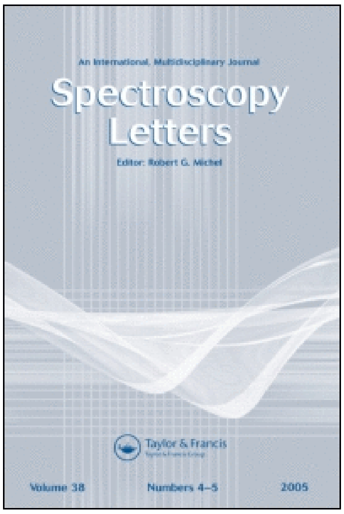

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STUDY OF PH DEPENDENCE OF 2-MERCAPTOBENZOTHIAZOLE BY SURFACE ENHANCED FT-RAMAN SCATTERING

Keywords: 2-mercaptobenzothiazole, chemisorption, Fourier transform surface enhanced Raman scattering (FT-SERS), silver surface.

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ABSTRACT

Fourier transform surface enhanced Raman spectrometer is used to characterize 2-mercaptobenzothiazole chemisorbed on silver surface from its aqueous solution of different pH values. The adsorbent conformation which determines its protection ability can change with pH value.

INTRODUCTION

Since the pioneering works by Fleischmann [1], Van Duyne [2], and Creight, surface enhanced Raman scattering (SERS) has found widely application in the characterization of a monolayer or sub-monolayer of adsorbed molecules on metal surface. In addition to the electrochemically roughened silver electrode, on which this phenomenon was first discovered, metal surfaces prepared by various processes have been employed for the measurements of the SERS spectra. Up to now, there are many methods to obtain a SERS-active substrate, which include metal sols [3], vacuum-deposited metal island films [4], and HNO_3 etched metal foils [5,6].

Organic sulfur derivatives coordinate strongly to some metal surfaces and form monomolecular film. Nuzzo and Allara showed that dialkyl disulfides formed oriented monolayer on metal from solutions [7]. The monolayer has well-organized microscopic characteristics and endows the attached metals with many special properties such as wetting, adhesion, and anti-corrosion. Up to now there are many problems to be solved about the relation of adsorbent state to its macro-property.

In this study we used silver film as substrate to investigate the chemical adsorption of 2-mercaptobenzothiazole in different pH value aqueous solutions with a fluorescence-free Fourier transform Raman spectrometer.

EXPERIMENTAL

Materials 2-mercaptobenzothiazole was obtained as a high-grade commercial reagent and was used without further purification (purity 99.9%). All other chemicals are analytical reagents.

Sampling methods of 2-mercaptobenzothiazole At room temperature, 10 ml 0.1-0.2 M silver ammonia complex was mixed with 5 ml 5% formaldehyde in a beaker, containing a few of pieces of clean glass plate (10-mm×10-mm×1-mm), a few of seconds later, the solution turns to gray and silver ions are reduced onto the plate to form a fine silver film. The thickness of silver film can be adjusted by controlling reaction time or temperature. Higher temperature and longer reaction time benefit thicker silver film. After withdrawing, the silver film is washed with distilled water and then dipped in 0.001 M 2-mercaptobenzothiazole aqueous solution. The pH value of the solution is adjusted by HCl or NaOH aqueous solution. The spectra are recorded 5 min. later after the change of pH value.

FT-Raman and FT-SERS spectroscopy measurement The spectra are recorded with a Bruker model RFS 100 Fourier Raman spectrometer with an air-cooled diode pumped Nd-YAG laser, and Ge-detector, cooled to liquid nitrogen temperature. The incident laser excitation is 1064 nm. The outputs are 30 and 350 mW for normal FT-Raman and FT-SERS measurement, respectively. The resolution is 4.0 cm^{-1}. The FT-SERS samples are dipped in the solution and recorded. There is a distance of 1 mm solution between the SERS sample surface and sample cell inside wall to ensure that there is fast adsorption equilibrium. The scattered light is collected at the angle of 180°.

RESULTS AND DISCUSSION

MBT is wisely used in the metal protection as corrosion inhibitor because it can easily ordinate metal. It can be adsorbed on silver, gold and copper electrode to form an assembled monolayer film [8, 9]. FIG.1 displays the FT-Raman spectrum of neat MBT (A) and its sodium salt solution (B). In FIG.1A the bands at 1495, 1252, 1130 cm^{-1} are due to the thione[9], the 1029 cm^{-1} band is caused by the C=S stretching vibration and it is lower than the normal C=S double bond because of the electron attraction of nitrogen. These bands disappear or get weak in the spectrum (FIG.1B) of the sodium salt solution. The band at 1392 cm^{-1} is characteristic of the N=C-S vibration. There is a broad band in the range of 300-450 cm^{-1}, which is caused by water. FIG.2 shows the FT-SERS spectra MBT adsorbed on silver surface. In FIG.2, the pH values of samples in A, B, C, D, E, F, G are 12, 10, 8, 6, 3, 2, 1, respectively. By comparison of FIG.1B and FIG.2 A thorough D, we find the SERS spectra are in fair agreement with that of sodium MBT solution except the relative intensity of bands. This similarity suggests the adsorbed MBT in neutral and basic medium and weak acidic medium (pH=6) is in the same form as the ionized thiol.

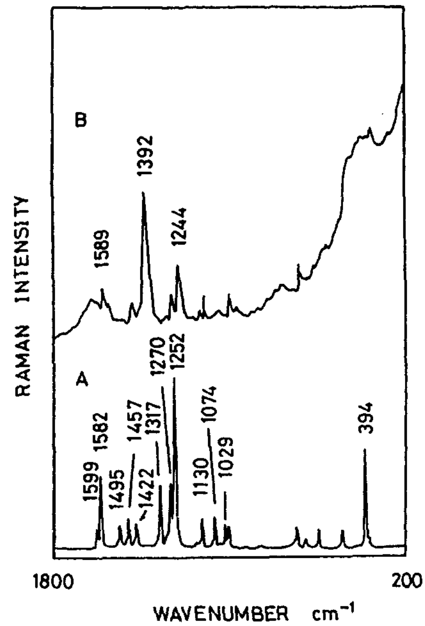

FIG.1 FT-Raman spectra of 2-mercaptobenzothiazole (A) and its sodium salt aqueous solution (B).

In aqueous solution MBT can exit in two forms, thiol or thione, just as displayed in FIG.3. The conformation can transform mutually, and is affected by the acidity. In FIG.1, the band at 1495, 1252 cm^{-1} and 1130 cm^{-1} are due to the vibration of thione. C=S stretching vibration can be observed at 1074 cm^{-1}, which is frequently lower than normal S=C bands because of the nitrogen attraction. The characteristic bands of thione in FIG.1B and, FIG.2A though 2E get weak, even disappear when MBT is in basic solution or is adsorbed on silver film from non-acidic solution.

An interesting phenomenon is the conformation change of 2-mercaptobenzothiazole attached to the silver surface with the variation of pH value. In FIG.2 the band at 1390 cm^{-1} due to N=C-S vibration loses

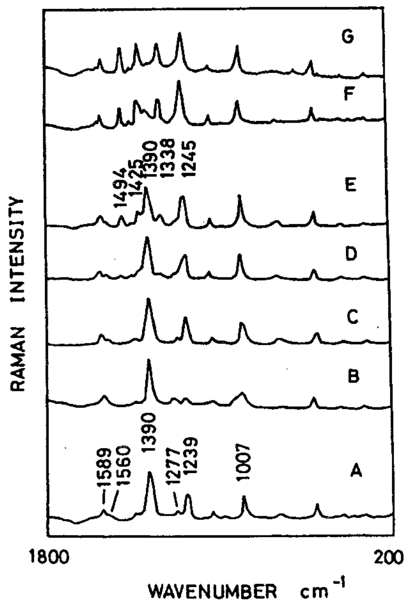

FIG.2 FT-SERS spectra of 2-mercaptobenzothiazole adsorbed on silver surface in different pH values, the pH value is 12, 10, 8, 6, 3, 2, 1 for A through G, respectively.

intensity, even disappears finally, while the band 1239 cm^{-1} which is attributed to the vibration of HN-C=S, gains intensity, and the bands at 1495, 1252 cm^{-1} and 1132 cm^{-1} due to thioacid amide gain intensity. When the pH value reaches 1, the adsorbed MBT thiol is isomerized to thione. During this process the band at 1599 cm^{-1} and 1582 cm^{-1} due to benzene ring in-plane vibration in FIG.1A have shifted to 1584 cm^{-1} and 1560 cm^{-1} and they undergo a continuous change, the former gets weak, and the later becomes intense. This is perhaps caused by the quaterization of nitrogen, which destroys the heterocylic ring, resulting in the change of adsorption state of the benzene ring. In FIG.2, the band at 1007 cm^{-1} is due to benzene ring in-plane breathing vibration; the band at 714 $cm^{-1}$was caused by the

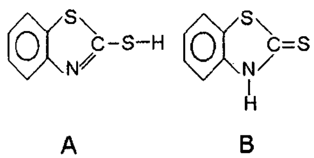

FIG.3 Structure of 2-mercaptobenzothiol (MBT) in aqueous solution, A: thiol, B:thione.

vibration of benzene ring out-of-plane. The intensity ratio of the band 1007 cm^{-1} to 714 cm^{-1} become larger with the decrease of pH value, which suggests that MBT tends to be adsorbed with the benzene ring perpendicular to the silver surface. This is harmful to the metal protection because of the disorderly arrangement of the benzene rings.

When the adsorbed MBT lies on surface with its molecular plane, the surface arrangement can obstruct the corrosion of harmful ions. In acidic medium MBT loses part of the ability to protect metal because of the perpendicular conformation.

The acid effect can also be observed in MBT adsorbed on copper surfaces and it is reversible. Now most circulating water operates as a weak basic medium, this is in agreement with the protection ability of MBT to the covered metal surface.

CONCLUSION

Fourier transform surface enhanced Raman scattering spectroscopy (FT-SERS) was used to characterized MBT adsorbed on silver surface. The normal FT-Raman and FT-SERS spectra lead to the conclusion that MBT can be adsorbed on the silver surface to form monolayers of their thiolates. The adsorption state is affected by pH value. In basic and weak acidic medium MBT is adsorbed in thiol, and in acid medium MBT tends to be adsorbed in thione. In basic medium MBT lies on the silver surface which is good for metal protection.

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