Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Structure 744–747 (2005) 75–78

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

# The SERS spectrum of 1,2-diaminoanthraquinone studied on silver colloid

José Guilherme S. Lopes, Paulo S. Santos*

*Laboratório de Espectroscopia Molecular, Instituto de Química, Universidade de São Paulo, Instituto do Milênio de Materiais Complexos,*
*Caixa Postal 26077, Cep 05513-970, São Paulo, SP, Brazil*

Received 6 September 2004; revised 3 December 2004; accepted 3 December 2004

## Abstract

1,2-Diaminoanthraquinone (1,2-DAAQ) was recently shown to recognize several anions selectively. In the presence of fluoride, it gives origin to a strongly coloured solution, as a consequence of a strong absorption band at ca. 550 nm. The detailed nature of such interaction is not known, although there are evidences for the formation of a hydrogen bonding involving the anion and the amino moieties. In particular, the use of resonance Raman spectroscopy, that would be one of techniques of choice for unveiling the nature of the chromophoric moiety responsible for the coloured solutions of 1,2-DAAQ with anions, is precluded by the intense fluorescence over the visible region. In the present work the SERS technique using silver colloid was employed to overcome such difficulties, besides aiming to reveal the interaction site of 1,2-DAAQ with the surface of the silver colloidal particles.

In this work it was possible to determine that the site of the 1,2-DAAQ/$F^-$ interaction is one of the amino moieties of the molecule. Such interaction involves a hydrogen bonding of moderate strength. As a consequence of such interaction, the CT transition involving the amino moiety and the $\pi$ system of 1,2-DAAQ is shifted to lower energies. In the presence of 1,2-DAAQ it appears two new bands at ca. 530 and 405 nm in the silver colloidal solution, assigned to silver aggregates of different sizes. Excitation of the SERS spectra at several wavelengths show that depending on the closeness of the excitation to the CT transition of 1,2-DAAQ, the RR contribution to the SERS enhancement can be significant.

The outstanding solvatochromic behavior of 1,2-DAAQ, as shown by its UV–Vis spectra in several solvents, is not reflected in the SERS spectra at two different solvents (dichloromethane and acetonitrile) that show slight differences both in frequency values and relative intensities.

*Keywords:* 1,2-Diaminoanthraquinone; Silver colloid; SERS; Anion sensor; Solvent effect and hydrogen bonding

## 1. Introduction

Although several cation recognizing species, like crown ethers, are know since long, the corresponding anion recognizing molecules are much more rare to find, and only in recent years received due attention [1].

Recently 1,2-diaminoanthraquinone (1,2-DAAQ) (Fig. 1) and related molecules have been investigated as species that recognize selectively several anions in organic solvents [2]. The interaction of 1,2-DAAQ with $F^-$, for instance, in solvents like dichloromethane or acetonitrile, gives origin to a strongly coloured solution. It has been proposed that such behavior results from the ionochromic shift of the band of 1,2-DAAQ at ca. 478 nm in dichloromethane to ca. 550 nm in the presence of fluoride. However, the nature of the specific interaction responsible for such substantial shift is unknown. The present work represents part of the effort aimed to clarify the nature of such interaction, making use of vibrational spectroscopy, and more particularly the SERS technique. The IR absorption spectrum of 1,2-DAAQ in dichloromethane in the presence of fluoride, with special care for the absence of water, shows conclusively that a hydrogen bonding involving the amino groups and the anion is present, as indicated by the shift of ca. 480 $cm^{-1}$ in the $NH_2$ anti-symmetric stretching mode.

Besides the scarcity of IR and Raman data on 1,2-DAAQ and related molecules, 1,2-DAAQ is strongly fluorescent,

---

* Corresponding author. Tel.: +55 11 3091 2163; fax: +55 11 3091 3890.

*E-mail address:* pssantos@iq.usp.br (P.S. Santos).

0022-2860/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2004.12.008

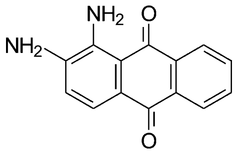

Fig. 1. 1,2-Diaminoanthraquinone (1,2-DAAQ) structure.

particularly in solution, what precludes the obtention of its Raman spectrum using conventional techniques. Such difficulty was overcome by the use of the SERS technique using a silver colloid. In the course of the present work it became clear that 1,2-DAAQ in the presence of silver colloid shows a substantial surface enhancement of its Raman spectrum. With the addition of 1,2-DAAQ to the silver colloid new absorption features at ca. 530 and 405 nm appear, as broad bands, that are assigned to surface plasmons of the metallic particles [3].

One of the outstanding features of 1,2-DAAQ is its substantial solvatochromism, whose origin is the shift of its strong CT band that, for instance, appears at ca. 478 nm in dichloromethane, at ca. 500 nm in acetonitrile and at ca. 538 nm in dimethylsulfoxyde. The molecular moieties more likely to be solvated are the very same more likely to interact with the colloid particles. In fact the SERS spectra of 1,2-DAAQ in dichloromethane and acetonitrile show just slight differences. The influence of the nature of the solvent on the molecular moieties that are preferentially enhanced in the SERS spectrum on a silver electrode has been recently investigated [4].

## 2. Experimental

The reagents 1,2-diaminoanthraquinone (1,2-DAAQ) and tetrabuthylammonium fluoride were purchased from Aldrich and used without further purification. The solvents were treated and dried before use, and the silver colloid prepared according to the procedure described by Creighton et al. [3].

Visible–UV spectra were obtained in a Shimadzu UV-3101PC spectrophotometer using a quartz cell of 1 mm pathlength. IR spectra were obtained in a Bomem MB-series using a liquid cell with ZnS windows and a 0.5 mm spacer. The Raman spectra were obtained in a Jobin Yvon U1000, consisting of a double monochromator equipped with a photomultiplier as detector. The laser lines used were from $Ar^+$ and $Kr^+$ lasers and the spectral resolution set at $5\ cm^{-1}$.

The IR spectra of saturated solutions of 1,2-DAAQ in dichloromethane, with and without fluoride were obtained after a careful treatment that minimizes the presence of water. More specifically, the dichloromethane solution containing tetrabuthylammonium fluoride was treated with a 4 Å molecular sieve, overnight. Only when the IR spectrum of this solution indicated the absence of water was 1,2-DAAQ added.

In the present work the SERS spectra on silver colloids were obtained by the mixture of a 1,2-DAAQ $1\times10^{-4}$ mol $L^{-1}$ acetonitrile solution with a silver colloid (3:1 v/v) or, alternatively by the extraction of 1,2-DAAQ ($1\times10^{-4}$ mol $L^{-1}$ in dichloromethane) to a silver colloid solution. In detail, the extraction procedure consists of shaking for ca. 15 min the silver colloid solution with 1,2-DAAQ dissolved in dichloromethane, what leads to the controlled aggregation of the silver colloid particles. By the use of UV–Vis spectroscopy the concentration of 1,2-DAAQ that is extracted to the colloidal solutions is estimated to be in the ($10^{-8}$–$10^{-10}$) mol $L^{-1}$ range.

## 3. Results and discussion

Fig. 2(a)–(d) shows, respectively, the UV–Vis spectrum of: 1,2-DAAQ in dichloromethane (a), 1,2-DAAQ in dichloromethane in the presence of fluoride (b), the silver colloid solution (c) and of the silver colloid in the presence of 1,2-DAAQ (d).

As can be seen in Fig. 2(a) and (b), the presence of fluoride gives origin to a strong band at ca. 550 nm, that can be understood as the shift of the band at 478 nm in the absence of fluoride. As revealed by the IR spectrum, Fig. 3, the interaction site of 1,2-DAAQ with fluoride is the amino group. In fact, 1,2-DAAQ contains two non-equivalent amino groups, but within the present results it is not possible to conclude which of them is involved in the interaction with the anion. On the other hand, the fact that fluoride causes a very substantial ionochromic shift of the CT transition of 1,2-DAAQ, suggests that such transition is very likely from the amino group to the π delocalized system of the molecule. The assignment of the electronic spectrum of 1,2-DAAQ has not yet been discussed in the literature, although the spectrum of 1,5-dihydroxy-anthraquinone has

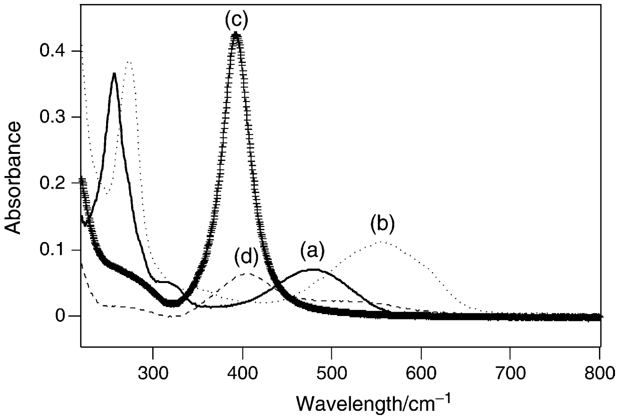

Fig. 2. UV–Vis spectra of: 1,2-DAAQ in dichloromethane (a); 1,2-DAAQ in dichloromethane in the presence of fluoride (b); the silver colloid solution (c) and the silver colloid in the presence of 1,2-DAAQ/$H_2CCl_2$ (d).