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Kinetic properties of layer-by-layer assembled cerium zinc molybdate nanocontainers during corrosion inhibition

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ABSTRACT

In the present study the loading of imidazole in between polyelectrolyte layers was carried out and the responsive release of imidazole was studied. Cerium zinc molybdate (CZM) was used as a core corrosion inhibitive nano pigment. The release rate of imidazole from CZM nanocontainer has been quantitatively estimated in water at different pH. The validation of quantitative analysis of release of corrosion inhibitor was carried out using the kinetic models. Results of electrochemical corrosion analysis of nanocontainer coatings on mild steel (MS) panel showed significant improvement in the anticorrosion performance of the nanocontainer/alkyd resin coatings.

1. Introduction

A problem of the modern day is rejection of materials due to corrosion which can be possibly prevented with an application of organic coatings that contain anticorrosion pigments. In recent times, numerous attempts have been focused on highly efficient corrosion inhibitive coating system with sustained release of the corrosion inhibitive agent [1]. Among the present pigments, zinc imparts anticorrosion properties by barrier and electrochemical mechanism [2]. Also molybdate conversion coatings have been investigated by many researchers as possible 'nonchromate' alternatives [3].

Technologies of encapsulation and release of various materials (e.g., drugs, oils, perfumes or corrosion inhibitors) are one of the rapidly developing research areas [4]. Nanocontainers and hollow spheres have been a subject of great scientific and industrial interest in the area of molecular biology, electronic materials, medical imaging etc. [5,6]. Furthermore, nanocontainers have been of concern to use as fillers, encapsulation of liquid agents, etc. The shells can be formed either by hydrolysis [7], in situ [8], in the presence of core materials. In the layer by layer assembly method the liquid active agent is encapsulated into the layer of oppositely charged polyelectrolyte layers. This method provides a good bonding of the organic functional groups to the metal surface, good barrier properties for corrosion protection. It is also important to note that these coatings remain active at lower temperature [9,10]. Nanopigment production using sonochemical approach is one important approach as it leads to generation of narrow size pigments with desired structures [11,12]. Following are some of the reports show the preparation of the layer by layer assembled nanocoatings. The preparation of shells on corrosion inhibitive nanoparticle that are constructed of corrosion inhibitor materials such as imidazole. To produce an inhibit impregnated polyelectrolyte shell, LbL deposition procedure involving both large polyelectrolyte molecules surrounded on inner and outer shell of the small quantity of a corrosion inhibitor has been pursued by many researchers [9,13]. Nanocontainers with a multifunctional shell can be prepared by using layer-by-layer (LbL) assembly of oppositely charged species (polyaniline and polyacrylic acid polyelectrolytes) on the surface [9]. PANI [14] is an important conducting polymer which may be used for the formation of a container because of its good environmental stability, high conductivity and low cost. It is also reported that PANI based coatings provided the protection to the metal surface against corrosive environments such as sulfuric acid solutions in the absence and presence of halide ions [15]. Kartsonakis et al. [16] have incorporated ceramic nanocontainers loaded with corrosion inhibitors into the conductive polymers coatings. The incorporation of ceramic nanocontainers loaded with corrosion inhibitor show significant enhancement in the corrosion resistance of these coatings that indicates that the presence of loaded

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nanocontainers into the conductive polymers coatings improved the corrosion protective properties of the films by increasing the total impedance values, and decreasing both anodic and cathodic currents relatively to coatings without nanocontainers. Kartsonakis et al. [17] also demonstrated the effect of loading of ceramic nanocontainers with corrosion inhibitor 2-mercaptobenzothiazole into hybrid organic–inorganic coatings on the corrosion protection of hot dip galvanized steel. In their report it has been reported that the corrosion resistance of these prepared coatings is found to be enhanced with loading of 4% w/w nanocontainers. Recently Kartsonakis et al. [18] have investigated the corrosion protection effectiveness of multifunctional epoxy coatings modified with pigments such as ceramic nanocontainers loaded with corrosion inhibitor, chloride and water traps, applied on AA2024-T3. Corrosion inhibitive efficiency has been reported to be improvement in the presence of the various used pigments. Saremi and Yeganeh [19] have applied mesoporous silica nanocontainer powders as corrosion inhibitor hosts and dispersed in the polypyrrole matrix. The more release of corrosion inhibitor from mesoporous silica nanocontainer has been reported at higher pHs and more aggressive chloride media indicating better protection to the substrates.

Further several kinetics models reported in the literature such as Zero order [20], first order [21], Higuchi [22], Hixson Crowell [23,24], and Korsemeyer Peppas [25] can be used to describe the corrosion inhibitor release from LbL assembled nanocontainers. These are several models available which can represent the corrosion inhibitor release as a function of time. The model equations can be derived from a theoretical analysis of the process e.g. zero order kinetics. In many cases prolonged release of corrosion inhibitor theoretical equations are not available, therefore in some case more adequate empirical equations can be used. Particle size, solubility, and types of corrosion inhibitor can influence the release kinetics. The kinetic study of the corrosion inhibitor release has been generally used to present the information about the diffusion processes and matrix degradation. Tyagi et al. [26] have studied different semi-empirical kinetic models to predict the release mechanism of benzotriazole in the solution maintained at different pH. The Korsmeyer–Peppas release model has been reported to be the best among the models used to predict the release of the corrosion inhibitor benzotriazole from silica nanocontainers.

A significant amount of work has been done in a past year, for the preparation of molybdate ion based anticorrosion coatings [11,27]. An investigation of molybdate behavior as a core material in LbL prepared nanocontainer has been not yet studied. Also it has been expected that initially release of imidazole will takes place with change in the pH of the environment which is acts as an active corrosion inhibitor in acidic as well as in basic environment and protects the substrate by the adsorption of the compact passive layer in its molecular or protonated form. Further once complete release of imidazole takes place then PANI and cerium inhibits the corrosion process thus protect the substrate from corrosion effectively [28]. With this objective in the present study CZM nanoparticles were used as a core material in the CZM nanocontainer. CZM nanocontainer was prepared by the deposition of polyaniline (PANI), imidazole and polyacrylic acid (PAA) layers on CZM nanoparticles in the presence of ultrasonic irradiation. The corrosion inhibitor (imidazole) is entrapped in between PANI and PAA layers. The responsive release and release rate of imidazole has been investigated quantitatively in aqueous media at different pH. The different theoretical and empirical equations have been used to study the release of corrosion inhibitor from LbL assembled CZM nanocontainer. The corrosion inhibition ability of CZM nanocontainer was evaluated by using dip test and electrochemical corrosion analysis method.

2. Experimental

2.1. Materials

Analytical grade zinc oxide (ZnO), cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$), sodium molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$), ammonium persulphate (APS, $(NH_4)_2S_2O_8$) as an initiator, sodium dodecyl sulfate (SDS, $NaC_{12}H_{25}SO_4$) as a surfactant and laboratory grade nitric acid (HNO_3) were procured from S.D. Fine Chem. and used as received without further purification. Analytical grade chemicals such as Myristic acid, imidazole, NaCl and methanol procured from Sigma Aldrich Chemical Co. and were used as received. Polyacrylic acid (PAA, M_w = 50,000 g mol^{-1}) was also procured from Sigma–Aldrich and were used as received. The monomer aniline (analytical grade, M/s Fluka) was distilled two times prior to use. Deionized water with conductivity of <0.2 μS/cm generated using the Elix 3 UV water purification system, has been used throughout the experimentation. Alkyd resin (Soya Alkyd Semidrying type) of Industrial grade was purchased from M/s Mahuli Paints, Pune, India. In this work Soya alkyd resin used has acid value = 06 and hydroxyl value = 56.

2.2. Preparation of cerium zinc molybdate nanocontainers

Ultrasound assisted chemical precipitation method reported by Patel et al. [11] was used for the synthesis CZM corrosion inhibitive nanopigment. Initially sodium zinc molybdate media were prepared by the chemical reaction between 0.2 M zinc oxide and 0.2 M sodium molybdate dihydrate solutions under ultrasonication. Stoichiometric amount of nitric acid was added dropwise to the above prepared mixture during the synthesis of sodium zinc molybdate media with the aid of ultrasonic irradiation. The reaction was carried out for 1 h in the presence of ultrasonic irradiation at 40 °C. Synthesis of CZM corrosion inhibitive nanopigment was carried out by chemical reaction between 0.025 M sodium zinc molybdate media and 0.016 M cerium nitrate hexahydrate solution in distilled water in presence ultrasonic irradiation for 40 min at 40 °C. The obtained precipitate was washed with hot deionized water (80–85 °C) 2–3 times in order to remove the impurity i.e. $NaNO_3$. Further, preparation of CZM nanocontainer has been implemented in a stepwise fashion. The steps are outlined here:

(1) Loading of a PANI layer onto nano CZM core by ultrasound assisted in-situ emulsion polymerization: Initially CZM nanoparticles (4 g in 150 ml water) were functionalized with 0.1 g Myristic acid solution in 5 ml methanol under ultrasonic irradiation at 60 °C for 30 min to accomplish hydrophobic properties of CZM nanoparticles. Myristic acid modification leads to adsorption of $C_{13}H_{27}COO^-$ functional group on the CZM nanoparticles surface which will create negative charge. Ultrasound assisted in-situ emulsion polymerization was used for encapsulation of treated CZM nanoparticles in PANI (positively charged) layer [15]. Encapsulation of CZM nanoparticles in PANI layer was accomplished as per below reported steps:

(i) Surfactant solution and initiator solutions were prepared separately by adding 1 g of SDS and 2 g of functionalized CZM nanoparticles (on the basis of monomer) in 100 ml deionized water and 3.5 g APS in 10 ml of deionized water respectively and then transferred to sonochemical reactor (Hielscher Ultrasonics GmbH, 22 kHz frequency 240 W power) as per method reported by Bhanvase and Sonawane [15].