



Layered double hydroxides as containers of inhibitors in organic coatings for corrosion protection of carbon steel

To Thi Xuan Hang, Trinh Anh Truc, Nguyen Thuy Duong, Nadine Pébère,
Marie-Georges Olivier

► To cite this version:

To Thi Xuan Hang, Trinh Anh Truc, Nguyen Thuy Duong, Nadine Pébère, Marie-Georges Olivier. Layered double hydroxides as containers of inhibitors in organic coatings for corrosion protection of carbon steel. Progress in Organic Coatings, 2012, vol. 74, pp. 343-348. 10.1016/j.porgcoat.2011.10.020 . hal-00864273

HAL Id: hal-00864273

<https://hal.science/hal-00864273>

Submitted on 3 Oct 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/>
Eprints ID : 8742

To link to this article : DOI:10.1016/j.porgcoat.2011.10.020
URL : <http://dx.doi.org/10.1016/j.porgcoat.2011.10.020>

To cite this version : Hang, To Thi Xuan and Truc, Trinh Anh and Duong, Nguyen Thuy and Pébère, Nadine and Olivier, Marie-Georges *Layered double hydroxides as containers of inhibitors in organic coatings for corrosion protection of carbon steel.* (2012) Progress in Organic Coatings, vol. 74 (n° 2). pp. 343-348. ISSN 0300-9440

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Layered double hydroxides as containers of inhibitors in organic coatings for corrosion protection of carbon steel

To Thi Xuan Hang^{a,*}, Trinh Anh Truc^a, Nguyen Thuy Duong^a, Nadine Pébère^b, Marie-Georges Olivier^c

^a Institute for Tropical Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Viet Nam

^b Université de Toulouse, CIRIMAT, UPS/INPT/CNRS, ENSIACET 4, allée Emile Monso – BP 44362, 31030 Toulouse Cedex 4, France

^c Université de Mons (UMONS), Faculté Polytechnique, Service de Science des Matériaux, 20 Place du Parc, Mons, Belgium

A B S T R A C T

The present work focuses on the use of layered double hydroxides (LDH) as containers for corrosion inhibitors in an epoxy coating. 2-Benzothiazolylthio-succinic acid (BTSA), used as corrosion inhibitor, was intercalated by co-precipitation in magnesium–aluminum layered double hydroxides. The obtained LDH–BTSA was characterized by infrared spectroscopy, X-ray diffraction and scanning electron microscopy. BTSA release from LDH–BTSA in NaCl solutions was investigated by UV–vis spectroscopy. The inhibitive action of LDH–BTSA on carbon steel corrosion was characterized by electrochemical methods and the protective properties of an epoxy coating containing LDH–BTSA were evaluated by electrochemical impedance spectroscopy. It was shown that the BTSA was intercalated in the layered double hydroxide and its loading was about 33%. The BTSA release was dependent on the NaCl concentration in the electrolyte. The polarization curves obtained on the carbon steel sample showed that the LDH–BTSA is an anodic inhibitor. Its efficiency was about 90% at a concentration of 3 g/l. The impedance results showed that the incorporation of LDH–BTSA (3%) in the epoxy matrix improved the corrosion protection of the carbon steel.

Keywords:

Organic coatings
Layered double hydroxides
Corrosion inhibitors
Release

1. Introduction

Organic coatings are widely used to prevent corrosion of metallic structures because they are easy to apply and cost effective. It is generally accepted that the coating efficiency is dependent on the intrinsic properties of the organic film (barrier properties), the substrate/coating interface in terms of adherence, the inhibitive or sacrificial pigments used and the degree of environment aggressiveness. Corrosion inhibitors are usually incorporated in organic coatings to provide active corrosion protection. In the past, chromates were the most commonly used inhibitive pigments. However, due to their high toxicity, many studies have been devoted to the development of more environmentally acceptable organic coatings.

Bentonite clays modified by environmentally friendly inorganic corrosion inhibitive species like cerium (III) bentonite, calcium (II) bentonite for protective coatings have already been studied [1–3]. The results showed that coatings containing Ce-exchange bentonite provide good corrosion protection, but lower than coatings containing chromates. Clays modified by organic corrosion

inhibitors were also investigated. Incorporation of modified clays in epoxy coatings provides both good barrier properties due to the lamellar structure of the clay and significant corrosion inhibition at the carbon steel/coating interface thanks to the presence of functional organic groups adsorbed at the metal interface [4–7].

Layered double hydroxides (LDH) are known as anionic clays. They are composed of positively charged hydroxide layers with a structure similar to that of brucite with intercalated anions and water molecules between the layers [8]. The general formula can be expressed as $M_n^{2+}M^{3+}(\text{OH})_{2+2n}(A_{1/m}^{m-})_x\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent cations occupying octahedral positions within the hydroxide layers, which are positively charged and A^{m-} is an interlayer exchangeable anion balancing the positive charges on the layers. The distance between hydroxide layers allows a wide range of anions (both organic and inorganic) of different sizes and orientations to be inserted [9–11]. The intercalated anions can be released and substituted by other anions from the environment. Application of LDH is based on adsorption, anion exchange capacity and mobility of the anion between the layers. LDH and LDH-derived mixed oxides have been widely used as adsorbents, ion exchangers, base catalysts, polymer additives and corrosion protection agents thus attracting extensive attention over recent decades [12–15].

LDH can be used to trap anionic inhibitors [16–19]. In this case, the release of inhibitor anions can be triggered by exchange with aggressive chloride ions. The anion-exchange pigment can

* Corresponding author. Tel.: +84 0912178768; fax: +84 4 37564484.
E-mail address: hang@vnd.vast.ac.vn (T.T.X. Hang).

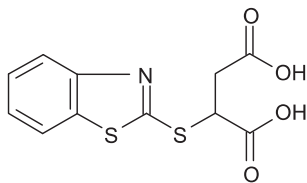


Fig. 1. Molecular structure of 2-benzothiazolylthio-succinic acid.

play a double role: absorbing the chlorides and releasing the inhibitive ions. LDH containing decavanadate or molybdate anions has been studied in application overlay for corrosion protection of aluminum alloys. However, coatings containing decavanadate intercalated in Zn/Al-LDH are not able to confer corrosion protection equivalent to that afforded by chromate anions [3,20]. Mg/Al-LDH and Zn/Al-LDH doped with divanadate anions as corrosion inhibitor were used in primers for corrosion protection of 2024 aluminum alloy. Electrochemical results and accelerated corrosion tests showed that coatings doped with Zn/Al-LDH give higher corrosion protection than chromate-based coatings [21].

The corrosion protection of aluminum alloys afforded by organic anions intercalated in LDH such as benzotriazolate, ethyl xanthate and oxalate salts has also been investigated [22]. The results show that inhibition efficiency depends on the structure of the organic anion. Inhibition efficiency increases in the order ethyl xanthate < oxalate < benzotriazolate. Benzotriazolate has been demonstrated to interact specifically with the aluminum alloy surface. 2-Benzothiazolylthio-succinic acid (BTSA) is a well-known corrosion inhibitor used in organic coatings. BTSA can be incorporated into the iron oxide layers which are always present on the steel surface and can form insoluble precipitates with ferrous ions [23].

The objective of the present work was to use magnesium–aluminum LDH as containers for corrosion inhibitors which can then be incorporated into an epoxy matrix for protection of carbon steel. BTSA was used as corrosion inhibitor and was intercalated by co-precipitation in the LDH structure (LDH–BTSA). The LDH–BTSA was characterized by infrared spectroscopy, X-ray diffraction and scanning electron microscopy. BTSA release from LDH–BTSA in NaCl solutions was investigated using UV–vis spectroscopy. The inhibition efficiency of LDH–BTSA and the protective properties of the epoxy coating containing it were evaluated by polarization curves and electrochemical impedance spectroscopy, respectively.

2. Experimental

2.1. Materials

Sodium hydroxide, magnesium nitrate hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and aluminum nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were purchased from Merck. BTSA was obtained from Ciba Company. The chemical structure of BTSA is shown in Fig. 1.

To characterize the inhibitive efficiency of LDH–BTSA, a rod of XC 35 carbon steel with 1 cm^2 cross-sectional area was used as working electrode. Its composition in percent 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 was used to leave 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 per-mutated water in an ultrasonic bath and dried in warm air.

For the coatings, carbon steel sheets ($150\text{ mm} \times 10\text{ mm} \times 2\text{ mm}$) were used as substrates. The sheets were ground with abrasive papers from 80 to 600 grades and cleaned with ethanol.

2.2. Synthesis of magnesium–aluminum layered double hydroxides (LDH)

The magnesium–aluminum LDH were synthesized using the co-precipitation method [24]. The preparation was performed in a nitrogen atmosphere to exclude CO_2 which would lead to the incorporation of carbonate in the LDH. A solution of 32.0 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.125 mol) and 23.4 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.0625 mol) in 125 ml of degassed and deionized water was added dropwise to a solution of 12.5 g of NaOH (0.313 mol) in 145 ml of degassed/deionized water. The pH of the solution was maintained at 8–10 by adding 1 M NaOH solution as needed. The resulting white precipitate was aged for 24 h at 65°C , and then filtered until the supernatant was completely removed. The sample was washed several times with deionized and degassed water, and finally dried at 50°C in a vacuum oven.

2.3. Synthesis of magnesium–aluminum BTSA layered double hydroxides

The LDH intercalated with BTSA were prepared following the same procedure as in Section 2.2, but using 0.313 mol of BTSA with the molar equivalent of NaOH in degassed/deionized water.

2.4. Epoxy coating preparation

The epoxy resin was an epoxy bisphenol A, Epotec YD 011-X75, epoxy equivalent weight is about 469–490 g/eq. The hardener was a polyamide, equivalent weight per active H is 266 g/eq. Both compounds were purchased from Thai Organic Chemicals Co. (Thailand). The LDH–BTSA was incorporated in the epoxy resin at a concentration of 3 wt.%. The LDH–BTSA was dispersed in the epoxy resin by magnetic stirring and then sonication. The liquid paint was applied by spin coating and dried at ambient temperature for 24 h. The dry film thickness was $30 \pm 3\text{ }\mu\text{m}$ (measured by Minitest 600 Erichen digital meter).

2.5. Analytical characterizations

Fourier transform infrared spectra were obtained using the KBr method on a Nexus 670 Nicolet spectrometer operated at 1 cm^{-1} resolution in the $400\text{--}4000\text{ cm}^{-1}$ region.

UV–vis spectra were obtained using a GBC Cintra 40 spectrometer.

X-ray diffraction measurements were performed with a Siemens diffractometer D5000 with $\text{Cu K}\alpha$ X-ray diffraction.

FE-SEM observations were carried out using a Hitachi 4800 spectrometer.

2.6. BTSA content in LDH–BTSA

The loading amount of BTSA in LDH–BTSA was determined using the following protocol: 0.05 g of LDH–BTSA and 0.5 ml of 6 M HNO_3 solution were mixed in a 10 ml volumetric flask, the balance was filled with ethanol. The concentration of BTSA in the resulting solution was determined by UV–vis spectroscopy at $\lambda_{\text{max}} = 283\text{ nm}$ [25]. The concentration was calculated using a calibration curve obtained from a series of standard solutions of BTSA from $1 \times 10^{-5}\text{ M}$ to $3 \times 10^{-4}\text{ M}$.

2.7. Release of BTSA from LDH–BTSA

The release of BTSA from LDH–BTSA was determined as follows: 0.5 g of LDH–BTSA was dispersed in 500 ml water/ethanol solution (volume ratio 8:2) with different NaCl concentrations under magnetic stirring. Aliquots (2 ml) of supernatant were withdrawn at

Table 1
Characteristic bands of FTIR spectra obtained for LDH, BTSA and LDH-BTSA.

LDH (cm ⁻¹)	BTSA (cm ⁻¹)	LDH-BTSA (cm ⁻¹)	Bond
450		447	Al-O
649		673	Mg-O
	758	764	Aromatic ring
1383		1376	NO ₃ ⁻
1632			-OH of H ₂ O
	1721		-COOH
		1405	-COO ⁻
		1583	-COO ⁻
	3062		-CH of aromatic ring
3441	3421	3433	-OH

different times and replaced by the same amount of fresh medium. The aliquots were filtered and their BTSA contents were determined by UV-vis spectroscopy at 283 nm.

2.8. Electrochemical characterizations

For the electrochemical measurements, a three-electrode cell was used with a large platinum auxiliary electrode, a saturated calomel reference electrode (SCE) and a working electrode with an exposed area of 1 cm² for the bare carbon steel and 28 cm² for the coated samples. Anodic and cathodic polarization curves, in the presence and absence of LDH-BTSA, were obtained after 2 h of immersion at a scan rate of 1 mV s⁻¹ starting from the corrosion potential. The electrochemical impedance measurements were performed using an Autolab PGSTAT30 over a frequency range of 100 kHz–10 mHz with six 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.

The corrosive medium was prepared from distilled water by adding NaCl (reagent grade). To evaluate the inhibitor efficiency in aqueous solution, ethanol (20%) was added to a 0.1 M NaCl solution to improve the BTSA solubility. To characterize the performance of the coatings, the NaCl solution concentration was 0.5 M. For each system, three samples were tested to ensure reproducibility.

3. Results and discussion

3.1. Characterizations of LDH-BTSA and epoxy coating containing LDH-BTSA

BTSA loading of LDH-BTSA was determined using UV-vis spectroscopy. The calibration curve determined from a series of standard BTSA solutions was:

$$C = 0.8518A$$

where C is the concentration of BTSA (in 10⁻⁴ mol/l) and A is the absorption intensity at 283 nm. The BTSA loading in LDH-BTSA was 33.2%.

The FT-IR spectra of LDH, BTSA and LDH-BTSA are shown in Fig. 2, and the characteristic bands of the spectra are given in Table 1. The IR spectrum of LDH shows a strong band at 1385 cm⁻¹ characteristic of the NO₃⁻ group [26]. In addition, the strong band at 450 cm⁻¹ and the broad one at 650 cm⁻¹ are attributed to the vibrations of Mg-O and Al-O. A very broad band at around 3450 cm⁻¹ belongs to OH stretching of the hydroxide layer and water [11,27]. The band at about 1631 cm⁻¹ can be attributed to the deformation vibration of water molecules in the interlayer domain. The spectrum of BTSA shows bands at 3421 cm⁻¹, 3062 cm⁻¹ characteristic of the OH and CH groups of the aromatic ring structure. The band at 1721 cm⁻¹ is attributed to the vibration of COOH. The band at 758 cm⁻¹ corresponds to the aromatic ring with four adjacent hydrogen atoms. The spectrum of LDH-BTSA presents

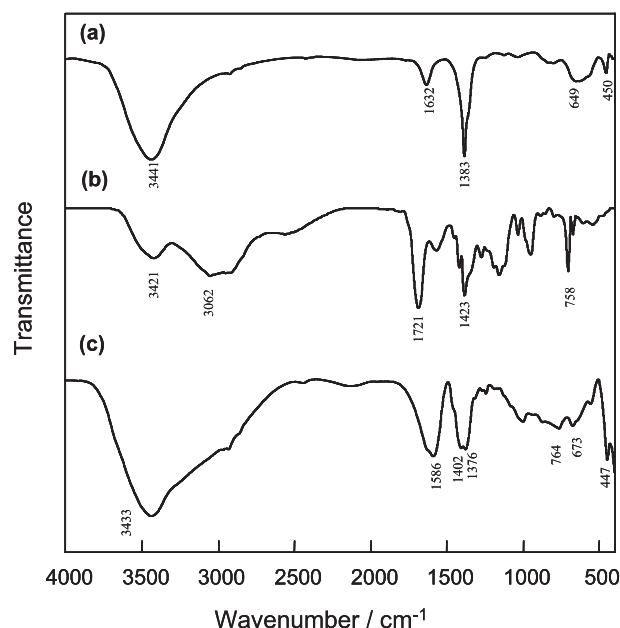


Fig. 2. FTIR spectra of (a) layered double hydroxide (LDH); (b) 2-benzothiazolylthio-succinic acid (BTSA); (c) layered double hydroxide containing BTSA (LDH-BTSA).

the bands characteristic of Mg-O and Al-O vibrations at 447 cm⁻¹ and 673 cm⁻¹. It can be seen that the band characteristic of the COOH group in BTSA at 1721 cm⁻¹ disappeared and a new band is observed at about 1600 cm⁻¹; this band is attributed to the vibration of the COO⁻ group. The band characteristic of the aromatic ring with four adjacent hydrogen atoms also appears at 764 cm⁻¹ in the LDH-BTSA spectrum. This result indicates the presence of the BTSA in the carboxylate form in the LDH interlayer space.

The XRD patterns of LDH, LDH-BTSA and epoxy coating containing 3% LDH-BTSA are shown in Fig. 3. In the XRD pattern of LDH, two distinct reflections (003) and (006) are observed. The value of the (003) reflection corresponds to the basal spacing of the hydroxide layer and is 0.81 nm, which is within the range of values reported in the literature (0.81–0.89 nm) [11,28,29]. In the XRD pattern of LDH-BTSA, the reflection peaks observed at 1.65 nm

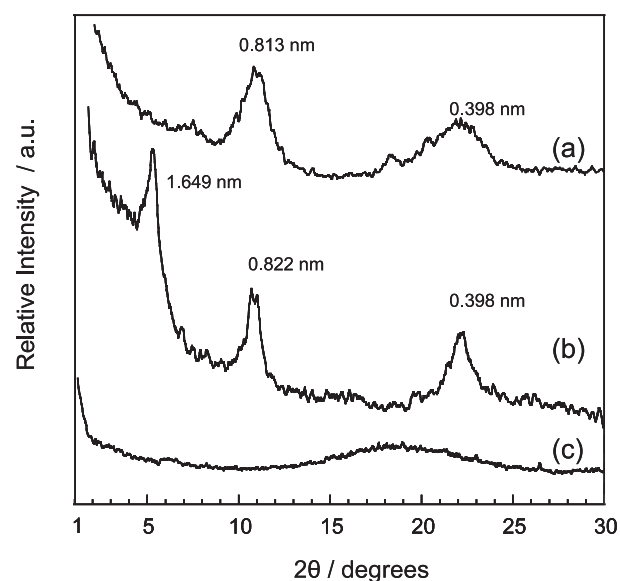


Fig. 3. XRD patterns of (a) LDH; (b) LDH-BTSA; (c) epoxy containing 3% LDH-BTSA.

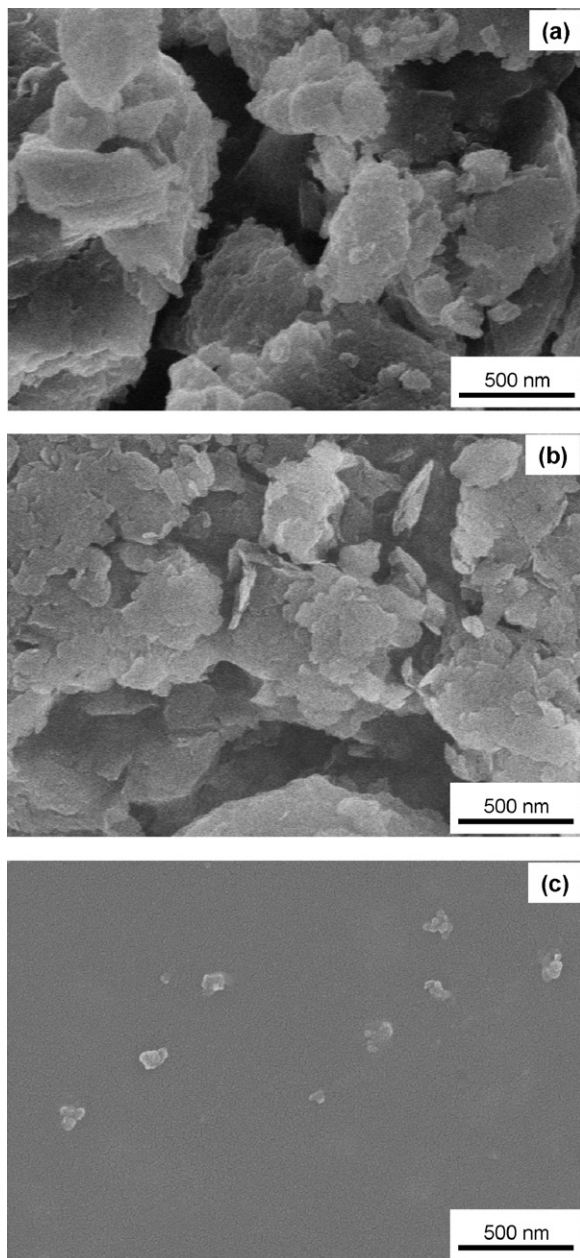


Fig. 4. FE-SEM images of (a) LDH; (b) LDH-BTSA; (c) epoxy containing 3% LDH-BTSA.

and 0.822 nm are attributed to the basal spacing. The d -spacing values of the LDH-BTSA, higher than that of pristine LDH, indicate that BTSA molecules were intercalated in the LDH structure. For the epoxy coating containing LDH-BTSA no diffraction peak was observed. This result could indicate that LDH-BTSA was exfoliated in the epoxy matrix or that the amount of LDH in the epoxy coating is too low to be detected by XRD.

SEM images of LDH, LDH-BTSA and epoxy coating containing 3% LDH-BTSA are shown in Fig. 4. Both LDH and LDH-BTSA have the typical plate-like morphology of LDH. The size of the LDH particles ranged from 50 nm to 200 nm. The size of LDH-BTSA particles was smaller, more homogeneous and more separated than those of LDH. For the epoxy coating containing 3% LDH-BTSA, the sheets of the LDH-BTSA can be clearly observed. The sheets are uniformly distributed through the epoxy matrix and have an average size of about 100 nm.

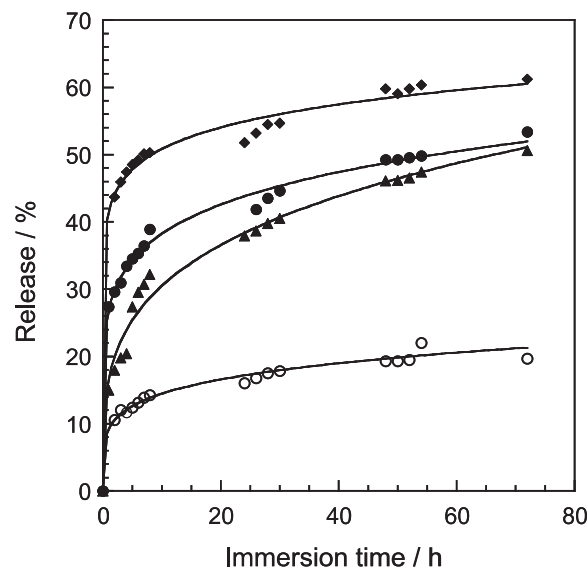


Fig. 5. Release curves of BTSA from LDH-BTSA NaCl solution at different concentrations: (○) 0%; (▲) 0.5%; (●) 1%; (◆) 3%.

3.2. Release of BTSA from LDH-BTSA

In neutral media, corrosion processes generally occur in the presence of aggressive anions in solution. Thus, inhibitor release in the presence of anions is sought in order to impede corrosion and confer self-healing properties to organic coatings. The release curves of BTSA from LDH-BTSA were determined in NaCl solutions having different concentrations and are shown in Fig. 5. It can be seen that release was rapid in the first hours of immersion (8 h) and then slowed down. This result is similar to the results reported in the literature [25]. By comparison with conditions without NaCl, BTSA release in NaCl solution was much higher and increased with an increase of the NaCl concentration. After 72 h of immersion in the ethanol/water mixture containing 0%, 0.5%, 1% and 3% NaCl, the release of BTSA was 20%, 50%, 53% and 61% respectively. These results confirm that the release of BTSA is based on an exchange reaction between BTSA and chloride ions. The rate of this exchange reaction increased with the NaCl concentration.

3.3. Corrosion inhibition effect of LDH-BTSA

The polarization curves for the carbon steel electrode obtained after 2 h of immersion in 0.1 M NaCl solution for three LDH-BTSA concentrations (1 g/l, 3 g/l and 5 g/l) are presented in Fig. 6. The curve obtained without LDH-BTSA is shown for comparison. In the presence of LDH-BTSA, a shift of the corrosion potential towards more positive values and lower anodic current densities can be observed. The cathodic curves were not modified with LDH-BTSA addition. The polarization curves proved that LDH-BTSA is an anodic inhibitor.

Fig. 7 shows the impedance diagrams, plotted in Bode coordinates, obtained for the carbon steel electrode after 2 h of immersion at the corrosion potential in the sodium chloride solutions with and without LDH-BTSA. The diagrams are characterized by a single time constant. The polarization resistances were extracted graphically and the values were used to evaluate the inhibitor efficiency [30].

$$E\% = \frac{R_p - R_{p0}}{R_p}$$

R_p and R_{p0} are the polarization resistances in the presence and the absence of LDH-BTSA respectively. R_{p0} is about 200 $\Omega \text{ cm}^2$ and

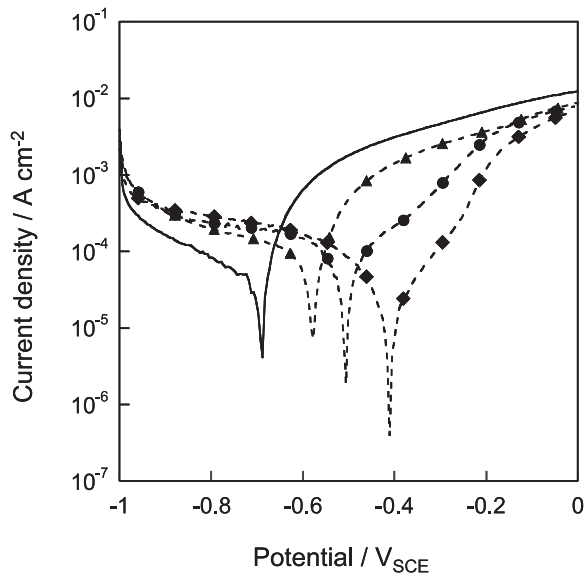


Fig. 6. Polarization curves obtained for the carbon steel electrode for three LDH-BTSA concentrations after 2 h of immersion in the 0.1 M NaCl solution: (●) 1 g/l; (◆) 3 g/l; (▲) 5 g/l; (—) without inhibitor.

the polarization resistances obtained in the presence of LDH-BTSA are higher. R_p increases when the LDH-BTSA concentration rises from 1 g/l to 3 g/l. For an LDH-BTSA concentration of 3 g/l, R_p is about 1600 Ω cm². For this concentration, the calculated inhibitor efficiency is about 90%.

3.4. EIS measurements on coated samples

Impedance diagrams were obtained at the corrosion potential to characterize the corrosion resistance of the carbon steel covered by the pure epoxy coating and the epoxy coating containing 3 wt.% LDH-BTSA. The diagrams obtained after different exposure times to the NaCl solution are presented in Fig. 8.

For the pure epoxy (Fig. 8a), at the beginning of immersion, the impedance diagrams are characterized by a single time constant and the impedance modulus is very high. In the low frequency

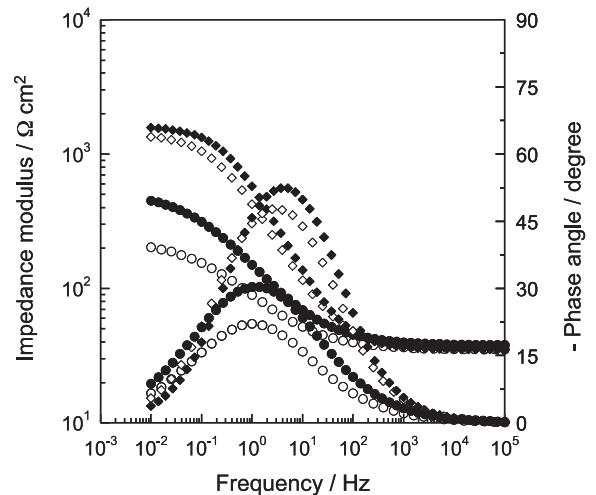


Fig. 7. Electrochemical impedance diagrams (Bode representation) obtained for the carbon steel electrode for three LDH-BTSA concentrations after 2 h of immersion in the 0.1 M NaCl solution: (○) without inhibitor; (●) 1 g/l; (◆) 3 g/l; (◇) 5 g/l.

domain, the impedance modulus decreased rapidly after 2 days of exposure to the aggressive solution and then progressively diminished with immersion time. After 35 days of exposure a modification of the low frequency part can be observed. For the epoxy containing 3 wt.% LDH-BTSA, independently of the immersion time, the diagrams present a single time constant (Fig. 8b). During the first two days of immersion, the impedance modulus decreased rapidly and then remained stable for longer immersion times.

It was proposed by Kittel et al. [31] and the group of Bierwaghen [32–34] that the impedance modulus at low frequencies (such as $|Z|_{1\text{ Hz}}$ or $|Z|_{10\text{ mHz}}$) measured versus exposure time could serve as an estimation of the corrosion protection of a painted metal. Fig. 9 plots $|Z|_{10\text{ mHz}}$ versus immersion time in 0.5 M NaCl solution for the carbon steel covered by pure epoxy and epoxy containing 3% LDH-BTSA.

For both coatings, the impedance modulus decreases rapidly during the first two days of immersion. After this exposure time, the modulus at low frequency continues to decrease for the pure epoxy. It remains relatively stable for the epoxy coating

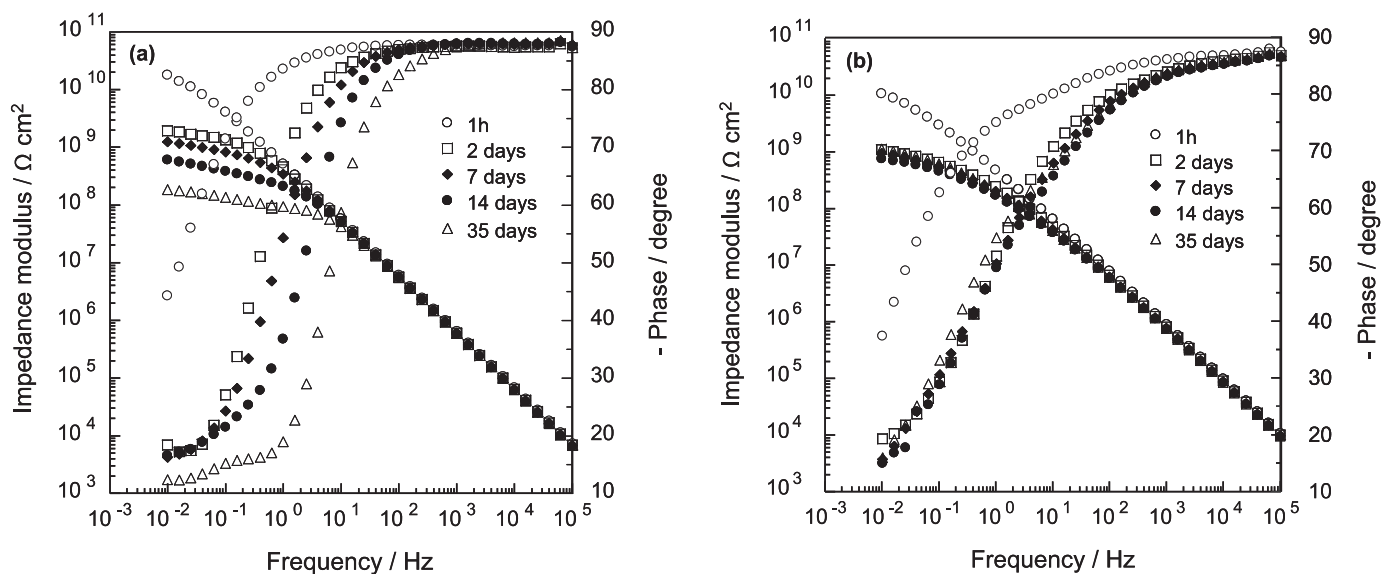


Fig. 8. Electrochemical impedance diagrams obtained after different exposure times to 0.5 M NaCl solution for the carbon steel covered by (a) pure epoxy coating and (b) epoxy coating containing 3 wt.% LDH-BTSA.

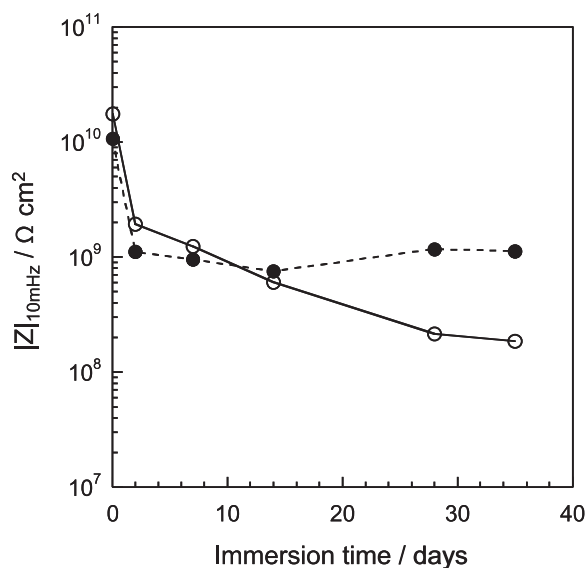


Fig. 9. $|Z|_{10\text{mHz}}$ versus immersion time in 0.5 M NaCl solution for the carbon steel covered by (○) pure epoxy and (●) epoxy containing 3 wt.% LDH-BTSA.

containing 3% of LDH-BTSA. By comparison with the pure epoxy, the impedance modulus of the LDH-BTSA containing coating is higher. These results show that the addition of LDH-BTSA improved the performance of the epoxy coating for the corrosion protection of the carbon steel.

After 35 days of exposure to 0.5 M NaCl solution, corrosion products were observed on the carbon steel covered by the pure epoxy coating, while no corrosion was observed for samples with coatings containing 3 wt.% LDH-BTSA.

4. Conclusions

LDH-BTSA were synthesized by the co-precipitation method. It was confirmed that BTSA was inserted into the galleries of the LDH and its loading was 33%. The release of BTSA from LDH-BTSA investigated for different NaCl solutions was dependent on the NaCl concentration. The BTSA release increased with the NaCl concentration. After 72 h in a 3% NaCl solution, 61% of the BTSA was released from LDH-BTSA. The polarization curves obtained on a carbon steel sample showed that LDH-BTSA is an anodic inhibitor. Its efficiency was about 90% at a concentration of 3 g/l. The presence of LDH-BTSA in an organic coating improved the corrosion protection of carbon steel.

This study has shown the feasibility of developing new formulations without toxic inhibitors.

Acknowledgments

The authors gratefully acknowledge the support of Vietnam's National Foundation for Science and Technology Development (NAFOSTED) through project no. 104.01.47.09 and CNRS (France).

References

- [1] G. Williams, H.N. McMurray, D.A. Worsley, *J. Electrochem. Soc.* 149 (2002) B154–B162.
- [2] S. Bohm, H.N. McMurray, S.M. Powell, D.A. Worsley, *Mater. Corros.* 52 (2001) 896–903.
- [3] S. Chrisanti, K.A. Ralston, R.C. Buchheit, *Corros. Sci. Technol.* 7 (2008) 212–218.
- [4] S.A. Garea, H. Iovu, *Prog. Org. Coat.* 56 (2006) 319–326.
- [5] T.T.X. Hang, T.A. Truc, T.H. Nam, V.K. Oanh, J.-B. Jorcin, N. Pébère, *Surf. Coat. Technol.* 201 (2007) 7408–7415.
- [6] T.A. Truc, T.T.X. Hang, V.K. Oanh, E. Dantras, C. Lacabanne, D. Oquab, N. Pébère, *Surf. Coat. Technol.* 202 (2008) 4945–4951.
- [7] T.T.X. Hang, T.A. Truc, M.-G. Olivier, C. Vandermiers, N. Guert, N. Pebere, *Prog. Org. Coat.* 69 (2010) 410–416.
- [8] A. Vaccari, *Appl. Clay Sci.* 14 (1999) 161–198.
- [9] S.P. Newman, W. Jones, *New J. Chem.* 22 (1998) 105–115.
- [10] F. Leroux, J.P. Besse, *Chem. Mater.* 13 (2001) 3507–3515.
- [11] A.I. Khan, D. O'Hare, *J. Mater. Chem.* 12 (2002) 3191–3198.
- [12] F. Cavani, F. Trifiro, A. Vaccari, *Catal. Today* 11 (1991) 173–301.
- [13] B.F. Sels, D.E. De Vos, P.A. Jacobs, *Catal. Rev.* 43 (2001) 443–488.
- [14] F.R. Costa, M. Saphiannikova, U. Wagenknecht, G. Heinrich, *Adv. Polym. Sci.* 210 (2008) 101–168.
- [15] G. Williams, H.N. McMurray, *Electrochem. Solid-State Lett.* 6 (2003) B9–B11.
- [16] R.B. Leggat, W. Zhang, R.G. Buchheit, S.R. Taylor, *Corrosion* 58 (2002) 322–328.
- [17] H. Wang, F. Presuel, R.G. Kelly, *Electrochim. Acta* 49 (2004) 239–255.
- [18] R.G. Buchheit, H. Guan, S. Mahajanam, F. Wong, *Prog. Org. Coat.* 47 (2003) 174–182.
- [19] P.V. Mahajanam, R.G. Buchheit, *Corrosion* 64 (2008) 230–240.
- [20] X. Yu, J. Wang, M. Zhang, L. Yang, J. Li, P. Yang, D. Cao, *Surf. Coat. Technol.* 203 (2008) 250–255.
- [21] M.L. Zheludkevich, S.K. Poznyak, L.M. Rodrigues, D. Raps, T. Hack, L.F. Dick, T. Nunes, M.G.S. Ferreira, *Corros. Sci.* 52 (2010) 602–611.
- [22] G. Williams, H.N. McMurray, *Electrochem. Solid-State Lett.* 7 (2004) B13–B15.
- [23] A. Braig, in: I. Sekine (Ed.), *Proceeding of the Symposium on Advance in Corrosion Protection by Organic Coatings III*, Electrochemical Society, Corrosion Division, 1998, pp. 18–31.
- [24] C. Nyambo, D. Chen, S. Su, C.A. Wilkie, *Polym. Degrad. Stab.* 94 (2009) 496–505.
- [25] D.P. Qiu, W.G. Hou, *Colloids Surf. A: Physicochem. Eng. Aspects* 336 (2009) 12–17.
- [26] Z.P. Xu, H.C. Zeng, *J. Phys. Chem. B* 105 (2001) 1743–1749.
- [27] P.S. Braterman, Z.P. Xu, F. Yarberry, *Handbook of Layered Materials*, Marcel Dekker, Inc., New York, 2004, p. 373.
- [28] J.C. Villegas, O.H. Giraldo, K. Laubernds, S.L. Suib, *Inorg. Chem.* 42 (2003) 5621–5631.
- [29] Y.F. Chao, *Appl. Clay Sci.* 40 (2008) 193–200.
- [30] M. Outirite, M. Lagrenée, M. Lebrini, M. Traisnel, C. Jama, H. Vezin, F. Bentiss, *Electrochim. Acta* 55 (2010) 1670–1681.
- [31] J. Kittel, N. Celati, M. Keddad, H. Takenouti, *Prog. Org. Coat.* 46 (2003) 135–147.
- [32] G.P. Bierwagen, D. Tallman, J. Li, L. He, C. Jeffcoate, *Prog. Org. Coat.* 46 (2003) 148–158.
- [33] R.L. De Rosa, D.A. Earl, G.P. Bierwagen, *Corros. Sci.* 44 (2002) 1607–1620.
- [34] B.R. Hinderliter, S.G. Croll, D.E. Tallman, Q. Su, G.P. Bierwagen, *Electrochim. Acta* 51 (2006) 4505–4515.