Vibrational Spectroscopy 87 (2016) 99–103

Contents lists available at ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec

Analysis of squaric acid and its complex with copper(II) ions adsorbed on silver nanoparticle surfaces by surface-enhanced Raman spectroscopy

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A R T I C L E I N F O

Article history:
Received 31 March 2016
Received in revised form 29 August 2016
Accepted 20 September 2016
Available online 21 September 2016

Keywords:
SERS
Squarate ion
Cu(II) complex

A B S T R A C T

Surface-enhanced Raman scattering (SERS) spectra of squaric acid (SA) and its complex with Cu(II) ion have been obtained on silver nanoparticle (AgNP) surfaces. The spectral deconvolution of the band assigned to symmetric carbonyl stretching showed the presence of two distinct coordination modes in the surface complex on AgNP even at high concentrations of Cu(II) ion. Additionally, in the presence of Cu (II), two bands have been observed in the low wavenumber range assigned to the Ag—O and Cu(II)—O stretching vibrations. An increase of the squaric acid-Cu(II) complex signal has also been shown with the increase of the cation concentration up to a molar ratio of 1:1 (SA:Cu(II)). At higher concentrations of Cu (II) ions the intensity ratio of the features assigned to the symmetric CO stretching for SA—Ag and Cu(II)-SA-Ag species was kept approximately constant. A relative population analysis suggests that an equilibrium between the species contributing to the SERS signal has been established, with the saturation of the surface with the Cu(II)-SA-Ag surface complex. The SERS analysis used here is a facile method for the detection and structural characterization of coordinated systems derived from squaric acid adsorption on SERS-active silver surfaces.

1. Introduction

Oxocarbons are chemical species formed only by carbon and oxygen atoms. The divalent anionic cyclic species with the general formula of $C_nO_n^{2-}$ have shown a high planar symmetrical structure including a large degree of electronic delocalization [1,2]. The known oxocarbonic cyclic divalent anionic species are: deltate ($C_3O_3^{2-}$), squarate ($C_4O_4^{2-}$), croconate ($C_5O_5^{2-}$) and rhodizonate ($C_6O_6^{2-}$). The squaric acid (SA), ($H_2C_4O_4$), is a neutral species, belongs to the oxocarbon family and has been shown to have two pK values: $pK_1 = 0.5$ and $pK_2 = 3.5$ [3]. There are different points of view about the behavior of SA in aqueous solutions in the literature; it has been suggested that SA is a very strong diprotic acid, which would dissociate completely to the squarate dianion, due to a strong stabilization promoted by the aromatic character of the latter [4]. On the other hand, it has also been suggested that, even though SA is a very strong acid, it should be predominantly in a non-dissociated form in aqueous solutions [5].

Extensive studies of the complex species formed between oxocarbons and transition metal ions have been carried out for a long time because those species present a broad spectrum of properties, important both in fundamental chemistry and applications. The high-symmetry properties of the oxocarbon dianions have made this family of compounds suitable probes to gather information about the formation of transition metal ion complexes [6–11]. The coordination of squarate with transition metals has been systematically studied using different spectroscopic techniques, such as UV–vis absorption, Electron Paramagnetic Resonance and vibrational spectroscopies, crystallography, etc. However, the works in literature have mostly been focused in the study of complexes in the solid state. As an example, Solans et al. obtained and characterized six different squarate-copper complex structures [6]. The authors indicated that squarate is not able to form complexes with Cu(II) in bis-bidentate or 1,2-bidentate coordination geometries. It was also suggested that for discrete and polymeric complexes the Cu(II) ion is present in pyramidal or octahedral coordination, respectively.

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http://dx.doi.org/10.1016/j.vibspec.2016.09.017
0924-2031/

In another study carried out by Santos et al. [7], the authors presented several structural insights of solid state squarate-Cu(II) complexes using a thorough analysis of Raman spectroscopy results. The complexes were obtained by reaction of squarate sodium salt with transition metal chlorides. The results suggested that the symmetry of the squarate was maintained in the complexes and that there is a delocalized interaction of the squarate anion with the metal cations.

Although SA has already been used as precursor for the synthesis of squarate complexes [12,13], the behavior of this acid as ligand for coordination with transition metals has been analyzed and characterized only in three cases to our knowledge [14–16]. Headley et al. characterized the structure of SA coordinated with Fe (II) and Ni(II) ions, obtained in a reaction in hot ethanol [15]. The authors' analysis suggested that the complexes are five-coordinate in a trigonal-bipyramidal geometry. Similar structure was reported by the same group for the case of SA-Co(II) complex [16]. In another study, Maharaj et al. suggested a different structure for the SA-Cu (II) complex formed by reacting SA and $CuCl_2$ in 2-propanol, in which the chloride acted as bridges in a supramolecular structure. In all the above cases, the characterization was carried out for solid state samples [14].

The aim of the present work was to study the complex of SA and Cu(II) adsorbed on silver nanoparticle (AgNP) surfaces using surface-enhanced Raman scattering (SERS) spectroscopy. Sant'Ana et al. reported the SERS spectra of squaric acid and derived species using gold and silver electrodes as substrates at different potentials and pH [17]. The results indicated the adsorption of SA is dependent of pH, co-adsorbed species and the applied potential. Additionally, it was shown that SA, hydrogen-squarate and squarate may be found at the electrode surface as a function of both solution pH and applied potential. It has also been demonstrated that SA may undergo degradation to carbon monoxide for long periods of interaction with Ag surfaces. In the present work, SERS spectroscopy was applied to understand the adsorption of SA and its complex with Cu(II) ions in solution using chloride-free silver colloid as a substrate.

2. Materials and methods

$AgNO_3$, $NaBH_4$, SA and $Cu(NO_3)_2$ were purchased from Sigma Aldrich, and used without further purifications. All the samples were prepared in ultrapure water obtained from a Synergy UV water purification system with a resistivity of 18.2 MΩ cm.

The AgNP colloidal suspension was obtained by addition of 10.0 mL of $AgNO_3$ (1.0 mM) dropwise to an ice-cold 30.0 mL of $NaBH_4$ solution (2.0 mM) under stirring, according to a well-known protocol [18].

UV–vis absorption experiments were carried out in a Shimadzu UV spectrophotometer (model UV-1800). The SERS experiments were carried out in a Senterra Raman spectrometer (Bruker) coupled to an Olympus microscope, using a backscattering configuration for excitation and collection of the data. The 632.8 nm wavelength of a He-Ne laser was used as excitation with a power at the equipment entrance of 5 mW. A 50x long-working distance objective (NA = 0.50) and a resolution of 3–5 cm^{-1} were chosen for data collection. The Raman signals were obtained with an integration time of 30 s, and the reported spectra are the average of at least 5 spectra obtained from the same sample. The Raman spectrum of solid SA was obtained with an integration time of 10 s. The Raman spectra of saturated solutions of SA and dianion squarate were acquired with a power of 20 mW and 30 s exposure time.

The SA-Cu(II) complexes were prepared by mixing 50% v/v a solution of pure SA (20 mM) with different concentrations of Cu $(NO_3)_2$ salt. The samples for SERS and UV–vis analyses were prepared by mixing an aqueous solution of free SA or SA-Cu(II) complex 50% v/v with the AgNP suspension, and the spectra were obtained immediately.

Geometry optimization and wavennumber calculations were carry out with the triple-ζ split valence B3LYP/6-311+G(d,p) [19,20] basis set for C, H and O atoms and the pseudo-potential LANL2DZ basis set [21–23] for Ag and Cu atoms, using GAUSSIAN03 [24].

3. Results and discussion

Fig. 1 shows the normal Raman spectra of SA in the solid and saturated solution (pH 0.84), the dianion squarate (pH 12.3), and two representative SERS spectra of SA at concentrations of 10 mM (pH 2.0) and 50 μM (pH 4.0). The Raman spectra of saturated aqueous solutions of SA and the dianion squarate show several differences. Most notably, the SA spectrum presents bands at 1062 and 1139 cm^{-1} and squarate ion has a single band at 1120 cm^{-1}. The band assigned to the symmetric C=O stretching vibration has low intensity and a position at 1790 cm^{-1} and 1804 cm^{-1} in squarate and SA spectra, respectively. The SERS spectrum of SA shows clear differences in comparison with those of normal Raman. For example, the band at 632 cm^{-1} in the normal Raman spectrum has very low intensity in the SERS spectrum. Another important difference is that the band corresponding to the symmetric C=O stretching vibration is weak in the normal Raman spectrum and is the most intense band in the SERS spectrum. This band also shifts from 1804 cm^{-1} in the normal Raman spectrum to 1772 cm^{-1} in the presence of silver nanoparticles. The intensity enhancement of the 1772 cm^{-1} band can be ascribed to the adsorption of SA on the nanoparticle surface through the C=O groups. The above spectral pattern in SERS is in agreement with the formation of a surface complex involving the interaction of the carbonyl moiety with the silver surface [17]. Though a specific trend in the SERS intensities as a function of SA concentrations could not be observed, it is noteworthy that it was possible to obtain SERS spectra with a reasonable signal-to-noise ratio for concentrations as low as 50 μM. A comparison of the SERS spectra shows that there are no prominent changes in the relative intensities and position of the Raman bands with the SA concentration. However, changes of SA concentration produce variation in the pH of aqueous solutions and considering the pK_a values of SA, it is expected that other species, as for example the hydrogen squarate ion, may also

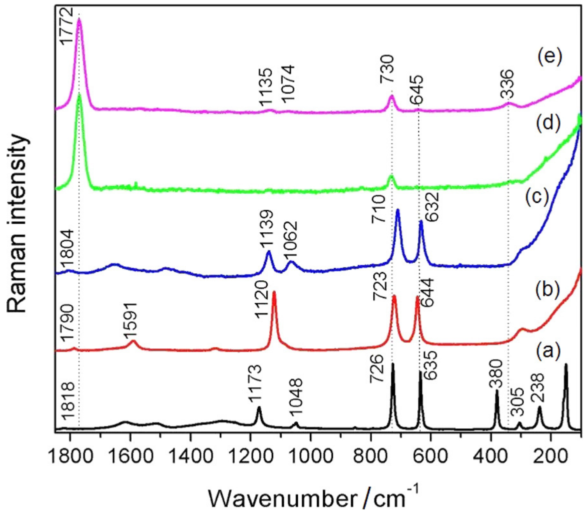

Fig. 1. Raman spectra of SA in solid state (a); saturated aqueous solutions of dianion squarate (b) and SA (c); and normalized SERS spectra of SA at concentrations of 5 μM (d) and 10 mM (e).