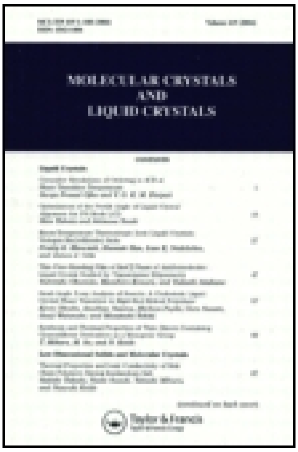

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Spectroscopic Characterization of the Inclusion Compound Formed by Polyaniline and β-Cyclodextrin

Gustavo M. Do Nascimento [a] , JosÉ E. P. Da Silva [a] , Suzana I. C. De Torresi [a] , Paulo S. Santos [a] & Márcia L. A. Temperini [a]

[a] Departmento de Química Fundamental, Instituto de Química, Universidade de São Paulo, CP 26.077, São Paulo, SP, CEP 05513-970, Brazil

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Spectroscopic Characterization of the Inclusion Compound Formed by Polyaniline and β-Cyclodextrin

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SUZANA I. C. DE TORRESI[a], PAULO S. SANTOS[a] and
MÁRCIA L. A. TEMPERINI[a]

[a]*Departmento de Química Fundamental, Instituto de Química,*
Universidade de São Paulo, CP 26.077, CEP 05513-970,
São Paulo, SP, Brazil

The encapsulation of emeraldine base (EB) was achieved by the thread of several β-CD units onto the polymer chain. The formation of the inclusion compound was confirmed by X-ray powder diffraction, IR and Raman spectroscopies. It was shown that despite encapsulation EB is still prone to the doping effect of HCl or iodine vapours.

Keywords: polyaniline; cyclodextrins; inclusion; molecular necklace; resonance raman

INTRODUCTION

Cyclodextrins (CDs) are very well known as host molecules in Inclusion chemistry, as their internal cavities are able to accommodate a variety of guest species [1]. More recently, it has been shown that CDs can be used as building blocks to form supramolecular structures known as "molecular necklaces", where several CD units thread onto a polymer chain [2]. In this context it should be highlighted recent investigations aimed to characterize the properties of the "molecular necklace" formed by the conjugated conducting polymer polyaniline and β-Cyclodextrin (β-CD) [3-4]. More specifically side investigations focused on the insulation effect of β-CD towards the oxidation by iodine of polyaniline, as well as on the effect of Cyclodextrin in inducing a change form the coil to the rod conformation of the polymer.

The present work aims to investigate in more detail, by means of resonance Raman, FTIR and X-ray diffraction techniques, the inclusion compound formed by β-CD and polyaniline as well as the effects of HCl and iodine vapours on the inclusion compound.

EXPERIMENTAL

PANI was prepared from the monomer, aniline, using the procedure described in the literature [5]. Emeraldine base (EB) was obtained from emeraldine salt by neutralization with NaOH aqueous solution. The inclusion compound was prepared by dissolving EB in N-methyl pyrrolidone (0.5 mg/mL) and this solution added to a saturated aqueous solution of β-CD. After three days it is observable the formation of precipitation nuclei and after five days the inclusion compound precipitates in the form of a blue fine powder that was filtered, washed with cold water and dried in a dissecator.

A mechanical mixture of EB and β-CD was prepared for comparison purposes, by mixing the two components in a 1:1000 ratio.

The IR spectra were obtained using a BOMEN MB-100 instrument and the sample dispersed in a KBr pellet. The X-ray powder diffractograms were obtained in a Phillips MPD-1880 diffractometer. The Raman spectra were obtained in Renishaw Raman Imaging Microscope system 3000, provided with an Olympus microscope and a CCD detector. Spectra were obtained with the 632.8 nm and 488.0 nm laser lines.

RESULTS AND DISCUSSION

The X-ray powder diffractograms of the inclusion compound (a), mechanical mixture of β-CD and EB (b), β-CD (c) and emeraldine base (d) are overlayed in figure 1, and as it can be observed there are new peaks in the diffractogram of the inclusion compound revealing that a new crystalline phase is formed. It should also be noticed that the inclusion compound is neatly crystalline despite the fact that polymer is mostly amorphous.

The FTIR spectrum in the 4000-2800 cm^{-1} region of β-CD, mechanical mixture (β-CD +EB) and inclusion compound are shown overlayed in figure 2. The fact to be highlighted is the substantial decrease in the integrated intensity of the band due to the OH stretching mode of water in the inclusion compound compared to its intensity in neat β-CD.

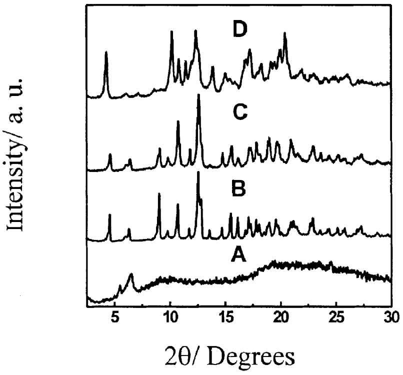

FIGURE 1 X-ray diffractograms of (A) IC, (B) Mechanical mixture, (C) β-CD and (D) EB.

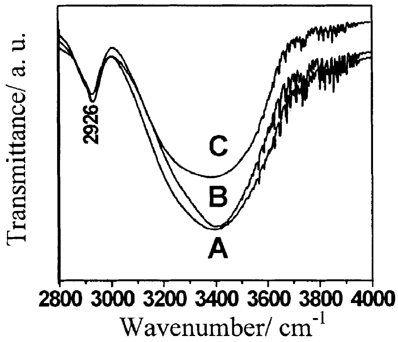

FIGURE 2 FTIR spectra of (A) β-CD, (B) Mechanical mixture and (C) Inclusion compound.

It is well known that the CD's cavities are normally filled with water molecules that have to be expelled for the inclusion of the guest molecules [6].

Figure 3 shows the Raman spectrum of the inclusion compound excited at 488.0 nm, and the Raman spectra excited at 632.8 nm of the inclusion compound (b), EB (c) and β-CD (d). As can be easily observed, excitation at resonance (632.8 nm) greatly enhances several EB vibrational modes, with no sign of the β-CD modes.

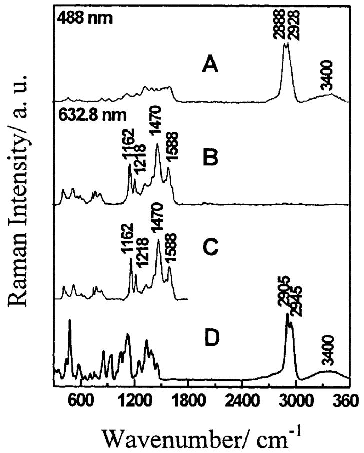

FIGURE 3 Resonance Raman spectra at λ_0=488.0 nm of (A) IC and λ_0=632.8 nm of (B) IC, (C) Mechanical mixture and (D) β-CD.

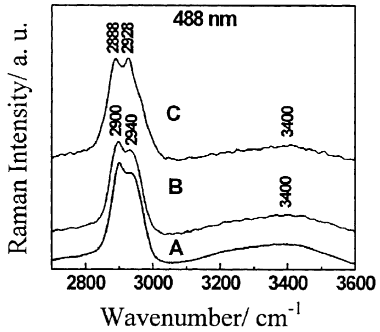

FIGURE 4 Resonance Raman spectra at λ_0=488 nm of (A) β-CD, (B) Mechanical mixture and (C) inclusion compound.

On the other hand, with excitation at 488.0 nm the EB modes are hardly seen and the β-CD modes in the inclusion compound show-up clearly. The 2800-3800 cm^{-1} region is expanded in figure 4 where the Raman spectra excited at 488.0 nm of (a) neat β-CD, (b) mechanical mixture and (c) inclusion compound are shown. It should be noticed that there is both a frequency shift and a change of relative intensities in the doublet at ca. 2900 cm^{-1} when one compares the inclusion compound with β-CD or the mechanical mixture. This is a further indication that the inclusion involves the interaction of the guest molecule with the interior of the β-CD cavity.

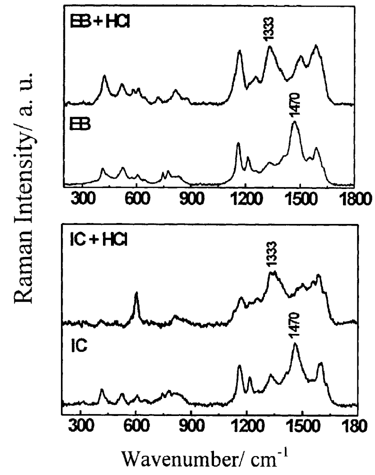

FIGURE 5 Resonance Raman spectra at λ_0=632.8 nm of EB and IC, after and before, exposure to HCl vapours.

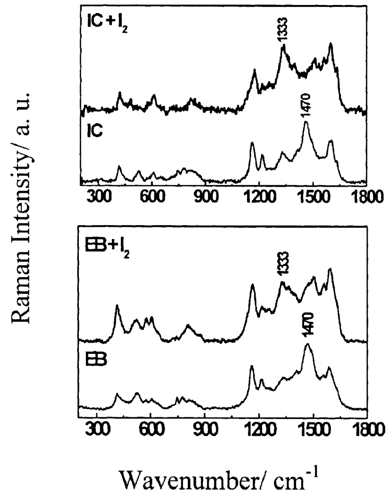

FIGURE 6 Resonance Raman spectra at λ_0=632.8 nm of EB and IC, after and before, exposure to iodine vapours.

The effects of exposing the inclusion compound to HCl and iodine vapours are shown in figure 5 and 6, respectively. Figure 5 shows for comparison purposes the Raman spectra of EB and inclusion componds before and after exposure to HCL vapours. As can be observed the 1480 cm^{-1} band of EB decreases in intensity and the one at 1330 cm^{-1} increases drastically. The same trend is observed in the spectrum of the inclusion compound revealing that inclusion does not preclude the doping effect.

Figure 6 shows the same behavior with relation to iodine vapours.Summing up, the inclusion of EB in β-CD leads to a new crystalline form that correspond to the thread of several β-CD units around the EB polymeric chain. On the other hand, in the inclusion compound EB is not completely encapsulated as shown by the doping effect of HCl or iodine vapours.

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