hydroxide at different pH levels. The appearance of the new peaks and peak shifts in the FTIR spectra suggests the formation of inner sphere complexes. When the initial pH is 5 or 7, the peaks appearing at approximately 1645 cm<sup>-1</sup>, which can be assigned to the C=O stretching vibration, indicate the formation of monodentate complexes between benzoate and aluminum hydroxide. The covalent property of the C–O–Al bond results in a strong band due to the C=O stretching vibration in the range of 1675–1620 cm<sup>-1</sup> (Socrates, 2001). The shoulder peak appearing at 1406 cm<sup>-1</sup> may be associated with the stretching of the C–O bond when monodentate complexes are formed. The doublet at 1607–1609 and 1566 cm<sup>-1</sup> is assigned to the asymmetric vibration of C–O bond in the bidentate or bridging complexes formed between benzoate and aluminum hydroxide. The bands appearing at 1439 cm<sup>-1</sup> are assigned to the symmetric vibration of the C–O bond in the bidentate or bridging complexes. Because the  $\Delta$  value 127 cm<sup>-1</sup> ( $\nu_{\text{as}} - \nu_{\text{s}}$  of COO<sup>-</sup>

in the complexes) is comparable to that of the ionic values ( $154\text{ cm}^{-1}$ ), it is believed that the bridging complexes are more likely to be formed than the bidentate complexes. Compared to the C–O bond in the free carboxylate anions, the asymmetric and symmetric vibrations of the C–O bond in the bridging complexes appear at higher frequency, which can be due to the increase in the force constant caused by the formation of the C–O–Al. The Al is heavier than C and O atoms and makes the C–O bond more restricted, therefore, larger force is necessary to make the C–O bond vibrate. Based on the above discussion, it is concluded that when the initial pH is acidic or neutral, monodentate and bridging complexes are to be formed between benzoate and aluminum hydroxide while bridging complexes predominate when the initial pH is alkaline.

The spectra of salicylate adsorbed on aluminum hydroxide at pH 5 and pH 7 are illustrated in Fig.2b. Spectral comparisons revealed that one peak at  $1666\text{ cm}^{-1}$  appeared at pH 5 and one strong peak at  $1711\text{ cm}^{-1}$  was observed at pH 7 in the spectra of adsorbed salicylate. These two bands can be assigned to the asymmetric vibration of C=O of monodentate complexes and precipitate, respectively (the formation of precipitate was observed when we carried out the experiment at pH 7). After adsorption onto aluminum hydroxide, the band at  $1578\text{ cm}^{-1}$ , which belongs to the asymmetric vibration of C–O bond in the carboxylate moiety, shifts to  $1551\text{--}1557\text{ cm}^{-1}$ . This band may be caused by asymmetric vibration of the bidentate or bridging complexes. The symmetric vibration of carboxylate moieties in the dissolved salicylate, appearing at  $1385\text{ cm}^{-1}$ , shift to higher frequency by  $15\text{ cm}^{-1}$  when salicylate is adsorbed on aluminum hydroxide. The peak at  $1400\text{ cm}^{-1}$  is assigned to the symmetric vibration of carboxylate group in the bidentate or bridging complexes. Because the  $\Delta$  value  $157\text{ cm}^{-1}$  ( $\nu_{\text{as}}\text{--}\nu_{\text{s}}$  of  $\text{COO}^-$  in the complexes) is comparable to that of the ionic values ( $191\text{ cm}^{-1}$ ), it is believed that the bridging complexes are more likely to be formed than the bidentate complexes. Complexation lead to red shift of the  $\nu_{\text{as}}(\text{COO}^-)$  in salicylate while blue shift of  $\nu_{\text{as}}(\text{COO}^-)$  in benzoate, which can be due to the effect of hydrogen bonding. However, after the formation of bidentate or bridging complexes, the asymmetric vibration of  $\text{COO}^-$  appears at similar frequencies no matter for salicylate or benzoate. The peak corresponding to the bending mode of the phenolic (Ph–OH) group in the free salicylate anions, at  $1341\text{ cm}^{-1}$ , shifts to lower frequency by about  $10\text{ cm}^{-1}$  and the Ph–O stretching band at  $1254\text{ cm}^{-1}$  also shifts to lower frequency. These evidences revealed the involvement of Ph–OH in the complexation reaction between salicylate and aluminum hydroxide and the weakening of the hydrogen bonding.

## 2.2 XPS analysis

The expected peaks from C 1s and O 1s core levels were clearly detected in all XP spectra, however, the O 1s spectra are not presented here because it is difficult to differentiate the O atoms contained in the organic acid from the O atoms contained in the adsorbent. Background subtracted high-resolution C 1s spectra of pure sodium

benzoate and benzoic acid adsorbed on aluminum hydroxide at different initial pH levels are shown in Fig.3. A standard line shape analysis with a Gaussian fitting function was applied. Three peaks, appearing at 285.0, 288.68 and 291.51 eV dominate the C 1s spectrum of pure sodium benzoate as illustrated in Fig.3a. The peak at 285.0 eV is associated with the binding energy of the C atoms in aromatic C–C/C–H and the peak at 288.68 eV can be attributed to binding energy of C atoms in the carboxylate group, while the peak at 291.51 eV is due to the  $\pi\text{--}\pi^*$  shake up satellite from the aromatic structure (Monteil-Rivera *et al.*, 2000).

Three peaks were observed in the C 1s spectrum of adsorbed benzoic acid on aluminum hydroxide at pH 4 as shown in Fig.3b. The peak at 289.14 eV is associated with the binding energy of the C atoms in the  $\text{COO}^-$  group, which shifts to a higher value by 0.46 eV after adsorption. This upward shift reveals the formation of inner-sphere complexes or chemical bonds between benzoic acid and aluminum hydroxide, which changes the electronic environment of the carbon atoms in the carboxylic moieties. Due to the stronger electron withdrawing capacity of Al(III) compared to  $\text{Na}^+$ , the formation of inner-sphere complexes between carboxylic group and Al(III) removed more valence electrons of carbon atom in the carboxylic group, resulting in the enhancement of effective nuclear

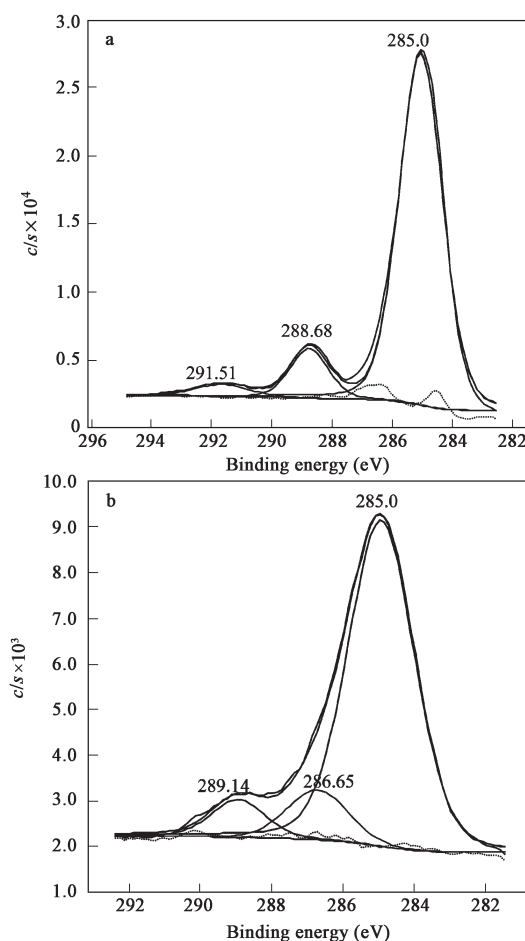


Fig. 3 XP spectra of sodium benzoate (a) and that of adsorbed benzoate on aluminum hydroxide (b).

charge experienced by the core-electron, thereby increasing the electron binding energy. The peak at 285.0 eV does not shift, which indicates that the C–C/C–H does not participate in the adsorption reaction.

For the solid sodium salicylate, four peaks are identified at 285.06, 286.54, 288.93 and 291.64 eV, as demonstrated in Fig.4a. Consulting the literature data (Han *et al.*, 2000; Tanner *et al.*, 2002), these peaks can be attributed to the aromatic carbon (C–C/C–H), carbon bound to a single oxygen (C–OH for this case), carboxylic carbon and the shake-up lines (satellites of the main lines), respectively. After adsorption on aluminum hydroxide, some peaks do shift and even new peaks appear, which strongly support the conclusion drawn from the ATR-FTIR evidence that the formation of inner-sphere complexes between salicylate and aluminum hydroxide surface. The shift of the binding energy at 286.54 in the pure sodium salicylate to 286.24 in the adsorbed salicylic acid on aluminum hydroxide, when the initial pH is 4, is an indication of the involvement of C–OH group in the complexation between salicylate with aluminum hydroxide. As hydrogen holds greater electronegativity, less valence electrons of the carbon in phenolic group are withdrawn by Al(III) after complexation and the binding energy of the core-electron experiences decrease. After adsorption on aluminum hydroxide, the binding energy of the carboxylic

carbon enhanced from 288.93 eV to 289.32 eV, which indicated the complexation between salicylate and Al(III) through the carboxylic moieties. Similar to the benzoate, the increase in the binding energy is attributed to the stronger electron withdrawing ability of Al(III) compared to Na. Two different bonding types of the carboxylate group to adsorbent surface have been proposed, namely, a bridging bond through two equivalent oxygen atoms and a monodentate (with two inequivalent oxygen atoms). The binding energy of the carbon atoms in the carboxylic groups is expected to be larger when bridging complexes are formed through the two oxygen atoms in the carboxylate group than when monodentate complexes are formed. However, they are difficult to be differentiated due to the poor resolution of the XP spectra. In the XP spectra of benzoate or salicylate adsorbed on aluminum hydroxide, the shake-up lines are not observed which can be due to the low concentration of benzoate or salicylate on the surface. The atomic concentration of carbon is 60%–70% in pure sodium benzoate and sodium salicylate while that of carbon on the surface of aluminum hydroxide due to the adsorption of benzoate or salicylate is only about 10%.

### 3 Conclusions

The ATR-FTIR spectra revealed that the ligand benzoate and salicylate do coordinate directly with the surface of hydrous aluminum hydroxide, thereby forming inner-sphere surface complexes. It is concluded that when the initial pH is acidic or neutral, monodentate and bridging complexes are to be formed between benzoic acid and aluminum hydroxide while bridging complexes predominate when the initial pH is alkalic. Monodentate and bridging complexes can be formed at pH 5 while precipitate and bridging complexes are formed at pH 7 when salicylate anions are adsorbed on aluminum hydroxide. The XP spectra demonstrated the variation of C 1s binding energy in the salicylate and phenolic groups before and after adsorption. It implied that the benzoate ligands are adsorbed through the complexation between carboxylate moieties and the aluminum hydroxide surface, while both carboxylate group and Ph–OH group were involved in the complexation reaction when salicylate is adsorbed onto aluminum hydroxide.

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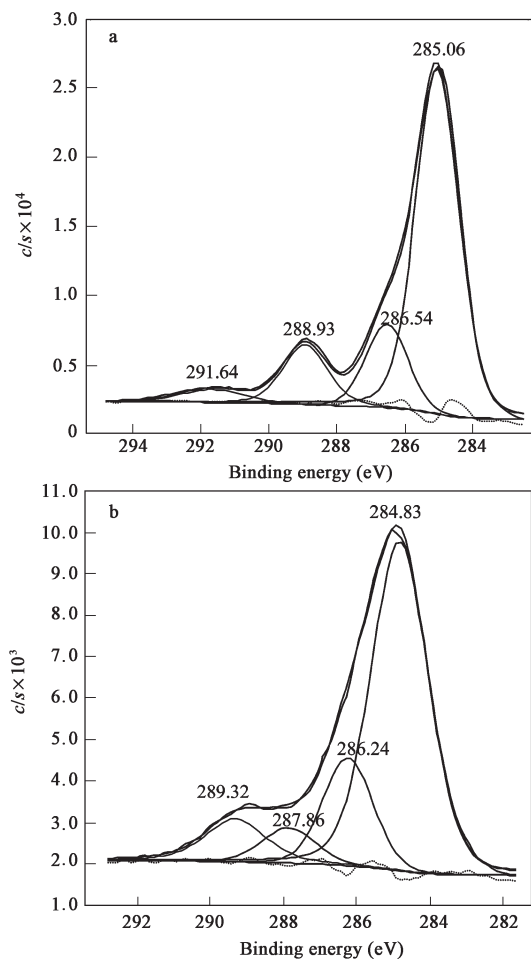


Fig. 4 XPS spectra of sodium salicylate (a) and that of adsorbed salicylate on aluminum hydroxide (b).

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