



Encapsulation and incorporation of sodium molybdate in polyurethane coatings and study of its corrosion inhibition on mild steel



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ABSTRACT

Sodium molybdate is evaluated as corrosion inhibitor for steel in brackish water; it is encapsulated by interfacial polymerization and the produced capsules are characterized. Electrochemical impedance spectroscopy and corrosion potential measurements were used to determine the short-time corrosion inhibition while polarization curves were used for the estimation of the inhibition efficiency. The capsules composition, the Na_2MoO_4 content and the release rate are then determined. Na_2MoO_4 shows corrosion inhibition for at least 15 h. Capsules consist of polyurea and polyurethane which are formed due to the reaction of the isocyanates with the water of the emulsion and the used surfactants, respectively. Most of the inhibitor is released within 90 min. Electrochemical Impedance Spectroscopy and Scanning Vibrating Electrode Technique show corrosion inhibition on artificially damaged areas for the coatings containing the corrosion inhibitor capsules.

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1. Introduction

Steel is the most common commercially used alloy since it combines good mechanical properties and relatively low cost. However, its main drawback is corrosion, which significantly decreases its lifetime and increases the cost of maintenance or replacement. Several protection strategies are used to decrease the effect of the corrosion. Protective coatings are typically used to isolate the metal from the environment, providing in many cases adequate corrosion protection [1]. However, coatings provide only passive protection and they fail to protect the metal when they are mechanically damaged. In many cases, inorganic anticorrosive pigments are added to provide active corrosion protection. Corrosion inhibitors hinder corrosion in areas where the coating has been mechanically damaged [2].

Corrosion inhibitors are compounds which when present in the electrolyte, interact with the metal and through various mechanisms, such as adsorption on the surface or formation of a passive layer, they hinder corrosion. Several compounds are used and studied as corrosion inhibitors such as chromates, heterocyclic organic compounds, rare-earth metal compounds, molybdates, phosphates and nitrates [2]. Chromates were commonly used as corrosion inhibitors in the past due to their high efficiency in aqueous media and their application for a wide range of metals and alloys. However, their use has been banned due to their high toxicity and carcinogenicity [2–4].

Molybdates are extensively used as corrosion inhibitors for steel but also for other metals. The exact mechanism of action of molybdates is not clear yet. Molybdates are expected to be oxygen-dependent inhibitors [5]. It is generally accepted that in the presence of O_2 , FeMoO_4 is formed which incorporates in the outer layers of the hydrated oxide film enhancing its stability [6–8].

Several studies are focused on the corrosion inhibition mechanism and the efficiency of the molybdates. Shams El Din and Wang performed a detailed study about molybdates in distilled and tap water [5]. They also studied the influence of the temperature, the electrolyte concentration and the presence of oxygen in the solution. Stranick studied the inhibition of molybdates in soft water for different acidities [9]. He showed that at low temperatures and high molybdate concentration active–passive behavior is exhibited and that high concentrations of molybdates substantially reduce the corrosion current density. The effect of the molybdates with other inhibitors was studied by Farr and Saremi [10]. They discovered that the efficiency of the molybdates is substantially increased when used with other corrosion inhibitors such as benzotriazole. However, it is not clear if there is a synergistic effect or a just cooperative inhibition. Saremi et al. studied the importance of the electrolyte hydrodynamics on the inhibition of molybdate in cooling water [11]. The work of Vukasovich and Robitaille provides more on the combination of sodium molybdate with organic and inorganic corrosion inhibitors. It was found that the combination of Na_2MoO_4 with other corrosion inhibitors can substantially enhance its efficiency [12]. All the aforementioned studies are focused on closed systems with low concentration of aggressive ions (Cl^-), where the corrosion inhibitor is dissolved in the electrolyte.

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Incorporation of the corrosion inhibitor in coatings is a common practice when they cannot be added directly to the electrolyte, for instance when metal are exposed to the environment. In our previous work, we incorporated cerium dibutyl phosphate (Ce(dbp)) in sub-micron plasma polymers and studied their electrochemical behavior [13]. An increase in the corrosion performance was noted but a decrease of the coating barrier properties over time was also observed. An extensive study about the replacement of chromates with other inorganic corrosion inhibitors in coatings was done by Sinko [14]. It was shown that the leaching of the inhibitor can promote osmotic blistering in the coating. Moreover, all the studied chromate alternative corrosion inhibitors were found to be significantly dependent on the environment. Zheludkevich et al. added Ce(NO₃) in sol–gel films and studied the effect on the corrosion inhibition. It was found that despite its beneficial contribution, when the inhibitor exceeds a critical concentration, which depends on the minimum efficient inhibitor concentration and its solubility, it significantly deteriorates the properties of the coating. Moreover, they concluded that corrosion inhibitor reservoirs play a crucial role in the storage and the release of the inhibitors [15,16].

A common way to decrease the influence of the corrosion inhibitors on the matrix and also to control their release is to encapsulate them prior to the incorporation into the coating [17]. Several techniques for encapsulation of corrosion inhibitors have been studied. Corrosion inhibitors have been added into oxide nanoparticles [16], have been encapsulated by using thermal phase separation, [18] or by using layered double hydroxide nanocontainers [19]. Interfacial polymerization is a common microencapsulation technique which has also been already used to encapsulate corrosion inhibitors [20].

Polyurethanes can provide high performance coatings however a lot of attention should be paid on the high cost and the special handling of the potentially hazardous isocyanates. For this reason, strict measures are required to avoid any kind of exposure to free isocyanates [21].

This is a study of encapsulation of corrosion inhibitors by inverse interfacial polymerization. It provides new insights on the incorporation of corrosion inhibitors in coatings and adds one more compound to the list of corrosion inhibitors that can be introduced by encapsulation. Sodium molybdate is encapsulated as corrosion inhibitor in polyurethane coatings on low-carbon steel. The main focus of the study is the encapsulation process and the characterization of the capsules since Na₂MoO₄ cannot be dissolved in the coating formulation while when encapsulated a suspension with the used polyol (castor oil) is formed. Further, the efficiency of the capsules in polyurethane coatings has been evaluated for short term corrosion exposure. The evaluation of the long term protection is part of the future study.

2. Materials and methods

2.1. Materials

Carbon steel SAE 1010 purchased from Q-lab was used as substrate. Sodium molybdate dihydrate of >99.5% grade and sodium chloride of >99.5% grade were purchased from VWR (PRO-LABO). For the inhibitor release test, Milli-Q water was used while for the preparation of other solutions double distilled water was used with conductivity <0.04 mS cm⁻¹.

For the preparation of the capsules methylene diphenyl diisocyanate (MDI) of >98% grade from ALFA AESAR was used. For the coatings formulation, a mixture of toluene diisocyanate (TDI) purchased from ALFA AESAR was used (80% 2,4-TDI, 20% 2,6-TDI). Glycerol anhydrous, Tween 80, Span 80 for synthesis and dibutyl tin dilaurate (DBTL) were purchased from Merck Millipore.

2.2. Encapsulation

For the encapsulation of the corrosion inhibitor, the interfacial polymerization technique was used following a procedure based on

the literature [22]. The ratio between lipophilic and hydrophilic surfactant was adjusted to achieve a stable emulsion [23].

Initially three solutions were made:

1. O1: 6.0 g Span 80 dissolved in 120 mL of toluene, out of which 30 mL was used for the preparation of the solution O2.
2. W1: 36.5 g of 31.5 wt.% Na₂MoO₄·2H₂O aqueous solution with 1.52 g of Tween 80. (containing 9.65 g Na₂MoO₄)
3. O2: 30 mL of O1 and 12 g MDI and 0.053 g DBTL used as catalyst.

The solutions O1 and W1 were poured into a 250 mL conical flask and stirred at 1200 rpm using a magnetic triangular bar for 1 h. The mixture was then stirred at 700 rpm and the solution O2 was added. The mixture was left at 700 rpm for 20 min at room temperature. The temperature was then increased to 63 °C (25 °C to 63 °C in <30 min) using an oil bath. During the encapsulation, MDI is expected to react with the water and the hydroxyl containing surfactants forming urea and urethane bonds, respectively (see Fig. 1).

After 4 h, the reacted emulsion was removed from the heating bath and the capsules were then decanted and filtered using a 3 μm to 5 μm mesh filtering paper. The filtered capsules were further washed with toluene and acetone, and dried overnight at 40 °C.

The synthesis yield ($\eta_{\text{synthesis}}$) was calculated based on the estimated encapsulated Na₂MoO₄:

$$\eta_{\text{synthesis}} = \frac{w_{\text{caps}} \times c_{\text{TGA}}}{w_{\text{NaMo}}} \times 100 \quad (1)$$

where w_{caps} is the total weight of the produced capsules, c_{TGA} the estimated by TGA wt.% concentration of Na₂MoO₄ in the capsules and w_{NaMo} the total amount of Na₂MoO₄ in the W1 phase.

This study focuses on the encapsulation process by inverse emulsions for corrosion inhibitors. Nevertheless, we are aware that several other aspects, such as the hazards from the use of isocyanates, the energy cost of the process and its economic viability, need to be investigated and improved in order to achieve a process that can be used in the industry.

2.3. Characterization of capsules with inhibitors

For the determination of the inhibitor release rate, capsules were dispersed in 50 mL of Milli-Q water, the conductivity of which was measured over time. The solutions were always stirred using a bar stirrer at 300 rpm and the conductivity was measured using a SCHOTT Instruments Lab 970 conductometer. In order to correlate the conductivity with the concentration of Na₂MoO₄ in the solution, released from the capsules, the conductivity of Na₂MoO₄ of different concentrations was measured and used as reference. The measurements were performed for 0.05 g, 0.1 g and 0.6 g of added capsules in solution.

Fourier Transform Infra-Red spectroscopy (FTIR) was used for the study of the composition of the produced capsules and coatings. FTIR measurements were performed with a Thermo Scientific Nicolet 6700 FTIR Spectrometer with a diamond crystal single bounce Attenuated Total Reflectance (ATR) set-up. The spectra were acquired between 600 cm⁻¹ and 4000 cm⁻¹ with an accumulation of 32 scans and a resolution of 4 cm⁻¹. Spectra acquisition was controlled by the OMNIC 8.1 software package (Thermo Electron Corporation, Madison, WI).

The thermogravimetric (TG) measurements were performed on a TA instruments TGA Q5000 using the Hi-Res mode [24,25] with dry air as the purge gas flowing at 25 mL min⁻¹.

For the observation of the capsules and the coatings, a JEOL JSM-IT300LV scanning electron microscope was used. The microscope was equipped with an Oxford X-Max energy dispersive spectrometer using a silicon drift detector. The accelerating voltage was 10 kV and the probe current was adjusted at 300 pA for the EDS mappings.

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