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Formylhymecromone and formylumbelliferon as corrosion inhibitors

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Abstract

Corrosion inhibitors derived from 4-methylumbelliferon namely 8-formylhymecromone and 4-formylumbelliferon have been synthesis and fully identified through spectroscopically techniques (Fourier transform infrared and nuclear magnetic resonance). The inhibition efficiencies for 8-formylhymecromone and 4-formylumbelliferon to reduce the damage impact of corrosion for mild steel in corrosive solution were investigated and they were 69.8% and 67.1% respectively based on weight loss method.

Keywords: 8-Formylhymecromone, 4-formylumbelliferon, corrosion inhibitor

1. Introduction

Nowadays organic compounds are very important due to biological applications [1-3]. Derivatives of coumarin have been extremely considerable, molecules that applicable in biological approaches [4–6]. Numerous of these derivatives have been confirmed as antimicrobial, anti-inflammatory [7], anticoagulant [8], antiHIV [9] and antitumor [10] compounds. Also these derivatives extremely employed in foods and additives [11], moreover they utilized in dyes and optics [12, 13]. Many coumarins act as preferable scavenger's agents [14]. Modification in the structure of coumarin shows inhibition of unit enzyme [15–19]. Inhibitors for corrosion act as resistance for the surface of mild steel in corrosive solutions to inhibit corrosion by adsorb the inhibitors molecules [20-25] in order to produce barriers to protect the mild steel surfaces [26-28]. Anticorrosion inhibitors that have the abilities to adsorb on the surface of metal were influenced by many factors, such as the metal surfaces natures, electrolyte types and inhibitors structures [29, 30]. Corrosion inhibitors have the abilities to forming stable complexes between inhibitor molecules and metal that act as protected barrier fir the surface of metal in corrosive solutions [31]. To develop my previously studies on applicable organic molecules, a synthesized umbelliferons namely 8-formylhymecromone and 4-formylumbelliferon that was characterize through infrared IR and nuclear magnetic resonance NMR techniques. The inhibition abilities were figured according to weight loss method.

2. Materials and Methods

2.1. Materials

Solvents and chemicals that wanted in this research were employed without extra purifications. Spectrum of infra-red has been performed utilizing FTIR-8300 Shimadzu spectrometer. CHN analyses were done 5500 Carlo Erba. Spectrum for NMR were obtained by 300MHz Bruker instrument with dimethylsulfoxied-d6 as solvent and TMS as internal standard.

2.2. Synthesis of 8-Formylhymecromone as 1st corrosion Inhibitor

A solution of glacial acetic acid (70 mL) that have hymecromone (10.20 g, 0.05 mol) and hexamethylenetetramine (21.0 g, 0.15 mol) were under refluxed for 7.0 hrs, then, 20% HCl (125 mL) has been add with refluxed gently for one hour. Extracted with diethyl ether, dried and using of dioxane and ethanol as recrystallization

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solution [32]. M.P. 177oC. FT-IR in cm-1: 3396.5 for hydroxyl group; 1748.3 for lactonic carbonyl; 16651.8aldehydic carbonyl. 1H NMR: 2.72 (s, CH3), 6.31 (s, C=CH), 6.97-7.05 (d, CH aromatic), 5.17 (s, O-H) and 11.16 (s, 1H aldehyde) [33].

2.3. Synthesis of 4-formylumbelliferon as 2nd corrosion Inhibitor

A solution of xylene (70 mL) that have hymecromone (10.20 g, 0.05 mol) and SeO2 (11.0 g, 0.10 mol) were under refluxed for 12.0 hrs. Filtered than evaporated to get yellow powder. M.P. 222oC. FT-IR in cm-1: 3243.7 for hydroxyl group; 1736.8 for lactonic carbonyl; 1689.1 aldehydic carbonyl. 1H NMR: 6.98 (s, C=CH), 6.78, 6.95 and 7.21 (d, CH aromatic), 5.45 (s, O-H) and 10.88 (s, 1H aldehyde) [34, 35].

2.4. Corrosion technique

Mild steel samples which were employing for this research as an electrodes were purchased through Metal Samples Company. 99.21% was the iron portion; 0.21% was the carbon portion; 0.38% was the silicon portion; 0.09% was the sulfur portion; 0.05% was the manganese portion and 0.01% was the aluminum portion. The efficient of inhibition for investigated chemical compound for surface of mild steel have the aria equal to 4.5 cm2 and have been cleaned regarding to reference [36]. Mild steel samples have been suspended based on the typical procedure in acidic solution 200mL., of hydrochloric acid without the inhibitors 8-Formylhymecromone (or 4-formylumbelliferon) and also with the inhibitor at the concentrations 0.001, 0.05, 0.10, 0.15, 0.2.0, 0.25 and 0.50 g/L for (1, 3, 5, 10, 24 and 72 h). The efficiencies of inhibition were figured regarding to equation 1

$$\mathrm{IE}(\%) = \left(1 - \frac{W_2}{W_1}\right) \times 100 \qquad 1$$

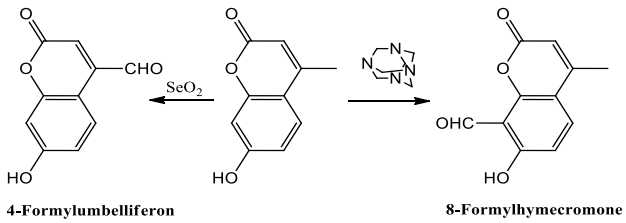
where W_1 and W_2 referred to weight of the sample of MS (mild steel) in presence of and absence 8-formylhymecromone (or 4-formylumbelliferon) respectively.

3. Results and discussion

3.1. Synthesis

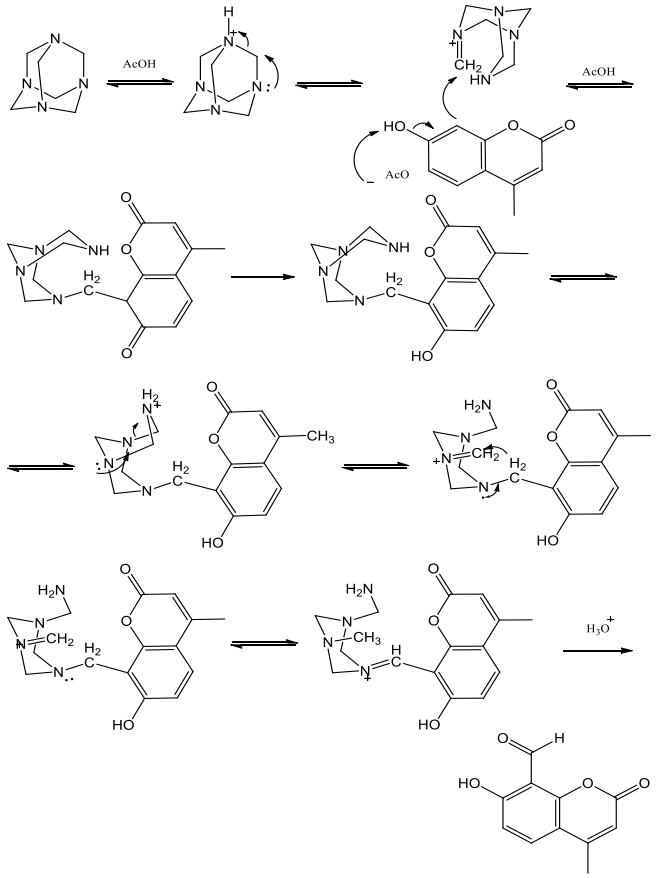
The inhibitor 8-formylhymecromone was synthesized in a modest product through reaction of same molar ratio of hymecromone and hexamine. The molecular formula of hymecromone. In infrared spectrum of hymecromone has a carbonyl absorption band for aldehyde group that appeared for 8-formylhymecromone. The Nuclear magnetic resonance spectrum demonstrated singlet at δ 12.16 ppm, due to the proton of C=O). 8-Formylhymecromone has been prepared from hymecromone as in Scheme 1.

Scheme 1: 8-formylhymecromone and 4-formylumbelliferon synthesis



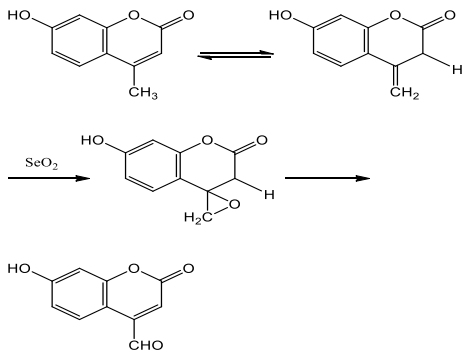
The mechanism of formyl formation via hexamethylenetetramine can be shown according to Scheme 2.

Scheme 2: Mechanism for the formation of 8-formylhymecromone



Oxidation of the methylene for 4-methylumbelliferon with SeO2 in acetic acid provides α-oxidation at position 4. 4-Methylumbelliferon oxidized in this way gave 4-formylumbelliferon in good yield. The chemo-selective reaction of SeO2 with 4-methylumbelliferon was described. This reaction was dependent on the nature of the methyl group. As in Scheme 3, the mechanism represent formation of ring with three bonds as an epoxide ring that hydrolysis to carbonyl group.

Scheme 3: Postulated mechanism for the synthesis of 4-formylumbelliferon.



3.2. Results of weight loss technique

Using of corrosion inhibitors in manufactures become the great economic manner due to surface protection for mild steel versus corrosive solutions [34]. Synthetic or natural inhibitors were the required materials employed industries oil and gas because of the formation of protect barrier for the surface of metals and alloys. The importance of utilizing corrosion inhibitors with the atoms nitrogen, oxygen and/or sulfur due to ability of these atoms to coordinate with metal and forming stable complex [37-40].

3.3. Concentration effect

Weight loss methodology that used to calculate the inhibition efficiencies of 8-formylhymecromone and 4-formylumbelliferon with the concentrations (0.05, 0.1, 0.15, 0.2, 0.25 and 0.5 g/L) for period of times (1, 3, 5, 10, 24 and 72 h) and fixed temperature (303K) in hydrochloric acid solution of for mild steel surface. The 8-formylhymecromone results which were showed in Figure 1, referred to the power of 8-formylhymecromone to diminish the corrosion that happened to the acidic solution of mild steel surface with highest inhibition efficiency 69.8% based on highest investigation concentration. The 4-formylumbelliferon results which were showed in Figure 2, referred to the power of 4-formylumbelliferon to diminish the corrosion that happened to the acidic solution of mild steel surface with highest inhibition efficiency 67.1% based on highest investigation concentration.

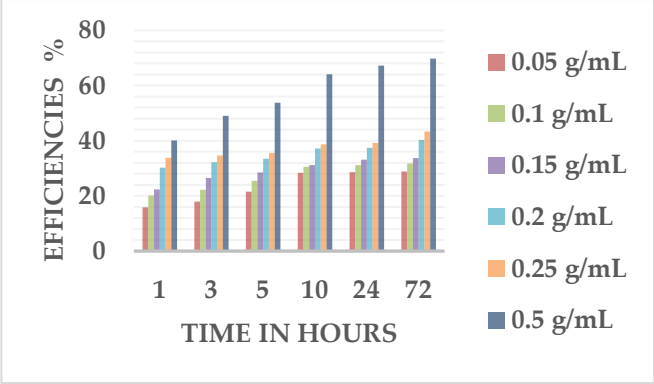


Figure 1: Function of time at concentrations of 8-formylhymecromone.

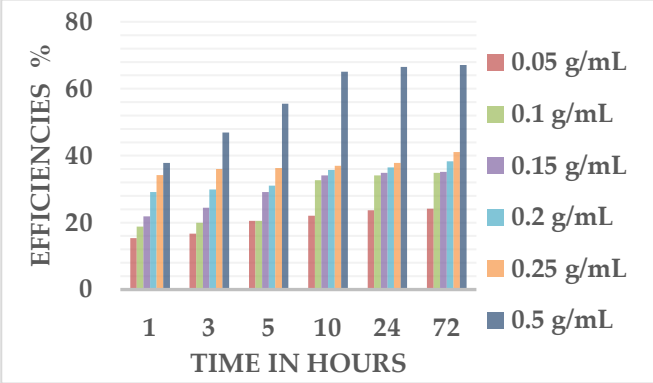


Figure 2. Function of time at concentrations of 4-formylumbelliferon

4. Conclusion

8-formylhymecromone and 4-formylumbelliferon as inhibitors for metal surface (MS) which were prepared from 4-methylumbelliferon. The structures of these compounds were elucidate according to proton-NMR and FT-IR spectroscopies. Inhibition efficiencies of the inhibitors 8-formylhymecromone and 4-formylumbelliferon in acidic solutions of 1M for MS has been studied. 8-formylhymecromone, showed a moderate action as inhibitor that with maximum efficiency 69.8% and 67.1% respectively at the maximum investigated concentrations of 8-formylhymecromone and 4-formylumbelliferon.

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