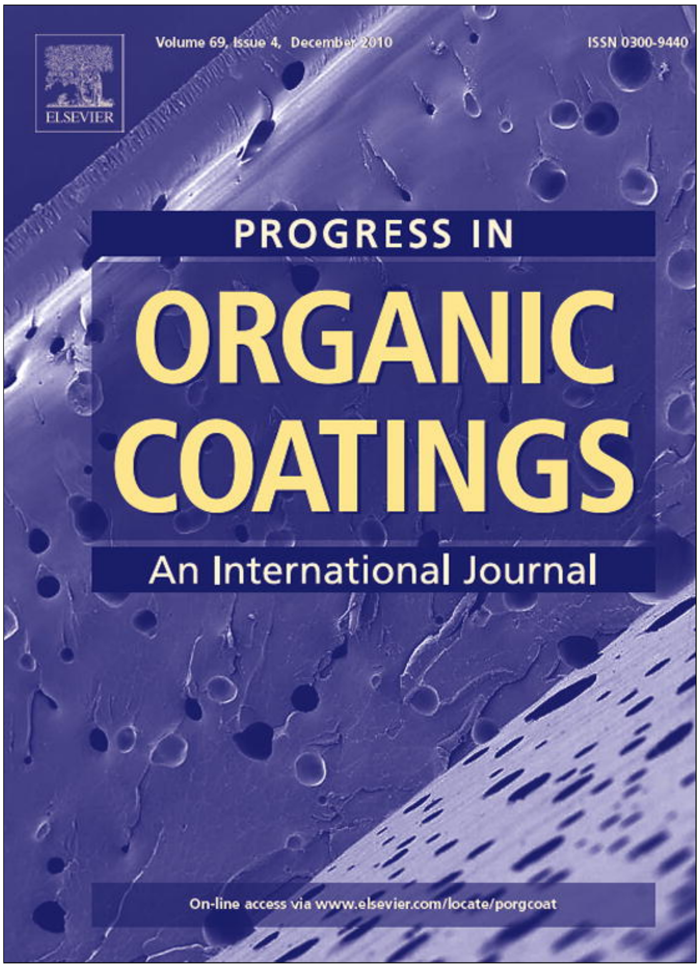

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Corrosion protection mechanisms of carbon steel by an epoxy resin containing indole-3 butyric acid modified clay

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ABSTRACT

This work is an extension of studies into the mechanisms of corrosion protection of mild steel by an epoxy resin containing organically modified clay (Hang et al. [1]; Truc et al. [2]). In a previous study (Truc et al. [2]), it was shown that indole-3 butyric acid (IBA)-modified clay improved the corrosion performance of epoxy. In the present study, it was shown that the IBA is an anodic inhibitor and its efficiency was about 93%. Exfoliation and dispersion of the IBA-modified clay in the epoxy coating were checked by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The improvement of the corrosion performance of the epoxy coating containing IBA-modified clay by comparison with pure epoxy coating was confirmed for a low film thickness (10 μm). Local electrochemical impedance measurements performed on scratched samples revealed the inhibitive action of IBA at the carbon steel/coating interface. It was shown that the inhibitor release from the IBA-modified clay was favoured for high pH values. Thus, in neutral media, the corrosion process which induces a local increase of pH will increase the self-healing performance.

1. Introduction

Mild steels are widely used in fabrication of reaction vessels, building applications, petroleum refinery, and automotive industry. Very sensitive to corrosion phenomena in acid [3–6] and neutral solutions [7–12], the steel is often protected by organic coatings. The coating efficiency is partly dependent on the inhibitive pigments incorporated into the coatings. Due to the problem of high toxicity associated with inhibitive pigments, such as strontium or zinc chromates, various studies have been carried out to develop more acceptable environmentally coatings. The most promising coatings confer self-repairing or self-healing properties. Different studies reported that particles such as hydrotalcite [13], zirconia [14] and silica [15] nanoparticles, porous titanium dioxide films [16] can be used as reservoirs for the storage and prolonged release of the inorganic and/or organic inhibitors. The self-healing ability of these reservoirs was mainly demonstrated on 2024 aluminium alloy substrate [13,14,16]. The interactions between the inhibitor and the nanocarriers can be due to the inhibitor adsorption on the oxide surface [17], cation or anion exchange capacity of containers [18] or by employing the layer-by-layer assembly approach [19]. One of the most important points in the design of new active coatings is to formulate nanocontainers that present good compatibility with the organic matrix that can encapsulate and maintain the active material.

Due to their rich intercalation chemistry, natural clays such as montmorillonite (MMT) can be organically modified in order to be compatible with an organic matrix. By replacing the hydrophilic Na^+ cations with more hydrophobic onium ions such as ammonium cations with long alkyl chains, an increase of the silicate interlayer was observed and concomitantly, the miscibility between organophilic clay and the polymeric matrix was enhanced. This property is widely used to improve mechanical and thermal properties of organic matrix [20–22]. In previous studies [1,2], it was shown that this methodology can be used to improve the corrosion protection of carbon steel by an epoxy resin containing MMT organically modified by organic inhibitors such as aminotrimethylphosphonic acid [1] or indole-3 butyric acid (IBA) [2]. It was seen that the barrier properties of the coatings were significantly improved in the presence of the modified clay by comparison

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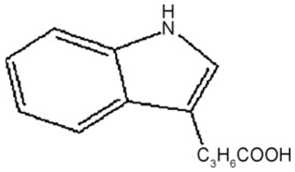


Fig. 1. Molecular structure of indole-3 butyric acid.

with the pure epoxy. In the case of IBA, although only a small quantity was incorporated into the coating, high corrosion protection was afforded.

The present study aims at investigating the inhibitive action of indole-3 butyric acid (IBA) on mild steel using electrochemical techniques. Particularly, the self-healing behaviour will be analysed by local electrochemical impedance spectroscopy (LEIS) and by measurement of the inhibitor release in water for different pH, quantified by total organic carbon content (TOC). Due to acid-basic properties, the IBA release should occur in a large pH range and more particularly when the interfacial pH will increase due to corrosion processes.

2. Experimental

2.1. Materials

To characterize the inhibitive efficiency of IBA, a rod of XC 35 carbon steel of 1 cm^2 cross-sectional area was used as working electrode. Its composition in percentage weight was C = 0.35, Mn = 0.65, Si = 0.25, P = 0.035, S = 0.035 and Fe to 100. A heat-shrinkable sheath left only the tip of the carbon steel cylinder in contact with the solution. For all experiments, the carbon steel samples were polished with SiC paper down to grade 1200, cleaned in permuted water in an ultrasonic bath and dried in warm air.

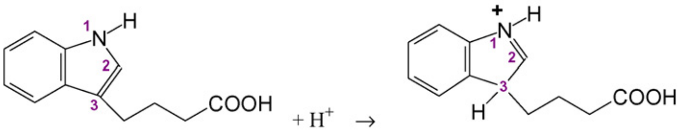
For the coatings, carbon steel sheets (150 mm × 10 mm × 2 mm) were used as substrates. They were polished with abrasive papers from 80 to 600 grades and cleaned with ethanol.

Indole-3 butyric acid (IBA), purchased from Sigma–Aldrich, was used as received. The chemical structure of IBA is shown in Fig. 1. The montmorillonite (MMT) was from Tuy Phong-Binh Thuan province in Vietnam. This clay consisted of a 2/1 ratio of silica to alumina, the swelling degree was 500% and the ion exchange capacity was 100–115 mequiv/100 g.

2.2. IBA modification of the clay

The pristine clay (3.0 g) was dispersed in distilled water (300 ml) containing concentrated hydrochloric acid (0.5 ml) and IBA (7.0 g). Then, the suspension was stirred at 70 °C for 24 h to afford a white precipitate. This precipitate was filtered and washed with water until no chloride was detected in the filtrate using a 0.1 M $AgNO_3$ solution. The IBA-modified clay was then dried at 80 °C in a vacuum oven for 2 days.

The pK_a of the IBA is 4.9 [23] corresponding to a weak acid. It was demonstrated [23] that the probability for the existence of different sites of protonation in alkyl substituted 3-carboxylic indoles is low and at low pH, the protonation occurs only on the indolic 3-carbon. Thus, in acidic medium, due to rearrangement of the π electrons, a positive charge will appear on the nitrogen atom:



The IBA content in the MMT, measured through thermogravimetric analysis was about 10 wt.% [2].

2.3. Coating

The epoxy resin was Epon 828 and the hardener was Epikure 207. Both compounds were purchased from Herison Co. (Germany). The IBA-modified clay was incorporated into the epoxy coating at a concentration of 2 wt.%. This concentration was chosen because in the previous work [1], the best corrosion protection was obtained with 2% clay content. An increase of the modified clay in the coating decreased the barrier properties and did not improve corrosion protection. The liquid paints (pure epoxy and epoxy resin containing IBA-modified clay) were applied by spin coating. After drying (ambient temperature for 24 h) the coatings were about 10 μm thick (measured by a Minitest 600 Erichen digital meter).

2.4. Analytical characterizations

XRD patterns were recorded on Siemens diffractometer D5000 with Cu K_α X-Ray diffraction. Transmission Electron Microscope (TEM) observations were done using a Philips CM200 at 120 kV and with a spot area of 250 nm.

2.5. Electrochemical characterizations

For the classical EIS measurements, a three-electrode cell was used with a large platinum auxiliary electrode, a saturated calomel reference electrode (SCE) and the working electrode with an exposed area of 1 cm^2 for the bare carbon steel and of 28 cm^2 for the coated samples. Anodic and cathodic polarization curves, in the presence and in the absence of IBA, were obtained after 2 h of immersion at a scan rate of 1 $mV\,s^{-1}$ starting from the corrosion potential. The conventional impedance measurements were performed using an Autolab PGstat30 over a frequency range of 100 kHz to 10 mHz with seven points per decade using 10 mV and 30 mV peak-to-peak sinusoidal voltage for the experiments with the bare carbon steel and for the coating, respectively. Local electrochemical impedance spectroscopy (LEIS) was carried out with a Solartron 1275. This method used a five-electrode configuration [24]. For local electrochemical impedance mapping (LEIM), the probe was stepped across a designed area of the sample. In the present case, the analysed part was an area of 3.2 cm × 2.4 cm, above the active zone. The step size was 1 mm in the *X* and *Y* directions. Admittance was plotted rather than impedance to improve the visualization of the mapping. The mappings were obtained at a fixed frequency of 10 Hz. To observe the self-healing process, a scratch was done manually with a cutting knife on the coated samples.

The corrosive medium was prepared from distilled water by adding NaCl (reagent grade). To evaluate the inhibitor efficiency in aqueous solution, 20% of ethanol was added to a 0.1 M NaCl solution to improve the IBA solubility (IBA solubility limit in water: 10^{-3} M). To characterize the coatings performance, the NaCl concentrations were 0.5 M for the conventional impedance and 0.001 M for the local impedance measurements, respectively. The local measurements were carried out in a low conductivity medium ($9.4 \times 10^5\ S\,cm^{-1}$) to optimize resolution. The electrolytic solution was in contact with air and at ambient temperature. For the electrochemical measurements, three trials were performed to ensure reproducibility.

2.6. Inhibitor release

The IBA release, from IBA-modified clay, versus pH was determined by measuring the total carbon content and the inorganic

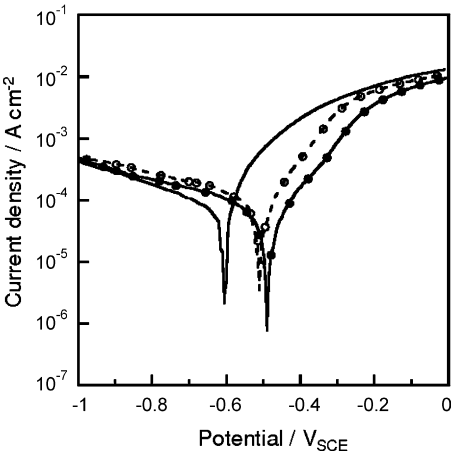


Fig. 2. Polarization curves obtained for the carbon steel electrode for two IBA concentrations after 2 h of immersion in the 0.1 M NaCl solution: (○) 5×10^{-4} M and (●) 5×10^{-3} M; (—) without inhibitor.

carbon content (TOC) in the liquid fraction using a TOC analyser (Shimadzu TOC-V$_{SCH}$). First, calibration curves were determined using a 1000 ppm concentrated sodium carbonate solution (inorganic carbon content) and a 1000 ppm concentrated phthalate solution (total carbon content). The calibration curves were obtained for these compounds between 0 ppm and 1000 ppm by dilution. 0.5 g of IBA-modified clay was incorporated in 3 ml of distilled water. pH was then adjusted using hydrochloric acid or sodium hydroxide. After 24 h of immersion and stirring, the solutions were filtered and the inhibitor release was determined on the liquid phase. The error on the measurement expressed in ppm is inferior to 2%.

3. Results and discussion

The inhibitive efficiency of IBA was first characterized by polarization curves and electrochemical impedance spectroscopy (EIS) at two concentrations. Then, MMT was treated with IBA by cation exchange reaction. The insertion of IBA between MMT clay platelets was investigated by X-ray diffraction (XRD). The dispersion and/or the exfoliation of the IBA-modified clay in the epoxy resin were observed by transmission electron microscopy (TEM). The protective properties of the epoxy resin containing IBA-modified clay were monitored by conventional impedance measurements at different immersion times up to 56 days and compared with those of the pure epoxy resin. In the present study, the coating thickness was thinner than in the previous investigation [2] to decrease the barrier effect and thus to better characterize the behaviour of the metal/coating interface. As a matter of fact, it was shown [25] that for an epoxy coating with a high barrier resistance, it was difficult to bring out the difference in corrosion resistance by the introduction of clay and the authors have suggested that an epoxy coating with a lower barrier resistance or higher permeability will be helpful in discriminating the corrosion behaviour by the introduction of clay into the matrix.

3.1. Inhibitor efficiency in solution

The polarization curves obtained for two IBA concentrations after 2 h of immersion are presented in Fig. 2. The curve obtained without inhibitor is also reported for comparison. In the presence of IBA, a shift of the corrosion potential towards more positive value and lower anodic current densities can be observed. This effect was more marked when the IBA concentration increased. The cathodic curves were not modified by IBA addition. From the polarization curves, it can be concluded that IBA can be classified as an anodic inhibitor. Fig. 3 reports the impedance diagrams obtained after 2 h of immersion at the corrosion potential with and without inhibitor. The diagrams are characterized by a single capacitive loop. The value of the polarization resistance can be used to evaluate the inhibitor efficiency [26].

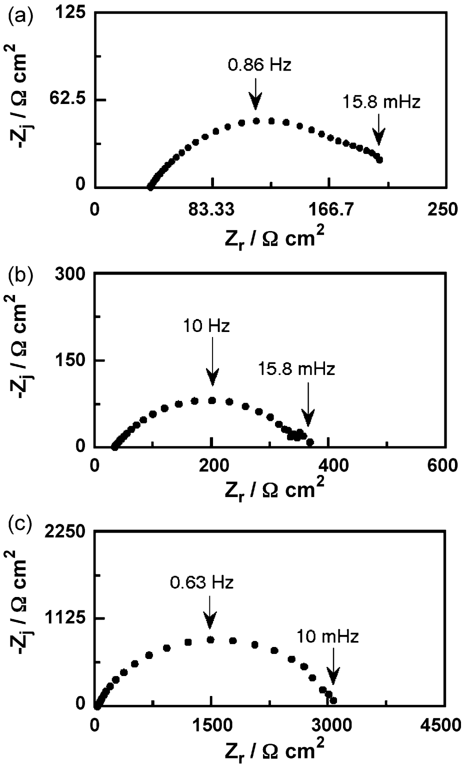


Fig. 3. Electrochemical impedance diagrams (Nyquist representation) obtained for the carbon steel electrode for two IBA concentrations after 2 h of immersion in the 0.1 M NaCl solution: (a) without inhibitor; (b) 5×10^{-4} M; (c) 5×10^{-3} M.

$$E\% = \frac{R_p^i - R_p^w}{R_p^w}$$

where R_p^i and R_p^w are the polarization resistances in the presence or in the absence of the inhibitor, respectively. R_p^w was about 200 Ω cm^2. For the lowest inhibitor concentration (5×10^{-4} M), the R_p value was similar. In contrast, for 5×10^{-3} M, R_p^i was about 3000 Ω cm^2. For this concentration, the calculated inhibitor efficiency was about 93%.

3.2. Characterization of IBA-modified clay

Fig. 4 shows X-ray diffraction patterns of the clay and of the IBA-modified clay. The peak corresponding to the d_{001} plane of the pristine clay appears at $2\theta = 7°$ and for the IBA-modified clay, it appears at $2\theta = 5.20°$. The peak d_{001} corresponds to the d-spacing of the lamellar structure of MMT. d-Spacing was calculated from Bragg's Law given in Eq. (1):

$$\lambda = 2d \sin\theta \tag{1}$$

where λ is the wavelength of the X-ray radiation, θ is the glancing angle and d is the interplanar spacing of the clay layers. From Fig. 4, the calculated d-spacing is 12.6 Å and 16.9 Å for the clay and for the IBA-modified clay, respectively. The increase in d_{001} spacing in the IBA-modified clay compared to pure clay is due to the exchange of cations by IBA which increased the gallery spacing.

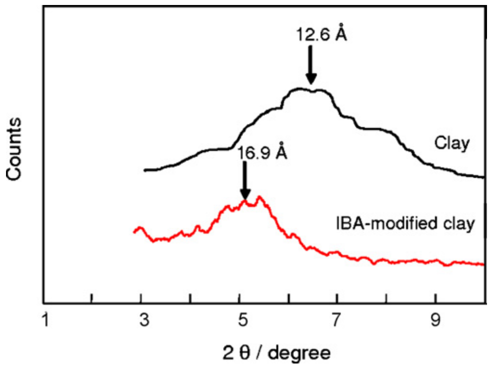


Fig. 4. X-ray diffraction spectra of (black) clay and (red) IBA-modified clay. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

3.3. TEM observations

Fig. 5 shows the photomicrograph obtained by TEM. The sheets of the nanoclays can be clearly observed. The exfoliated state is not complete. Some sheets are free and exfoliated but most of the platelets maintain an interconnected structure with a higher interfoliated distance confirming inhibitor incorporation between the sheets. The dispersion of IBA-modified clay in the matrix was not complete and some aggregates were observed. Nevertheless, its distribution was uniform through the whole coating thickness proving that any settling is induced during air drying.

3.4. Conventional impedance results

In the previous papers [1–2], it was shown that the barrier properties of the epoxy coating were significantly higher in the presence of IBA-modified clay by comparison with the pure epoxy and that the improvement of the barrier properties was mainly due to the clays incorporation for short immersion times, and, to the combined effect of clays and inhibitors for longer periods [1]. In the present paper, the thickness of the coating (10 μm instead of 20 μm) was decreased to limit the barrier effect and thus to better characterize the metal/coating interface. The impedance diagrams plotted after three different exposure times are presented in Figs. 6 and 7 for the pure epoxy coating and for the epoxy coating

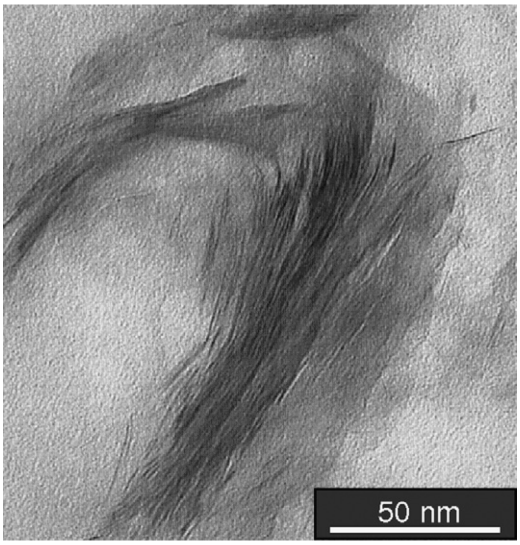


Fig. 5. Micrograph obtained by TEM of the epoxy coating containing 2 wt.% of IBA-modified clay.

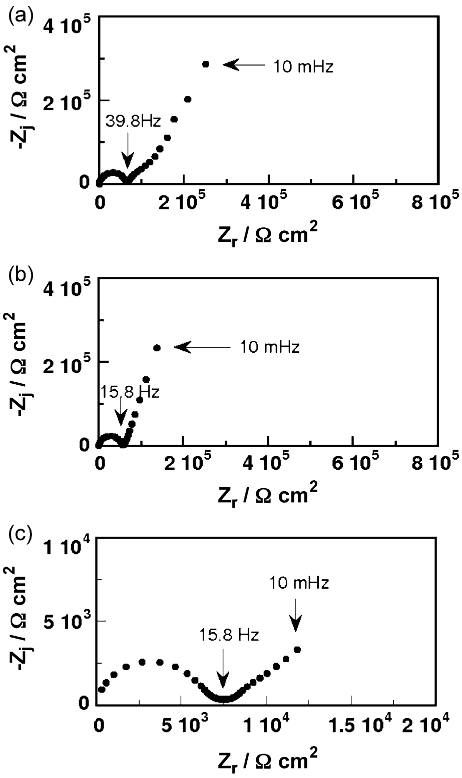


Fig. 6. Electrochemical impedance diagrams obtained for the carbon steel covered by the pure epoxy coating after (a) 7 days, (b) 14 days, (c) 56 days of exposure to 0.5 M NaCl solution.

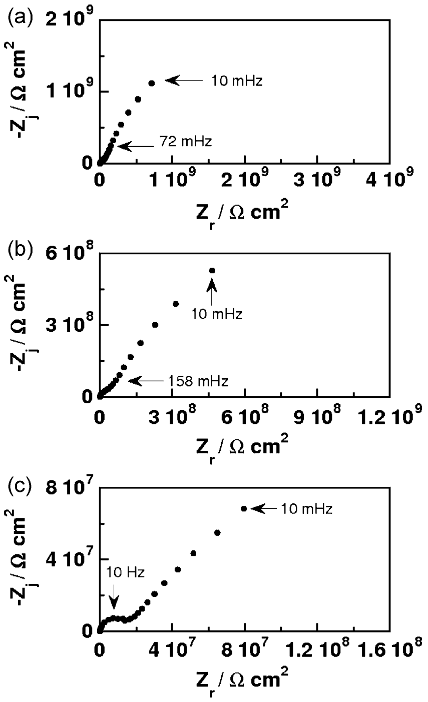


Fig. 7. Electrochemical impedance diagrams obtained for the carbon steel covered by the epoxy coating containing 2 wt.% IBA-modified clay after (a) 7 days (b) 14 days, (c) 56 days of exposure to 0.5 M NaCl solution.

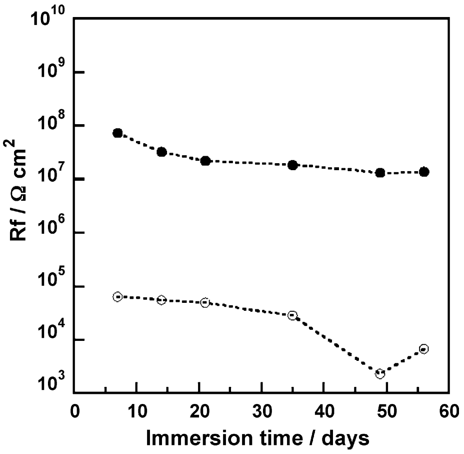


Fig. 8. R_f versus immersion time in 0.5 M NaCl solution for the carbon steel covered by (○) pure epoxy and (●) epoxy containing 2 wt.% IBA-modified clay.

containing 2% IBA-modified clay, respectively. It can be seen that the shape of the impedance diagrams is relatively similar: a high frequency capacitive loop which is related to the organic coating and represents the electrolyte resistance in the pores of the coating and in the low-frequency range a straight line which corresponds to the corrosion reaction on the metal surface and mainly accounts for diffusion through defects and pores on the coating. The main result is that the impedance was significantly higher for the coating containing IBA-modified clay. As in the previous studies [1,2], the values associated with the HF loop (R_f) and the impedance modulus at low frequency ($|Z|_{10\,\mathrm{mHz}}$) were extracted from the impedance diagrams to follow, respectively, the variation of the barrier properties (Fig. 8) and the corrosion protection (Fig. 9) with immersion time.

For the pure epoxy coating, both the R_f and the $|Z|_{10\,\mathrm{mHz}}$ were significantly lower (more than 3 decades) than for the epoxy coating containing IBA-modified clay. The decrease of R_f for the system containing IBA-modified clay was not significant during the exposure time to the aggressive solution (Fig. 8). This result confirmed that the introduction of the clay particles in the organic coating led to a significant improvement of the barrier properties. For the pure epoxy coating, the decrease of R_f with exposure time was followed by an increase of R_f after 50 days. This could be attributed to the presence of corrosion products which can seal the pores of the coating. The decrease of the modulus at low frequency versus immersion time (Fig. 9) was more significant for the pure epoxy coating than for the coating containing IBA-modified clay. For the coating containing IBA-modified clay, the modulus decreased less than one decade during 56 days of exposure reaching a value about 10^4 times higher than that measured without clay. These results clearly show that the addition of IBA-modified clay markedly improved the corrosion resistance of the carbon steel. It is noteworthy that after the impedance tests, the carbon steel covered by the pure epoxy coating was strongly corroded. Corrosion products can be visible after only 7 days of immersion. In contrast, for the coating containing IBA-modified clay, the sample had the same appearance than before immersion: there was no corrosion product. By comparison with the previous study [2], it can be emphasized that the decrease of the coating thickness led, for the pure epoxy coating, to a significant decrease of the barrier properties. Surprisingly, for the coating containing IBA-modified clay, the barrier properties and the modulus at low frequency were poorly dependent on the coating thickness. These results underline that the presence of IBA-modified clay played a major role on the performance of the coating.

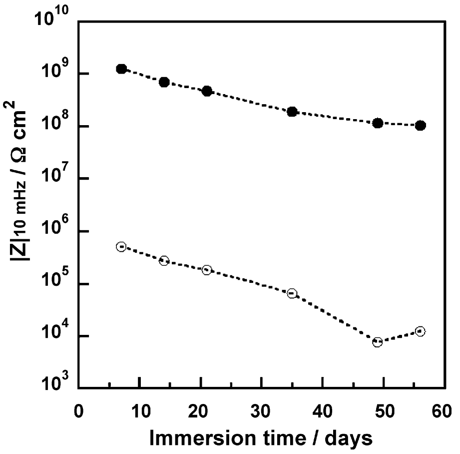


Fig. 9. $|Z|_{10\,\mathrm{mHz}}$ versus immersion time in 0.5 M NaCl solution for the carbon steel covered by (○) pure epoxy and (●) epoxy containing 2 wt.% IBA-modified clay.

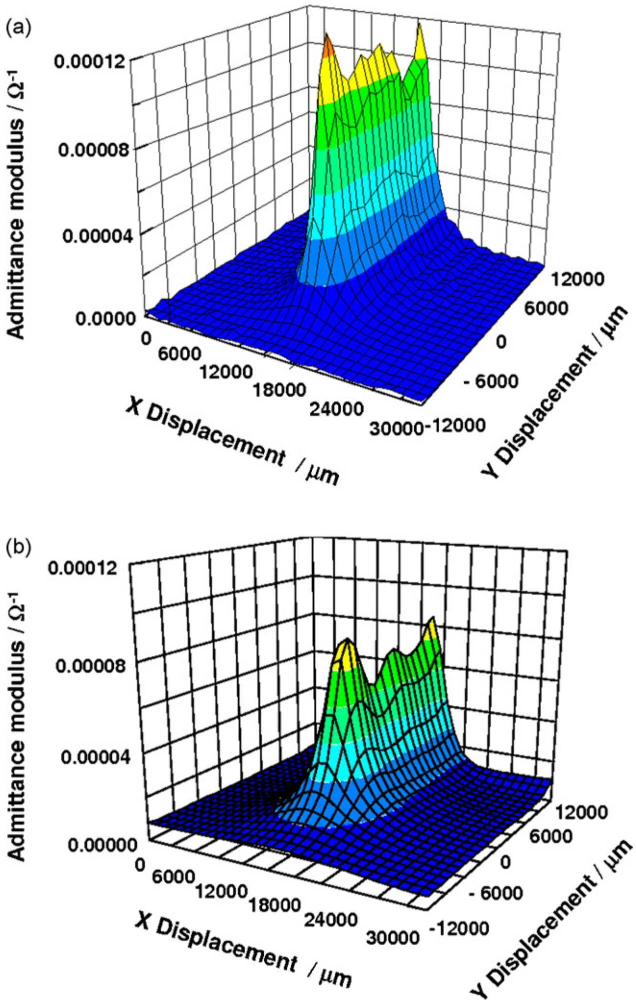


Fig. 10. LEIS carried out at 10 Hz for the pure epoxy coating around the scratched area (a) after 1 day and (b) after 12 days of immersion in the aggressive solution.

3.5. Local electrochemical impedance spectroscopy

Figs. 10 and 11 present LEIS maps obtained after two exposure times to the 0.001 M NaCl solution for the pure epoxy coating and for the epoxy containing 2% IBA-modified clay, respectively. For the pure epoxy, when the exposure time to the aggressive

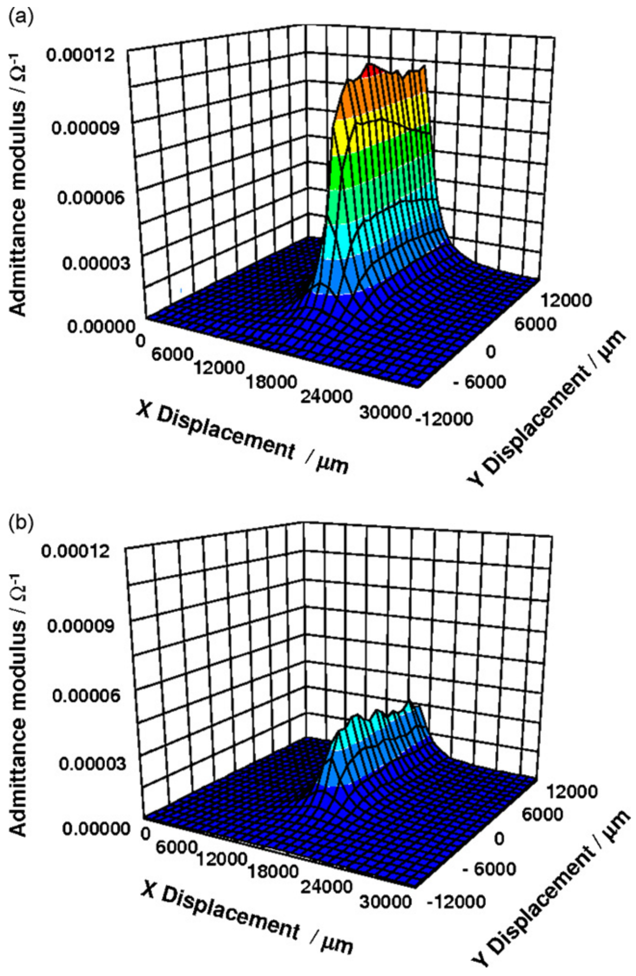


Fig. 11. LEIS carried out at 10 Hz for the epoxy coating containing 2 wt.% of IBA-modified clay around the scratched area (a) after 1 day and (b) after 12 days of immersion in the aggressive solution.

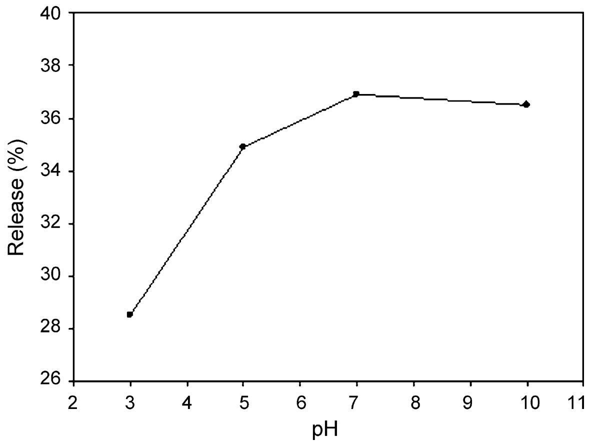


Fig. 12. Release (%) of IBA versus pH in distilled water.

solution increases the admittance increases (impedance decreases) on the edge of the scratch. This behaviour corresponds to a loss of adherence of the coating [24]. Inside the scratch, the lower admittance values, measured after 12 days of immersion, can be attributed to the presence of corrosion products. After the test, visual observation revealed the presence of brown, rusty and poorly adherent corrosion products. For the epoxy coating containing 2% IBA-modified clay (Fig. 11), when the immersion time increases there is no admittance variation around the scratch and the admittance decreases in the scratch. These results show a corrosion inhibition in the scratch. This is due to the self-healing process by the leaching of IBA from the epoxy coating. After the test, dark corrosion products are visible on the scratch.

3.6. *Inhibitor release from the IBA-modified clay*

In neutral solution, corrosion process generally induces a local increase of pH due to the reduction of dissolved oxygen. Thus, in neutral and alkaline media, the inhibitor release is expected in order to impede corrosion and confer self-healing properties to the coating. As shown in Fig. 12, the inhibitor release was higher when the pH increased. This can be explained by the fact that at pH lower than the pK_a (4.9), the global charge of the IBA is positive due to –N$^+$-H functional group. The clay having a deficit in positive charge, electrostatic bonds can be created between the clay and the inhibitor limiting the IBA release. When the pH increased and became higher than the pK_a, the nitrogen function was no more charged and the interactions between the clay and the inhibitor were reduced. This can explain the increase of the inhibitor release for pH higher than 5. Moreover, for alkaline pH, the carboxylic functional group is a protons donor and can be partially dissociated leading to a negative global charge which again induces poor interactions between the clay and the inhibitor. However, the complete release of the inhibitor from the IBA-modified clay was not observed which can be explained by the incomplete exfoliation of the IBA-modified clay in the adjusted pH water. This incomplete exfoliation probably impedes inhibitor diffusion through the platelets and limits inhibitor release incorporated between the non-exfoliated sheets. These results are in good agreement with the LEIS measurements and confirm that the pH increase, due to the corrosion process occurring in cathodic area, is favourable to the release of inhibitor and self-healing behaviour. The inhibitor release will reduce the cathodic delamination process of the organic coating [24].

4. Conclusions

In a previous work [2], it was shown that IBA-modified clay allows the corrosion performance of epoxy coatings to be improved both by an increase of the barrier properties of the film and by the inhibitive action of IBA at the carbon steel/coating interface. In the present paper, the study mainly focussed on the inhibitor efficiency, on the self-healing properties conferred to the epoxy matrix after a scratch and on the inhibitor release from the clay. The polarization curves showed that the IBA is an anodic inhibitor of the carbon steel. Its efficiency, evaluated from EIS data, reached 93%. XRD measurements confirmed the incorporation of the IBA between the clay platelets. The exfoliation of the clay in the epoxy matrix was not complete and aggregates, uniformly distributed in the organic matrix, were observed. The self-healing performance offered by the modified clay was clearly shown by LEIS measurements on scratched samples. The inhibitor release from IBA-modified clay was superior for the higher pH which constitutes an interesting point to inhibit corrosion process in neutral media. Finally, in agreement with our previous results, the performances of the coating in terms of corrosion resistance were improved by the IBA-modified clay incorporation in the epoxy matrix and by comparison with the previous results a decrease of the film thickness has maintained high barrier properties.

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