Inclusion compounds of dibenzylthiourea with hydroxypropylated-cyclodextrins for corrosion protection of carbon steel in acidic medium

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In this work the complexation of the guest molecule (dibenzylthiourea-DBT) with α and β forms of hydroxypropylated cyclodextrins was evaluated in solution and in the solid state by different techniques. It was shown that the inclusion complexes were obtained and the aromatic moieties of DBT are points of interaction in the structure of the guest. The inhibitory action of these inclusion compounds in carbon steel corrosion in acidic medium was evaluated by polarization curves, electrochemical impedance diagrams and weight loss measurements. There is an enhancement of the inhibitory action against the carbon steel corrosion in HCl solution when the DBT was encapsulated in inclusion compounds whereas the alone hydroxypropylated cyclodextrins did not present an inhibitory effect. It was concluded that these inclusion compounds could be a good alternative to introduce molecules with low solubility in aqueous media and still increase their inhibitory action.

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1. Introduction

The use of corrosion inhibitors is an important method to protect metallic materials against corrosion in acidic medium. The acid solutions are widely used in industry for various purposes, such as acid pickling, acidification of petroleum wells, among others [1]. In general, inhibitors used in acid medium are organic compounds that contain N, O and S atoms in their structures [2]. The inhibition efficiency should increase according to the order of progressively stronger coordination bond, that is O < N < S [3]. The inhibitor that simultaneously has N and S atoms shows enhanced performance when compared to those that present either N or S [2]. Therefore, thiourea and its derivatives are known as effective corrosion inhibitors to iron and steel in HCl [1], H₃PO₄ [2], H₂SO₄ [4,5], HNO₃ [6], HClO₄ [7] and HCOOH [8] media. However, some organic compounds present limited water solubility which prevents their complete solubilization in the corrosion medium. In this case, some

additives that allow the formation of host-guest compounds must be used to achieve the maximum inhibition performance [9].

Cyclodextrins (CDs) are among these additives that form inclusion compounds with organic compounds. CDs are oligosaccharides that are composed of circularly linked 6 to 8 D-glucose units (corresponding to α, β and γ forms) in a configuration that resembles a torus shape. Therefore, the CD structure presents a cavity whose interior has a hydrophobic character that allows encapsulating organic guests. In contrast, the presence of hydroxyls in the CD rim makes the outside-cavity environment hydrophilic. This property permits to increase the solubility of some organic guests in aqueous medium by encapsulation in the CD torus. Taking this into consideration, cyclodextrins have been used in applications such as catalysis [10], controlled delivery of drugs [11], separations [12], and removal of organic contaminants from effluents [13].

There are some descriptions in the literature about the use of cyclodextrins to encapsulate corrosion inhibitors such as 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) [9] and 2-mercaptobenzothiazole (MBT) [14]. Inhibition efficiency is said to

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be over 90%.

In order to get over solubility issues concerning the dissolution in aqueous medium of most of the organic corrosion inhibitors we introduce the study and the use of encapsulated dibenzylthiourea in hydroxypropylated-cyclodextrin hosts. Firstly, the complexation of the guest molecule with α and β forms of CD was evaluated in solution and in the solid state. For this purpose, measurements of UV absorption, UV circular dichroism, FTIR and NMR spectroscopies and differential thermal analysis were carried out. The inhibitory action of the inclusion compounds between DBT and each CD in carbon steel corrosion in acidic medium was evaluated by weight-loss measurements and electrochemical techniques (electrochemical impedance and polarization curves), as well as by surface analyses using Scanning Electron Microscopy (SEM).

2. Experimental

2.1. Synthesis of the inclusion compounds of hydroxypropylated-cyclodextrins and dibenzylthiourea

Dibenzylthiourea, synthesized as described in the literature [15], and hydroxypropyl-alpha- or −beta-cyclodextrin, were mixed in a molar ratio of 1:2 in aqueous medium (3 mL of water or 1:1 water:ethanol mixture). This solution was maintained under magnetic stirring for 24 h at room temperature and then the solvent was evaporated. The residual solid was collected and ground in agate mortar.

In order to aid the solid-state characterization of each inclusion compound, mechanical mixtures were prepared mixing dibenzylthiourea and hydroxypropyl-alpha- or -beta-cyclodextrin in a 1:2 M ratio, respectively, in an agate mortar until forming a homogeneous solid.

2.2. In-solution characterization of inclusion compounds

For the UV absorption experiments, 1×10^{-3} mol L^{-1} stock solutions of dibenzylthiourea (DBT), 2-hydroxypropyl-alpha-cyclodextrin and 2-hydroxypropyl-beta-cyclodextrin (HPCDs) were prepared and used in order to have a set of solutions with DBT/(DBT + HPCD) molar fraction varying from 0 to 1.0. All these solutions were analyzed in a Varian Cary spectrophotometer.

For the ^{1}H NMR experiments, solutions were prepared employing 0.6 mL of DMSO-d_6 as the solvent, 5 mg of DBT and HPCD in order to have 1:10 DBT:HPCD molar ratios. HPCD solutions presenting the same concentrations as in the mixtures were also analyzed. The spectra were collected in a Bruker spectrometer DRX 400 with 300 MHz frequency using a wide band reverse probe of 5 mm in a single gradient in z.

Solutions of DBT:HPCDs presenting 1:10 M ratio in DMSO were analyzed by UV circular dichroism spectroscopy. The blank essays were carried out using the HPCDs solutions having the same concentrations. The spectra were acquired using a JASCO 815 spectrometer.

2.3. Solid-state characterization of inclusion compounds

The Fourier-transform Infrared Spectroscopy (FTIR) analysis was performed using KBr pellets prepared in order to contain 150 mg of KBr and 3 mg of the sample. The measurements were carried out in a FTIR spectrometer Nicolet Magna-IR 760, with 16 accumulation and 4 cm^{-1} resolution in the 4000-400 cm^{-1} interval. Spectra of the inclusion compounds and the mechanical mixtures were subtracted from those of the corresponding cyclodextrins using the OMNIC XP software (Nicolet).

Differential Thermal Analysis (DTA) curves were collected in a Shimadzu DTG 60 equipment. Approximately 5 mg of each sample were weighted in an alumina pan. Each run was performed having the set temperature of 175 °C under argon atmosphere (50 mL min^{-1}) with a heating rate of 10 °C min^{-1}.

2.4. Electrochemical procedure

Working electrodes were prepared from steel specimens with the following composition (wt.%): C: 0.18, P: 0.04, S: 0.05, Mn:0.30, Si: trace and Fe: balance. C-steel specimens were mechanically cut into 3.0 cm × 1.0 cm × 1.0 cm sections. Prior to each measurement, the sample surfaces were abraded with 400, 600 and 1200 grade emery paper, washed with double-distilled water, degreased with acetone and dried in warm air.

All electrochemical measurements were conducted in a conventional three-electrode Pyrex cell where the working electrode exposed surface area to the electrolyte was of 0.78 cm^2. A saturated calomel electrode (SCE) and a large-area platinum wire were used as the reference and auxiliary electrodes, respectively. The electrolyte was a 1 mol L^{-1}HCl solution prepared from 37 wt% HCl (purchased from Merck Co. Darmstadt − Germany) and double distilled water. In the DBT study the electrolyte was a 1 mol L^{-1}HCl solution containing 3% (v/v) of ethanol (purchased from Vetec Química Fina Ltda., Duque de Caxias − Brazil). All experiments were carried out in 100 mL of non-stirred and naturally aerated electrolyte maintained at 25 °C.

In all experiments, the carbon steel electrode was allowed to reach its stable open-circuit potential (OCP), which occurred after 1 h. After this time, electrochemical impedance measurements were performed over a frequency range of 100 kHz to 10 mHz at the stable open circuit potential with an AC wave of 10 mV (rms). Potentiodynamic anodic and cathodic polarization curves were performed using as can rate equal to 1 mV s^{-1},from−300 mV up to +300 mV in relation to the stable open-circuit potential. The polarization curves were obtained immediately after the electrochemical impedance measurement.

The electrochemical experiments were performed using anAutolab PGSTAT 128 N potentiostat/galvanostat, controlled byGPES 4.9 electrochemical software from Metrohm Autolab (The Netherlands). The inhibition efficiency (n%) was calculated from the electrochemical impedance diagrams and the potentiodynamic polarization curves, as follows (equations (1) and (2)), respectively):

$$n\% = (R_{ct} - R_{ct,0}/R_{ct}) \times 100 \qquad (1)$$

where $R_{ct,0}$ is the charge-transfer resistance in the absence of the inhibitor and R_{ct} is the charge-transfer resistance in the presence of the inhibitor (DBT, HPαCD, HPβCDor the HPαCD:DBT and HPβCD:DBT complexes in a molar ratio of 2:1), obtained from the electrochemical impedance diagrams.

$$n\% = \left(j_{corr,0} - j_{corr}/j_{corr,0} \right) \times 100 \qquad (2)$$

where $j_{corr,0}$ is the corrosion current density in the absence of the inhibitor and $j_{corr}$is the corrosion current density in the presence of the inhibitor (DBT, HPαCD, HPβCDor the HPαCD:DBT and HPβCD:DBT complexes in a molar ratio of 2:1), obtained from Tafel plots.

2.5. Weight loss experiment

The same C-steel specimens used in the electrochemical measurements were abraded with 100 grade emery paper, sandblasted,