

Surface-enhanced Raman scattering and cyclic voltammetry studies of synergetic effects in the corrosion inhibition of copper by polybenzimidazole and mercaptobenzimidazole at high temperature

K. T. CARRON, M. L. LEWIS

Department of Chemistry, Wyoming University, Laramie, WY 82071, USA

JIAN DONG, JIANFU DING, GI XUE* and YU CHEN

Department of Chemistry, Nanjing University, Nanjing 210 008, People's Republic of China

The inhibition of copper corrosion by polybenzimidazole and mercaptobenzimidazole at room and high temperature was assessed by *in situ* surface-enhanced Raman scattering (SERS) and cyclic voltammetry (CV). It was found that a very compact protective layer, produced by immersion in polybenzimidazole and mercaptobenzimidazole mixture solutions, showed better anticorrosive performance than each single inhibitor component even at high temperatures. This synergetic effect of the two components was explained by the physico-chemical mechanism of corrosion inhibition of polymeric coatings. Meanwhile, the results implied that the SERS active substrate prepared by the HNO₃ etching method was particularly useful for *in situ* characterization of many problems in high-temperature surface chemistry which otherwise could not be accomplished by the usual SERS active substrates.

1. Introduction

Mercaptobenzimidazole (MBIH) is a powerful corrosion inhibitor for copper immersed in solution, i.e. metal attack by a variety of corrosive media is strongly reduced in the presence of dissolved MBIH. Early studies of its chemical behaviour on copper surfaces did not reveal the exact inhibition mechanism [1–3]. Investigations by spectroscopic and electrochemical methods on the chemisorption of MBIH on a freshly etched surface of copper metal found that MBIH reacted readily with the metal to form mercaptoimidazolates [4, 5]. Under acidic, alkaline and some other severe conditions, the complex film shows attractive anti-corrosive behaviour.

Recently, there has been great emphasis in using polymers as corrosive inhibitors [6], for example, different heterocyclic polymers, polythiopropionate, polymaleic acid and polyalkyloamide/alkenyl copolymers were developed for protecting steel in sea water, tap water, in acidic environments, etc. Relatively few polymeric inhibitors for copper have been reported, especially in high-temperature studies. Poly-*N*-vinylimidazole and poly-4-vinylimidazole were demonstrated to be effective anticorrosive agents for copper [7]. In this study, a two-component inhibitor, of polybenzimidazole (PBIMH) mixed with MBIH, for copper at elevated temperatures is reported. The rea-

sons why PBIMH is preferred are as follows. PBIMHs have imidazole rings which tend to form complexes with the metal surface [8–11]. The polymer can easily form thin films of relatively higher stability than small molecules on a copper surface. It is known that the higher stability would enhance the adhesion of the film to the substrate.

In the present work, surface-enhanced Raman scattering (SERS), and cyclic voltammetry (CV) were utilized to characterize the adsorbed layers on the copper surface. Vibrations of the adsorbed species on incidence of electromagnetic radiation give rise to characteristic frequencies that serve as fingerprints for the identification of the adsorbed species. SERS is also ideal for probing the interfaces between polymer films and metallic substrates, as long as the films are not so thick that normal Raman scattering from the bulk of the polymer is more intense than SERS from the interface [12]. As far as we know, there are difficulties in conducting SERS experiments under high temperature. It is impossible for electrochemically roughened electrodes or metal colloids to exhibit *in situ* SERS effect well above 100°C, because these two systems require a water medium. In contrast, HNO₃-etched metal foils show stable SERS effect at high temperature, unlike vacuum-deposited metal-island films. This point, which has been demonstrated in a previous

*Author to whom all correspondence should be addressed.

work [13], also makes it possible for us to take advantage of the *in situ* SERS technique to study the temperature effect on the corrosion inhibition of organic coatings. Therefore, a further aim of this work was to apply this surface-sensitive spectroscopy in high-temperature studies.

2. Experimental procedure

PBIMH and MBIH were purchased from Aldrich Chemical Co. SERS active copper substrates (0.025 mm thick) were prepared by etching in HNO_3 solution as described previously [14, 15]. Corrosion inhibitors were dissolved in ethanol or *N,N*-dimethylformamide (DMF), solution-cast on to freshly etched copper substrates, and air dried. A heating cell was mounted in a SPEX-1401 Raman spectrometer for high-temperature studies. The incident laser excitation was the 647.1 nm line from a Kr^+ laser source.

Cyclic voltammetry was performed using a Model 79-1 voltammeter. A saturated calomel electrode (SCE) served as the reference electrode and a platinum wire was used as counter electrode. Sweeping in a one-compartment cell in this work was at a rate of 250 mV s^{-1} in acetate buffer solution pH 6.0, $[\text{Na}^+] = 1.0 \text{ M}$.

3. Results and discussion

3.1. SERS study on PBIMH and MBIH coatings on copper

Fig. 1a is a room-temperature SERS spectrum of PBIMH chemisorbed on a copper surface. All the Raman bands appearing can be assigned to vibrational modes of PBIMH if compared with the similar spectrum of PBIMH on a silver substrate [16], except in the region of $400\text{--}630 \text{ cm}^{-1}$. The very broad band ranging from $400\text{--}630 \text{ cm}^{-1}$ shown in the present copper substrate spectrum is attributed to a metal surface oxide [17, 18]. No observable signals can be detected in this region in the first 3 min after chemically cleaning the copper surface. Therefore, the onset and the intensity of the oxide band was monitored as a measure of the surface oxidation of copper substrates with films of either PBIMH or MBIH cast on to the surface, and discussion will be centred on this vibrational frequency region in the following studies.

The appearance of oxide bands in the copper SERS spectrum implies that a PBIMH-covered surface does not possess substantial resistance to oxygen permeation. It is obvious that oxygen permeability decreases with decreasing chain mobility, e.g. by cross-linking, by decreasing the hydrophilic character of the macromolecules and by increasing the density of molecular pack-up to crystalline structures. Even though the PBIMH chain is rigid, it cannot suppress oxidation even at room temperature. This may be due to the fact that there are pinholes on the metal surface that are not covered by the polymer.

Upon heating to 200°C for 8 h, the oxide band intensity became more prominent (Fig. 1b), indicating acceleration of surface oxidation. It is noticeable that

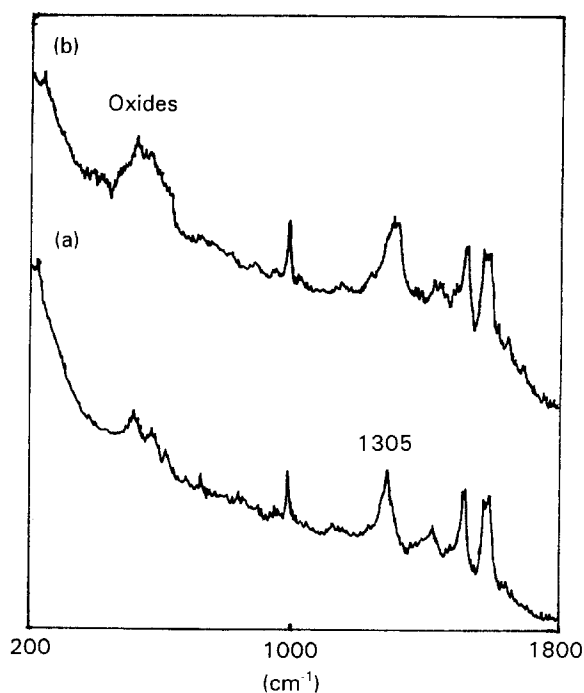


Figure 1 SERS spectra of polybenzimidazole on copper foil, (a) at room temperature, (b) heated to 200°C for 8 h.

the SERS effect remains so strong at this temperature that Raman signals originating from adsorbed PBIMH are still of high quality. Preliminary work on HNO_3 -etched silver foils showed that this kind of SERS active substrate possesses satisfactory thermal stability at a relatively high temperature [13]. Because many catalytic reactions occur at high temperatures, SERS on HNO_3 etched metal foils seems to be a very promising technique for mechanistic studies of the reactions.

Fig. 2a shows the room-temperature SERS spectrum of MBIH on a copper surface. Oxide bands were undetectable simply because of the powerful anticorrosive property of MBIH. We have postulated that MBIH can react with the copper surface in the presence of oxygen, yielding cuprous mercaptobenzimidazolate compactly covering the surface [4, 5] (see Fig. 3). However, the surface reaction product is brittle and can be destroyed easily upon heating. Fig. 2b shows that copper oxide films grew rapidly after the MBIH cast foils had been heated at 200°C for 1 h. If the Cu^+ MBI^- film was heat resistant, one would expect some oxidation inhibition under elevated temperature. This prompts us to utilize polymeric materials to overcome this weakness as long as polymer degradation does not commence under the applied temperature. PBIMH is well known for its heat resistance. A simple method for employing PBIMH is mixing with MBIH.

Fig. 4a shows a room-temperature SERS spectrum of PBIMH and MBIH coadsorbed from a solution of their mixture. Here a HNO_3 -etched copper foil was first pretreated in a 1% DMF solution of PBIMH for 5 min, then in a DMF mixed solution of 1% PBIMH and MBIH for 1 min. No oxide bands were detected on the copper surface. The distinction between Fig. 4a and Fig. 1a is the appearance of a strong 1286 cm^{-1} band due to the adsorption of MBIH. Other bands, for example, the 1305 cm^{-1} band in

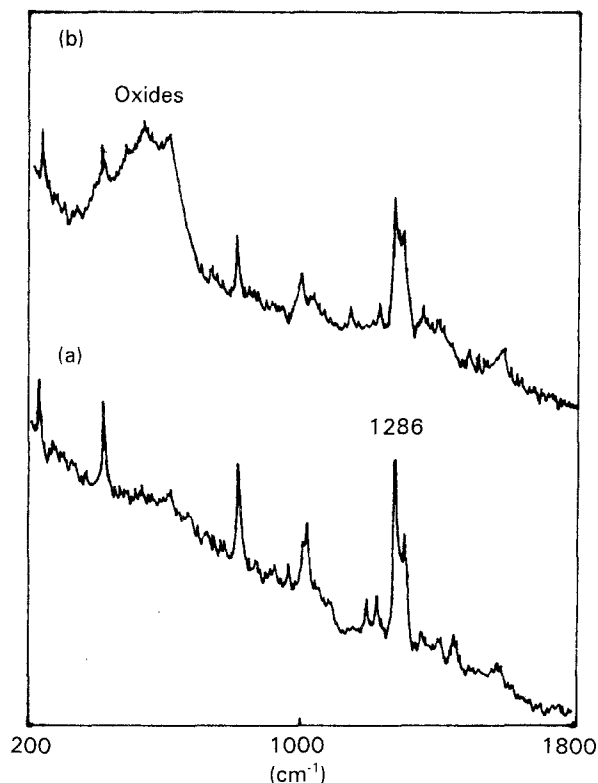
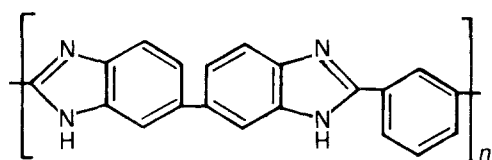
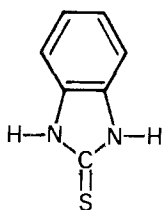


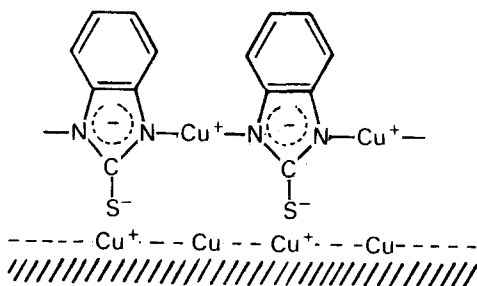
Figure 2 SERS spectra of mercaptobenzimidazole on copper, (a) at room temperature, (b) heated to 200 °C for 1 h.



(a)



(b)



(c)

Figure 3 Chemical formulae of (a) PBIMH, (b) MBIH and (c) the surface reaction product of MBIH with copper surface, cuprous mercaptobenzimidazolate.

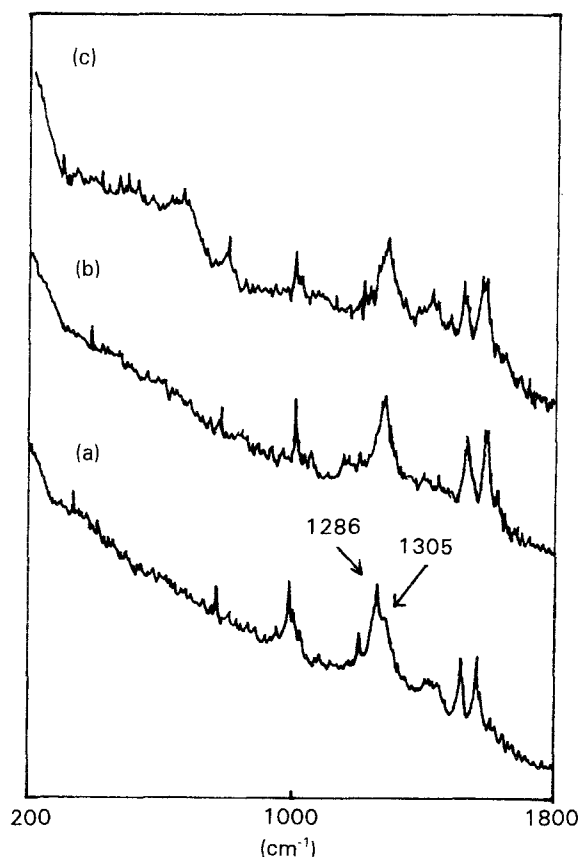


Figure 4 SERS spectra of copper pretreated with PBIMH and MBIH, (a) at room temperature, (b) heated to 200 °C for 10 h, (c) heated to 200 °C for 125 h.

Fig. 3a, may be attributed to those from PBIMH. As illustrated in Fig. 3a, oxidation cannot be suppressed by PBIMH. We therefore conclude that the surface loci left by PBIMH have been filled with MBIH.

Fig. 4b shows that oxide film formation did not occur even when the treated copper had been heated to 200 °C for 10 h. This property is very important, because copper surfaces treated with either PBIMH or MBIH alone oxidize in 1 h at 200 °C. This corrosion inhibition effect is synergistic and may be explained by the physicochemical mechanism of corrosion protection by organic coatings [19]. The physicochemical mechanism consists in blocking the diffusion of corrosive agents, such as water and oxygen, and of corrosion stimulants. This barrier action of organic coatings may be enhanced significantly by fillers, pigments or extenders which greatly increase the length of diffusional pathways through the cross-section of the coating films. It has been confirmed, therefore, that MBIH is prone to react with copper surface under mild conditions [4, 5], and the surface reaction product, cuprous mercaptobenzimidazolate, produced in the interfacial region, acted as a barrier and greatly retarded the oxidation. This was ascertained by a prolonged heating test in which oxide bands were ultimately observable after heating at 200 °C for 125 h, as shown in Fig. 4c.

3.2. CV measurement of PBIMH and MBIH coatings on copper

A further electrochemical study, complementary to SERS measurements, was carried out using cyclic

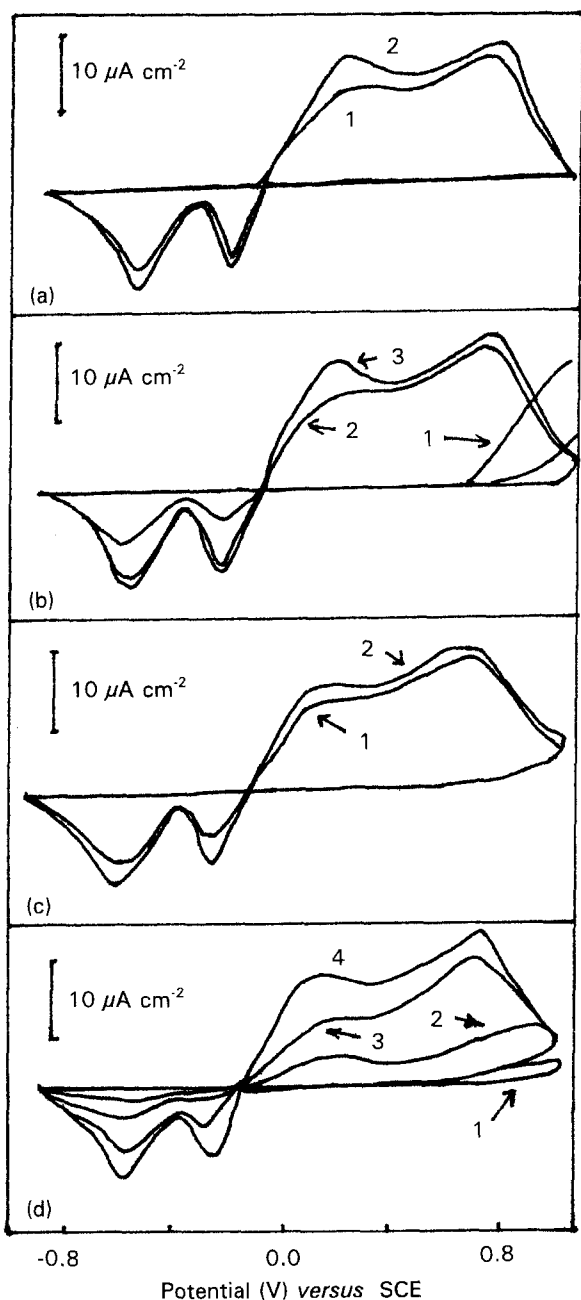


Figure 5 Cyclic voltammetry of copper pre-treated with (a) nitric acid, (b) MBIH solution for 15s, (c) PBIMH solution for 15s, (d) PBIMH and MBIH solution for 15s. The numbers indicate the scan number.

voltammetry (CV). The CV of bare copper electrode which had been etched by HNO_3 was characterized by two major peaks, each apparently associated with a multiple electrode process, as suggested by the shape and structure of the peaks (Fig. 5a). In acetate buffer at pH 6.0, the production of Cu_2O or CuO_2^{2-} leads ultimately to the formation of Cu^{2+} in solution. The first oxidation peak is associated with the formation of Cu_2O and the second peak corresponds to the production of CuO and/or $\text{Cu}(\text{OH})_2$. On the reverse scan, the first reduction peak involves the reduction of Cu^{2+} to Cu^+ species and successive peaks correspond to complex reduction reactions producing Cu^0 . The results agree with the conclusions drawn in previous investigations [20, 21].

Prior immersion of the copper electrode in MBIH for 15s results in the initial sweep voltammogram

shown in Fig. 5b. On the second and successive sweeps after immersion treatment, the currents of the first oxidation peak ($\text{Cu}^0 \rightarrow \text{Cu}^+$) increase relative to the second oxidation peak ($\text{Cu}^+ \rightarrow \text{Cu}^{2+}$), and the peak currents observed on the reverse sweep increase in magnitude. In the initial sweep the reaction $\text{Cu}^0 \rightarrow \text{Cu}^+$ is inhibited. The anode current was observed above 0.70 V. This suggests that CuO is the predominant oxidation product on the forward scan. On the reverse scan, the oxide film is at least partially reduced, first to Cu_2O , then to Cu^0 . The film on the surface is removed in the second cycle so that reactions proceed as depicted in Fig. 5a.

The CV obtained from PBIMH pretreated copper electrode is shown in Fig. 5c. This trace is to some extent similar to that in Fig. 5a, indicating oxidation and reduction occurred at the bare portion of the copper surface.

Copper electrode pretreated with PBIMH and MBIH mixture solution produces the CV shown in Fig. 5d. The anodic oxidation reactions of copper were inhibited in the first cycle, and a small anodic current was observable only near the switching potential. This behaviour is more pronounced than that in Fig. 4b. Subsequent cycling resulted in the gradual increase of the anodic and cathodic peaks. However, comparing Fig. 5d with 5b, one finds that the peak currents are much less for copper electrode coadsorbed with PBIMH and MBIH than those for MBIH-modified electrode in their corresponding cycles. This means that the protective mixture coating covered the electrode surface in a much tighter manner, as illustrated by high-temperature SERS results.

4. Conclusion

There is evidence for the production of a very compact protective layer on copper surfaces by immersion in PBIMH and MBIH mixture solutions. This surface-adsorbed layer is a mixture of PBIMH and $\text{Cu}^+ \text{MBI}^-$, either of which shows less corrosion inhibitive properties than their mixture. The synergistic effect can be attributed to the barrier action of the $\text{Cu}^+ \text{MBI}^-$ layer. No complete film coverage would be expected for PBIMH alone. The film of $\text{Cu}^+ \text{MBI}^-$ on copper can be easily destroyed by heating or by repetitive cycling voltammetrically. The protective mixture coating on copper not only covers the surface entirely, but also prevents permeation of oxygen, therefore showing better resistance to heat than the single components. The feature of two-component inhibiting systems is important, because localized corrosion may be inhibited by rebuilding of the protective layer.

Above all else, it must be pointed out that *in situ* SERS on HNO_3 -etched metal foils shows the ability to characterize surface chemistry at high temperature. This feature is also significant, because there are many reactions occurring at relatively high temperatures whose mechanisms might be revealed by SERS, but not by other SERS sampling techniques, such as roughened metal electrodes and aqueous metal sols.

Acknowledgements

This work was partially supported by the National Science Foundation EPSCOR Program, USA (Grant RII-8610680), and by the Coordination Chemistry Laboratory, Nanjing University.

References

1. D. CHADWICK and T. HASHEMI, *Surf. Sci.* **89** (1979) 649.
2. M. K. PATEL, *J. Ind. Chem. Soc.* **54** (1977) 815.
3. D. THIERRY and C. LEYGRAF, *J. Electrochem. Soc.* **132** (1985) 1009.
4. G. XUE, X. HUANG and J. DING, *J. Chem. Soc. Faraday Trans.* **87** (1991) 1229.
5. G. XUE, X. HUANG, J. DONG and J. ZHANG, *J. Electroanal Chem.* **310** (1991) 139.
6. R. A. DICKI and F. L. FLOYD (eds) "Polymeric Materials for Corrosion Control", ACS Symposium Series 322 (American Chemical Society, Washington, DC, 1986).
7. F. P. ENG and H. ISHIDA, *J. Mater. Sci.* **21** (1986) 1561.
8. G. XUE, S. JIANG, X. HUANG and G. SHI, *J. Chem. Soc. Dalton Trans.* (1988) 1487.
9. G. XUE, J. ZHANG, G. SHI and Y. WU, *J. Chem. Soc. Perkin Trans., II* (1989) 33.
10. G. XUE, P. WU, Z. BAO, J. DONG and R. CHENG, *J. Chem. Soc. Chem. Commun.* (1990) 495.
11. G. XUE, Q. DAI and S. JIANG, *J. Am. Chem. Soc.* **110** (1988) 2393.
12. F. J. BOERIO, *Thin Solid Films* **181** (1989) 423.
13. G. XUE and J. DONG, *Anal. Chem.* **63** (1991) 2393.
14. G. XUE, J. DONG and M. ZHANG, *Appl. Spectrosc.* **45** (1991) 756.
15. K. T. CARRON, G. XUE, M. L. LEWIS and LANGMUIR, *ibid.* **7** (1991) 2.
16. G. XUE, J. DONG and J. ZHANG, *Macromolecules* **24** (1991) 4195.
17. N. T. MCDEVITT and W. L. BAUN, *Spectrochim. Acta* **20** (1964) 799.
18. F. J. BOERIO and L. ARMOGAN, *Appl. Spectrosc.* **32** (1978) 509.
19. W. FUNKE, in "Polymeric Materials for Corrosion Control", edited by R. A. Dickie and F. L. Floyd, ACS Symposium Series 322 (American Chemical Society, Washington, DC, 1986) p. 222.
20. C. McRORY-JOY and J. M. ROSAMILIA, *J. Electroanal. Chem.* **136** (1982) 105.
21. D. D. MacDONALD, *J. Electrochem. Soc.* **121** (1974) 651.

Received 30 April 1992
and accepted 11 January 1993