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Vibrational study of the salicylate interaction with metallic ions and surfaces

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Abstract

Infrared and Raman spectroscopy are used in this work to study the metallic complexes of salicylic acid with silver and copper, comparing the interaction between salicylate and the cations (Ag^+ and Cu^{2+}) in the metal complexes with the SERS spectra when adsorbed on colloidal metal surfaces of the same metals. The salicylate complexes with the above metals were compared to those of Na^+, Fe^{3+} and Al^{3+} cations. A different interaction mechanism is deduced for salicylate in the metal complex and when adsorbed on the metal surface. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Salicylic acid; Infrared; Raman; Metallic complexes; SERS; Adsorption

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1. Introduction

The ability of soil organic matter to bind metals of different nature and inorganic matrices is of a great importance regarding the metal richness of soils in relation to the plant nutrition [1,2]. One of the most relevant metal binding sites existing in humic substances is the salicylate moiety (Fig. 1). The interaction of salicylate with metallic ions and mineral interfaces has been already studied in relation to environmental aspects [3–5]. Another point of interest regarding the salicylate molecule is its presence in many commercial drugs [6,7]. The study of the interaction of this molecule with ions is, thus, an interesting topic which deserves a deep research.

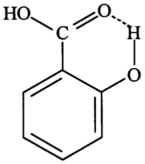

Fig. 1. H-bond in salicylic acid.

In this respect we believe that a comparative study of the interaction of salicylate with metal cations and metal surfaces could also afford a valuable information concerning the ability of this molecule to bind metals under different states. This could also serve to understand the different

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binding possibilities that this molecule can demonstrate in soils or physiological systems. Surface-enhanced Raman spectroscopy (SERS) is a technique which has been largely used to study the interaction of an adsorbate on metal surfaces. The high sensitivity of this technique allows for a selective study of only those molecules which are directly adsorbed onto the surface.

The aim of this work is to develop a vibrational study (infrared and Raman) of metallic complexes of salicylic acid with Ag^+ and Cu^{2+} and their comparison with the SERS spectra of this molecule when adsorbed on colloidal metal surfaces of the same metals: Ag and Cu. Although in the literature one can find SERS studies regarding the adsorption of metallic complexes [8,9], few studies has been undertaken dealing with a comparison between the interaction of a ligand with the same metal under different states: cation, in the metallic complex, and surface, when this ligand is adsorbed on it. The salicylate complexes with the above metals were compared with those of Na^+, Fe^{3+} and Al^{3+} cations, corresponding to cations that interact through an electrostatic interaction (Na^+) and cations that are known to strongly interact with salicylate through a coordinate bond, in the case of Fe^{3+} and Al^{3+} [10,11]. The assignments of the vibrational bands corresponding to salicylic acid and salicylate were made on the basis of data found in the literature [12–15].

2. Experimental

2.1. Materials

Sodium salicylate was purchased from Sigma. $FeCl_3$, $Al(NO_3)_3$, $AgNO_3$, $CuCl_2$, $NaBH_4$ and trisodium citrate were purchased from Merck.

2.2. Preparation of metal complexes

The salicylate complexes with Cu^{2+}, Fe^{3+} and Al^{3+} in solid state were obtained by mixing a 1 M aqueous solution of sodium salicylate and an 1 M solution of $CuCl_2$, $FeCl_3$ or $AlCl_3$ aqueous solutions, with the following volume ratios: 2:1 in the case of salicylate/Cu^{2+}, and 3:1 in the case of salicylate/Fe^{3+} and salicylate/Al^{3+} complexes. The salicylate complex with Ag^+ was obtained by mixing a 0.1 M aqueous solutions of Na salicylate and a 0.1 M aqueous solution of $AgNO_3$. After mixing the above solutions an spontaneous precipitation of the corresponding metal complex was observed. The suspensions were centrifuged and the precipitate obtained was washed three times with triply distilled water. Then, these were dried at 60–90°C and, afterwards, they were kept in a desiccator. Salicylic acid in the solid state was prepared by adding hydrochloric acid to a 0.5 M Na salicylate aqueous solution until $pH = 3$. At this pH the salicylic acid precipitated due to its insolubility in water. Then the precipitate was washed several times and dried as indicated above.

2.3. Preparation of colloids

The silver colloid was prepared by the Creighton method [16]: 10 ml of an aqueous $AgNO_3$ solution (10^{-3} M) were added drop by drop to 30 ml of an ice-cold aqueous $NaBH_4$ solution (2×10^{-3} M) and vigorously stirred; the resulting initial colloid showed a yellow color. Afterwards, the Ag colloid becomes brown, but on stirring the resulting colloid, the final colour becomes again light yellow.

The Cu-coated Ag colloid was prepared by dissolving the $AgNO_3$ in a previously obtained Cu colloid up to a final concentration of 10^{-3} M, and subsequent reduction of the mixture by means of an ice-cold aqueous sodium borohydride solution (2×10^{-3} M), following the same procedure described above. The Cu colloid was prepared by using the procedure of Creighton et al. [17] with some modifications: A 1 ml aqueous solution of $CuSO_4$ (10^{-2} M) was added to 16 ml of a trisodium citrate solution (2.8×10^{-3} M), and 6 ml of a freshly prepared solution of $NaBH_4$ (2×10^{-2} M) and sodium hydroxide (2×10^{-2} M) was added drop by drop with vigorous stirring. The resulting brown colloid must be aged for at least 1.5 h to be employed in SERS measurements. After this time the colloid becomes dark red due to its partial aggregation.

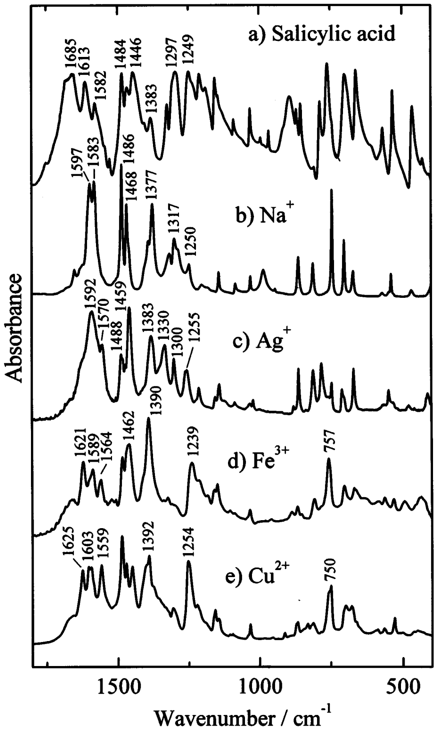

Fig. 2. FTIR spectra in KBr of salicylic acid (a), Na^+ salicylate (b) and salicylate complexes with (c) Ag^+; (d) Fe^{3+} and (e) Cu^{2+}.

Samples for SERS measurements were prepared by adding aliquots of an initial 0.1 M sodium salicylate aqueous solution to 1 ml of the corresponding colloid (Ag or Ag on Cu colloids) until reaching a 1.7×10^{-2} M final concentration. This relatively high concentration was necessary for aggregating the colloid without adding any aggregation agent that could influence the interaction of salicylate with the metal.

2.4. Instrumentation

IR spectra were recorded with a Perkin-Elmer FTIR 1725 spectrophotometer. FT-Raman spectra were recorded with a Bruker RFS 100/S by using a Nd:YAG laser source at 1064 nm, the output power was 50 mW. The samples in the solid state were prepared by placing a small amount of the compound in a brass metallic cylinder with a small hole in the centre. FT-Raman spectra were recorded by using a 180° geometry and a 4 cm^{-1} resolution. The final spectra were the result of 1000 scans accumulation.

SERS spectra in the visible were recorded in a U-1000 Jobin-Yvon Raman spectrophotometer, using the 514.5 nm radiation line of a Spectra-Physics 165 Model Ar^+ laser. The laser power at the sample was about 40 mW, and the SERS spectra were the result of five scans average recorded at a 1 cm^{-1} per second rate. Samples for SERS measurements were placed in a 2 mm diameter capilar. A 90° geometry was employed in this case with a 4 cm^{-1} resolution.

3. Results and discussion

3.1. FTIR spectra of salicylate complexes

FTIR spectra of Na^+, Ag^+, Cu^{2+} and Fe^{3+}, salicylates and salicylic acid in KBr are displayed in Fig. 2. The broad band appearing in the 1700 – 1650 cm^{-1} region in the FTIR spectrum of salicylic acid, which is assigned to $C=O$ stretching of aromatic carboxylic acids, is absent in the spectra complexes spectra, while the bands attributed to the carboxylate moiety, appearing at about 1590 cm^{-1} ($\nu_{as}(COO^-)$) and about 1380 cm^{-1} ($\nu_s(COO^-)$) are evident in these complexes, thus indicating that the acid is dissociated in the presence of the metal. However, the above carboxylate bands undergo different shifts depending on the interacting metal. The strongest changes are seen for the $\nu_{as}(COO^-)$, which is one of the most intense in the IR spectra. In the case of sodium salicylate, this band is split in two components appearing at 1597 and 1583 cm^{-1}. But in the case of Fe^{3+} and Cu^{2+} complexes the $\nu_{as}(COO^-)$ mode is markedly weakened. This variation may indicate a significant change in the symmetry of these modes induced by the interaction with the metal.

The bands attributed to aromatic ring also undergo remarkable changes. In general, we observed more changes again in the case of Fe^{3+} and Cu^{2+} complexes. The bands appearing at 1613 and 1582 cm^{-1} are displaced to opposite directions in the presence of the cation: to 1621

(Fe^{3+}) and 1625 cm^{-1} (Cu^{2+}) the first; and to 1570 (Ag^{+}), 1564 (Fe^{3+}) and 1559 cm^{-1} (Cu^{2+}), the second. In the case of sodium salicylate no significant displacement is observed for the lower component, while the upper one is down shifted to 1597 cm^{-1}. The ring stretching bands appearing in the 1400–1500 cm^{-1} region also undergo evident changes. But the stronger variations are seen in the case of the ring bands of the 1300–1350 cm^{-1} region which are remarkably weakened in the Fe^{3+} and Cu^{2+} complexes. All these results corroborate the strong influence of these two metals in the salicylate ring vibrations [10,11].

Finally, the metal has also an influence on the ν(C-OH) bonds of salicylate. This effect is different in Ag^{+} and Cu^{2+} in relation to Fe^{3+}. The 1249 cm^{-1} band is up shifted in the complexes of the two first cations to 1255 and 1254 cm^{-1}, respectively, while in the Fe^{3+} is strongly down shifted to 1239 cm^{-1}. The marked down shift undergone with Fe^{3+} may indicate a breakdown of the intramolecular H-bond existing in the molecule (Fig. 1), as a consequence of the interaction with the metal.

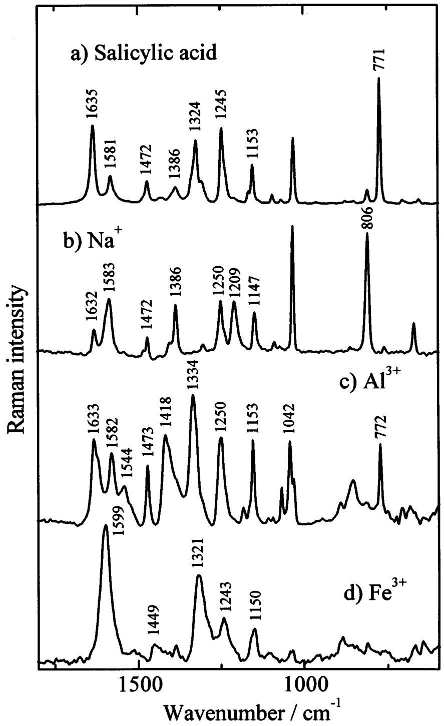

Fig. 3. FT-Raman spectra of salycilic acid (a), Na^{+} salicylate (b) and salicylate complexes with (c) Fe^{3+} and (d) Al^{3+}.

3.2. Raman spectra of salicylate and its complexes with Fe^{3+} and Al^{3+}

Fig. 3 displays the FT-Raman spectra of salicylic acid, sodium salicylate and the complexes with Fe^{3+} and Al^{3+} in solid state. In the sodium salycilate, the ionization of the carboxyl group in the complex is suggested by: (1) the marked weakening of the 1635 cm^{-1} band, which may contain contributions from ring stretching motions as well as $\nu(C=O)$ vibrations of carboxylic acid group; (2) the intensity decrease of the 1324 cm^{-1} band, assigned to a $\nu(C-O)$ mode in the carboxylic acid group coupled to ring stretching vibrations; (3) the enhancement of the bands appearing at 1583 cm^{-1}, attributed to $\nu_{as}(COO^{-})$ in combination with ring stretching motions; and (4) the appearance of a new bands at 1386 cm^{-1}, due to $\nu_{s}(COO^{-})$; at 1209 cm^{-1} attributed to $\nu_{as}(COO^{-})$ coupled to phenolic $\nu(C-O)$ motion (15); and at 671 cm^{-1}, that may correspond to $\delta(COO^{-})$. All these facts corroborates the assignments found in the literature for salicylate. On the other hand, the observation of the $\nu(C=O)$ band of carboxylic acid group at a lower frequency in the FT-Raman when compared with the FTIR spectrum (Fig. 2a) can be explained on the basis of the different state of salicylic acid in solid and in KBr.

The FT-Raman of the Fe^{3+} shows many differences in relation to the sodium salt that corroborates the existence of a strong interaction of this ion with salicylate. The spectrum is dominated by two intense bands appearing at 1599 and 1321 cm^{-1}. The ring stretching motions of the 1500 – 1400 region, corresponding to ν_8 and ν_9 of the Green nomenclature [13] are markedly reduced, indicating a strong influence of this metal in the aromatic system. Moreover, the intensity decrease of the $\nu_{s}(COO^{-})$ mode at 1385 cm^{-1} and the down shift of the $\nu(C-O)$ mode at 1243 cm^{-1} also indicates a strong interaction of Fe^{3+} with both the carboxylate and the phenolic groups, as it was also deduced from the IR spectrum. This simultaneous interaction lead to a subsequent

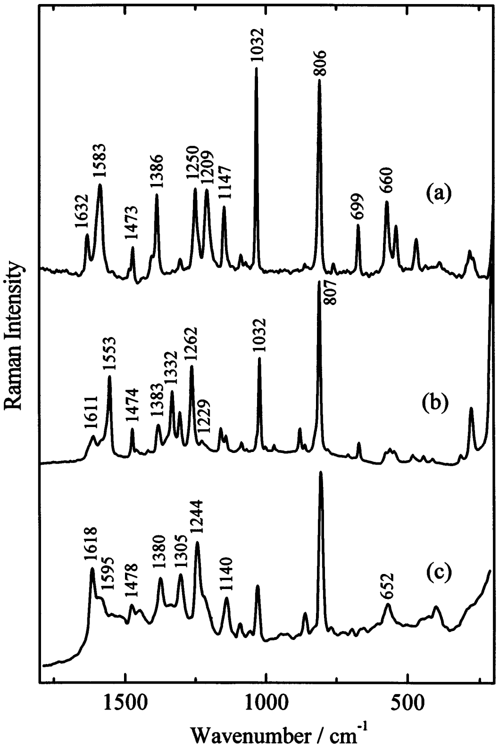

Fig. 4. (a) FT-Raman spectrum of Na^+ salicylate; (b) FT-Raman spectrum of Ag^+ salicylate complex; and (c) SERS of salicylate on Ag colloid (1.7×10^{-2} M, $\lambda_{ex} = 514.5$ nm).

electronic modification of the aromatic π system [10,11].

In the case of Al^{3+} salicylate complex we also observed changes concerning the ring stretching bands and the carboxylate, but the 1250 cm^{-1} band of phenol group is not down shift and the Raman spectrum in general does not undergo a so deep modification as in the case of Fe^{3+}, suggesting that the interaction of Al^{3+} with salicylate is weaker. It is worthy noting in this complex the up shift and enhancement of the 1633 cm^{-1} band, and the strong up shift of the $\nu_s(COO^-)$ band to 1418 cm^{-1}. All these facts suggest a strong charge transfer from the cation to the salicylate through a back donation mechanism.

3.3. Raman of salicylate complexes with Ag^+ and Cu^{2+}: comparison with SERS spectra

The FT-Raman spectrum of Ag^+ salicylate complex is shown in Fig. 4b compared with the SERS on Ag colloid (Fig. 4c) and that of the sodium salt (Fig. 4a). The Raman of the complex in solid state shows strong features at 1553 and 1262 cm^{-1}, along with the intense bands of C – H ring deformation appearing at 1032 and 807 cm^{-1}. The up shift of salicylate $\nu(C-O)$ band at 1250 cm^{-1} towards 1262 cm^{-1} in the Ag^+ complex (Fig. 4b) indicates that the hydroxyl group may not participate in the interaction with the metal as in the case of Fe^{3+}. However, the interaction with the carboxylate group may cause a great distortion of the aromatic system as indicated by the appearance of a strong band at 1553 cm^{-1}. The SERS spectrum (Fig. 4c) shows a different behavior in relation to the solid complex. The salicylate band at 1250 cm^{-1} is down shift to 1244 cm^{-1}, thus suggesting the participation of the phenol group in the interaction with the surface, as has been also referred by other authors studying the adsorption of salicylate on silica [18,19]. This different interaction is also suggested by the enhancement of the 1305 cm^{-1} band in the SERS spectrum and the lower intensity of that at 1332 cm^{-1}, which undergoes an up shift to 1340 cm^{-1} in the SERS. The involvement of both the phenol and carboxylate groups in this vibrations is also indicative of an interaction of salicylate through these two groups.

The spectrum of sodium salicylate shows a weak band at about 2600 cm^{-1} that may correspond to the $\nu(O-H)$ motion of an alcohol bond involved in a H-bond [7], which is not seen in the SERS of salicylate (result not shown), thus corroborating the possible breakdown of the intramolecular H-bond due to the simultaneous interaction of salicylate through the carboxylate and the phenolic group. Nevertheless, the existence of a close hydroxyl group may induce a possible reorientation on the molecule that is not completely perpendicular in relation to the surface, as deduced from the absence of any $\nu(C-H)$ band in the high wavenumbers region.

The FT-Raman spectrum of Cu^{2+} salicylate complex is shown in Fig. 5b compared with the SERS spectrum on mixed Cu/Ag colloid (Fig. 5c) and that of sodium salicylate (Fig. 5a). The high fluorescence background of Cu^{2+} complex observed exciting at 1064 nm avoids obtaining a good Raman spectrum (Fig. 5b). The excitation with a visible line induces a so high fluorescence that no band can be seen in the Raman spectrum. As in the case of Fe^{3+} complex, we observed a down shift of the ν(C – O) band to 1240 cm^{-1}, and an intense band at 1535 cm^{-1}, which may correspond to that observed for the Ag^{+} and Al^{3+} complexes at 1553 and 1544 cm^{-1}, respectively. Moreover, the carboxylate $\nu_s(COO^-)$ band is up shifted to 1392 cm^{-1}. This may indicate a simultaneous interaction with both the phenol and carboxylate groups as in the case of the Fe^{3+} complex. However, the differences observed between the FT-Raman spectra of Cu^{2+} and Fe^{3+} complexes (Fig. 5b and Fig. 3d, respectively) contrasts with the high similarity of the FTIR spectra of these complexes (Fig. 2c and e). This disparity may be a consequence of the higher contribution in Raman of ring modes, which may be differently changed in each complex, depending on the interaction strength between the cation and the ligand. According to this, the down shift observed for the ν(C–O) band to 1240 cm^{-1} could not be attributed to a direct interaction of Cu^{2+} with the phenol group, but rather to a strong distortion of the ring vibrations which are also reflected in a change of the above phenol band.

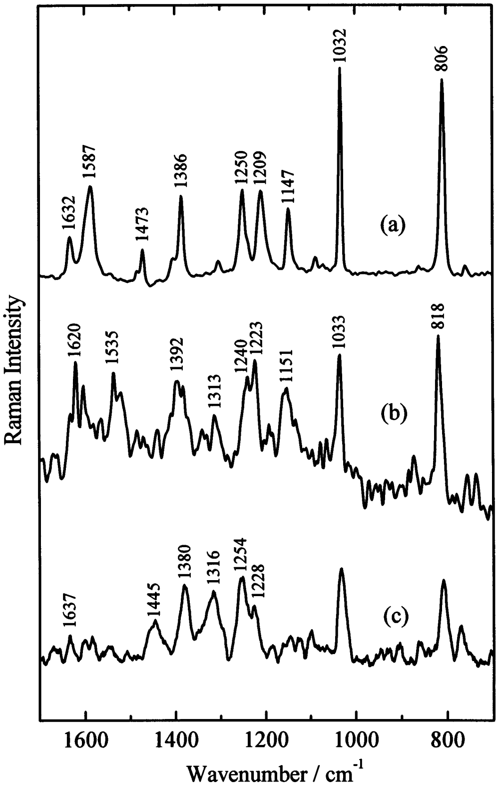

Fig. 5. (a) FT-Raman spectrum of sodium salicylate; (b) FT-Raman spectrum of Cu^{2+} salicylate complex; and (c) SERS of salicylate on Cu/Ag colloid (1.7×10^{-2} M, $\lambda_{ex} =$ 514.5 nm).

The SERS of salicylate could not be obtained on Cu colloid. For this reason we have tried to obtain the SERS spectrum of salicylate on a mixed colloid composed by Cu and Ag with the goal of increasing the affinity of the Cu surface with respect to this ligand. The SERS spectrum of salicylate adsorbed on this mixed colloid is very weak (Fig. 5c). The spectral profile is in general different in relation to the SERS on Ag or the Ag^{+} complex, thus indicating that the observed SERS spectrum may correspond to the salicylate interacting with metallic Cu surface. Moreover, this spectrum shows many differences in relation to that of Cu^{2+} complex: the ν(O–H) band is not down shifted, while the carboxylate band does not undergo the up shift observed for the Cu^{2+} complex, thus revealing a weaker interaction of salicylate with the metallic Cu surface through these groups. This can be the cause of the weaker SERS intensity. However, strong changes can be observed in the bands corresponding to the aromatic ring, since a marked weakening is observed for the bands appearing in the 1650 – 1400 cm^{-1} region and a prominent band is seen at 1316 cm^{-1}.

4. Conclusions

The interaction of salicylate with metallic cations has a distinct influence on the different molecular moieties that integrate this molecule: carboxylate, hydroxyl and aromatic ring. In solid state Fe^{3+} strongly interacts with the carboxylate and hydroxyl groups simultaneously, while Ag^{+}, Cu^{2+}, and Al^{3+} only interact with the carboxylate, although these cations induce strong changes in the aromatic ring. The interaction of salicylate with the colloidal metal surfaces seems to take place through a different mechanism with regard to the metal complexes. On Ag colloid the interaction involves both the hydroxyl and the carboxylate groups, in contrast to what happens in the solid complex and in agreement with the salicylate interaction found with silica surface. Nevertheless, on Cu/Ag colloids the interaction is weaker than in the solid complex and seems to affect mainly the aromatic ring.

Acknowledgements

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