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Acetamidocoumarin as a based eco-friendly corrosion inhibitor

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Abstract : Eco-friendly corrosion inhibitor derived from coumarin namely3-acetamidocoumarin was synthesized by reaction of salicylaldehyde and aceturic acid. The chemical structure of 3-acetamidocoumarin had been elucidation some spectroscopic techniques (Fourier transform infrared (FT-IR) and proton Nuclear magnetic resonance (NMR)) and elemental micro analysis (CHN). Inhibition efficiency of the synthesized inhibitor in corrosive solution was evaluated based on weight loss technique. Increasing in inhibition efficiency (IE %)was achieved by rising of concentrations of the green inhibitor and reach to 91% at the highest concentration, also the IE %, decrease with the rising of temperature. To establish the activity of 3-acetamidocoumarin as a perfect corrosion inhibitor, scanning electron microscopy (SEM) was utilized as another technique. From SEM technique we understand the mechanism of protection and it accomplished by adsorption of the eco-friendly inhibitor molecules on the MS (mild steel) surface and formation of protective film of the inhibitor on surface of the MS.
Keywords: 3-acetamidocoumarin, salicylaldehyde, aceturic acid, green corrosion inhibitor, eco-friendly.

1. Introduction

MS had been mostly utilized for the manufactures in the gas-oil industries because of the excellent, mechanistic features [1]. Various issues showed during transport of gas-oil in the pipeline, due to migrating of ions arrive to impinge with metal because of the denaturation of the emulsion solution (oil-aqueous), that induce corrosion approach 2 moreover, the corrosion has been enhance by the existence of salts in the oil and the corrosive solution which had been applied widely [3].In concentrated hydrochloric or sulfuric acids, the corrosion methods harvest the damages in the mild steel composite. Several sort of inhibitors that are immensely, applied to hold the corrosion case of MS when offered to concentrated hydrochloric or sulfuric acids, that vary from organic molecules to Nano-composites[4-8].Usually, the capability to form powerful coordination bonds and, as a conclusion, the inhibition performance rise according to subsequent: Oxygen(O)<Nitrogen(N)<Sulfur(S)<Phosphorous(P)[9]. Scanning, of organic compounds which applied as corrosion inhibitors have been a significant field of studies, due to its advantage in several industries[10]. Organic compounds have heterocyclic rings or heteroatoms have been chosen and become an excellent inhibition as applied with acids and bases [11]. Concerning to a continuance published articles[12–16], we focus on the utilized organic compounds with heteroatoms as new corrosion inhibitors[17-29]. 3-Acetamidocoumarin has been prepared in clarity to be applied as a corrosion inhibitor. Elucidation of chemical structure of 3-acetamidocoumarin had

been confirmed according to some spectrochemical techniques named Fourier transform infrared spectroscopy and Nuclear magnetic resonance spectroscopy in addition to elemental analysis. The using of 3-acetamidocoumarin as corrosion inhibitor is based on the truth, of containing oxygen and nitrogen atoms that made the inhibitor molecules have high efficiently towards inhibition of corrosion of MS in acidic solution. Chemical structure for the 3-acetamidocoumarin has been demonstrated in Figure 1.

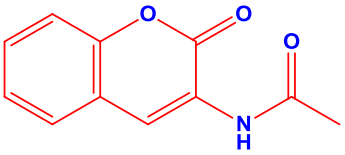

Figure 1.The structure of 3-acetamidocoumarin.

Experimental

Materials:

The chemicals that where utilized in our search were provide by Sigma-Aldrich and/or Fluka and applied with no addition procedure. Fourier transform infrared spectra were applied on a FT-IR 8300 Shimadzu Spectrophotometer. Nuclear magnetic resonance spectra had been done by using 300 MHz Bruker-DPX spectrometer with TMS as internal standard. Elemental micro analysis CHN, was carried out utilizing a 5500-Carlo Erba analyzer. A melting point instrument model Gallenkamp M.F.B.600.010 F had been applied to detect the melting point of corrosion inhibitor.

Synthesis of corrosion inhibitor (3-acetamidocoumarin).

Reflux of aceturic acid (58.5 g, 0.5 mol), salicylaldehyde (92.7 g, 0.76 mol) with acetic anhydride (0.5 mL, 0.053 mol) and few drops of piperidine at 130 °C for 8hrs, then cool to room temperature. Solid was separated out washed with diethyl ether, dried and recrystallized from ethanol to producewhite solid of 85% yield of3-acetamidocoumarin. Melting point was199°C; $NMR_{spectroscopy}$: σ2.19 (s, 3H for methyl group); σ 6.73 (d, for 1H of alkene); σ 7.38-7.55 (m, for 1H ofbenzene ring); σ8.44 (s, 1H, amine).$IR_{spectroscopy}$: 3307.3 cm^{-1} for amino group; 3087.1 aromatic ring; 1711 cm^{-1} for lactone group and 1681 cm^{-1} for carbonyl group.$CHN_{analysis}$ for $C_9H_7NO_2$ were C 65.90% (C 65.02%)H5.01% (H 4.46%), N 7.11% (N 6.89%).

Weight loss measurements:

The necessary samples of Mild steel (MS) had been obtained from Metal Samples Company and were applied as active electrodes consideration and recognize the composition (wt%) as: 99.21(Iron), 0.21(Carbon), 0.38(Silicon), 0.09(Phosphorous), 0.05(Sulfur), 0.05(Manganese) and 0.01 (Aluminum). The samples had been cleaned regarding to ASTM methodology principles G1-03 [30]. All methodologies have been done in aerated, non-stirred one normal of hydrochloric acid with several concentrations of 3-acetamidocoumarin as an investigated inhibitor. MS samples of 25mm×20mm×0.25mm and using distilled water two times for washing, rinsed with ethanol, acetone and dried. Weighing accurately, suspended in 1L of 1.0 M hydrochloric acid at several concentrations of the 3-acetamidocoumarin (0.0, 0.05, 0.1, 0.15, 0.20, 0.25 and 0.50 mM) for 1, 2, 3, 4, 5, 10, 24 h. After each immersion time, samples were occupied, washed, dried, weighed accurately and the weight loss methods were done in triplicate.

Scanning Electron Microscopy (SEM) Morphologies:

SEM examination was done at the Electron Microscopy Unit/UKM with SEM/TM1000 Hitachi Tabletop Microscope at 2000× magnification. Realization of the MS samples was carried out for submerged in corrosive solution, with and without of 3-acetamidocoumarin for three hrs. SEM. The morphology of the surface of the metal samples had been researched by SEM directly after the weight loss method.

Results and discussion

The synthesis of 3-acetamidocoumarin had been carried out by refluxing of a mixture of salicylaldehyde with aceturic acid and piperidine as a strong base. Reaction sequence for the formation the green inhibitor that derived from coumarin is outline in Figure 2.

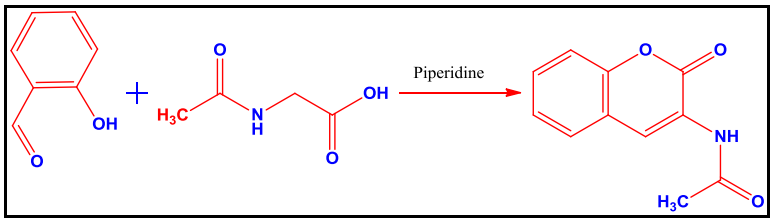

Figure 2.Preparation of 3-acetamidocoumarin.

The FT-IR spectrum of 3-acetamidocoumarin showed absorption peaks for amino and carbonyl groups at 3307.3 cm^{-1} and 1681 cm^{-1}respectively. The 1H-NMR spectrum exhibited a singlet at δ 6.73 (d, for 1H)ppm due to proton for alkene group. Suggested mechanism may be based ona mechanism namely carbanion as in Figure 3.

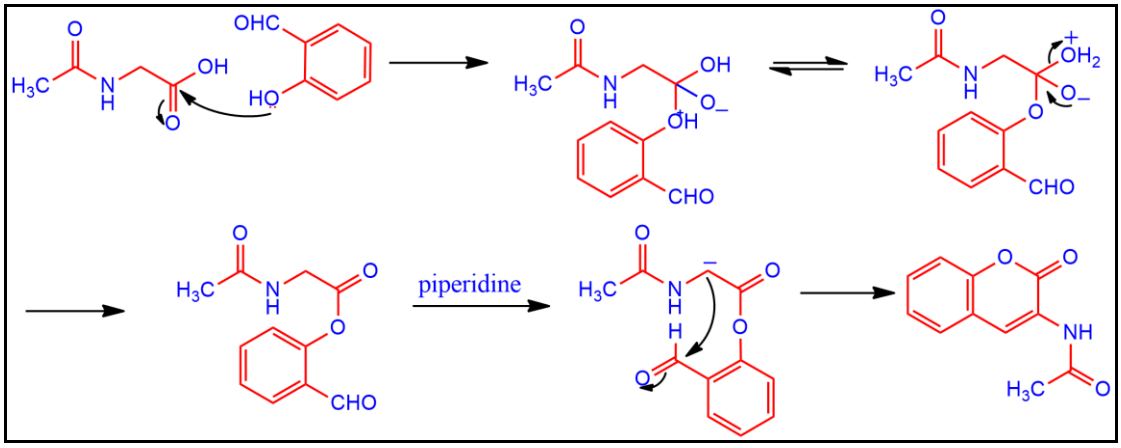

Figure 3. The reaction mechanism or the formation of 3-acetamidocoumarin

Concentration Impact

The impact of increment of 3-acetamidocoumarin in corrosive solution on the corrosion of mild steel was examined based on weight loss technique for a period of time (1, 2, 3, 4, 5, 10 and 24 h) at 303 K. The values of corrosion rate and inhibition efficiency with and without 3-acetamidocoumarin was shown in Figures 4 and 5.The corrosion rate and the inhibition efficiency IE (%) had been estimated based on Equations 1 and 2 respectively:

$$C_R(Corrosion\ rate) = 87.6\ W/at\rho \qquad (1)$$

Where, w is the weight loss, ρ is the density of mild steel, a is the area of specimen and t is the time of immersion.

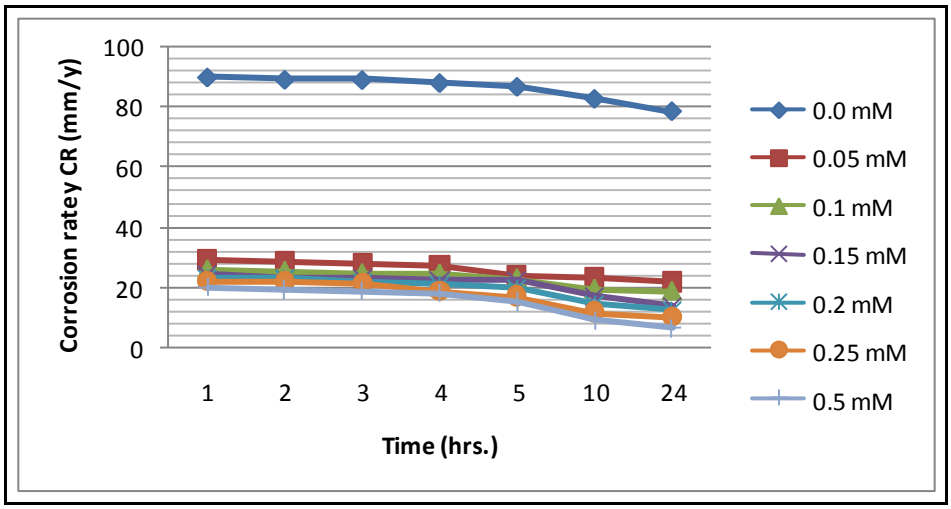

Figure 4.Impactof 3-acetamidocoumarin concentration andtime on corrosion rate of mild steel at 303 K.

$$\text{IE\% (Inhibition Efficiency)} = \frac{w_1 - w_2}{w_1} \times 100 \qquad (2)$$

where the W and W' were the weight of the mild steel samples without and with inhibition.

The corrosion rates were markedly decreased and the inhibition efficiency was enhanced with the increasing concentration of 3-acetamidocoumarin. The improvement ofIE(%) with the higher concentration is revealing of the raise in the range of protection efficiencies of 3-acetamidocoumarin.

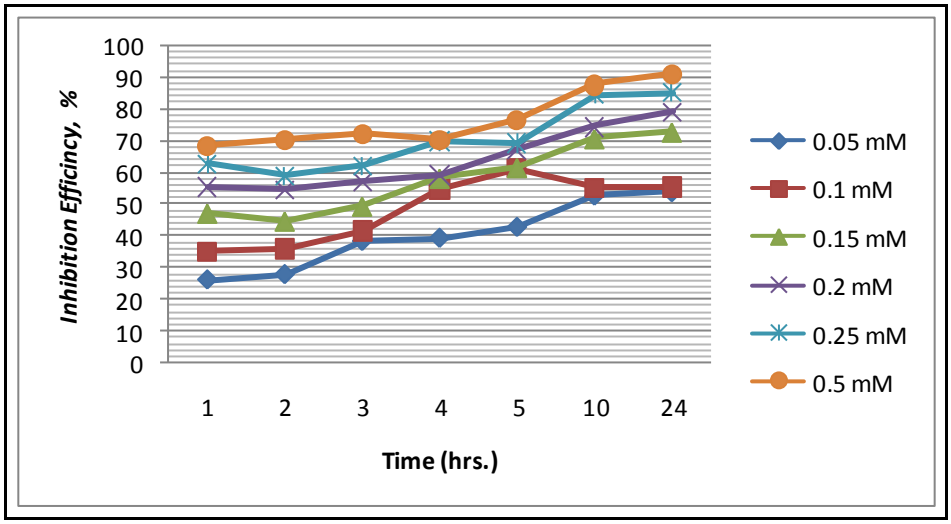

Figure 5.Impact of 3-acetamidocoumarin concentration and time on inhibition efficiency of mild steel at 303 K.

Temperature Impact

A differentiation of the inhibition efficiency of 3-acetamidocoumarin on mild steel in corrosive solution with various concentrations (0.0, 0.05, 0.1, 0.15, 0.20, 0.25 and 0.50 mM) of 3-acetamidocoumarin at temperatures (303, 313, 323 and 333 K) indicated that IE improved with enhancement of concentration of 3-acetamidocoumarin and also decreased with higher temperature as shown in Figure 5.For the adsorption process of inhibitor molecules, the heat of adsorption is markedly negative, and this specified an exothermic reaction. This is the cause that the inhibition efficiency decreases at a higher temperature.

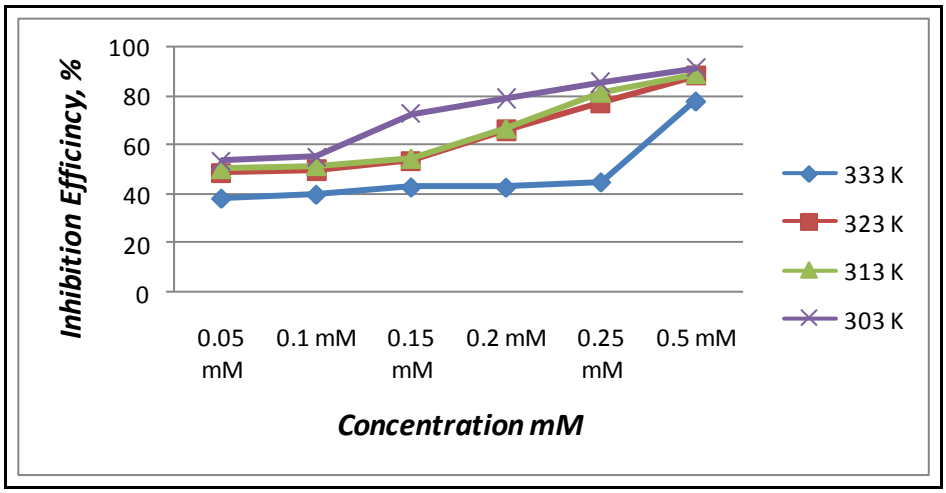

Figure 6.Impact of temperature on inhibition efficiency of 3-acetamidocoumarin at various concentrations

SEM

Regarding to Figure7, as predictable, significant corrosion of mild steel appeared where the MS (mild steel) surface, that was primarily smooth and clean, turn into harsh. The MS surface was markedly attacked by corrosive solution. Regarding to Figure 8, MS surface dose not afford, significant corrosion. 3-acetamidocoumarin has the ability to completely protective potentiality the MS from the corrosion exposure relevant by corrosive solution.

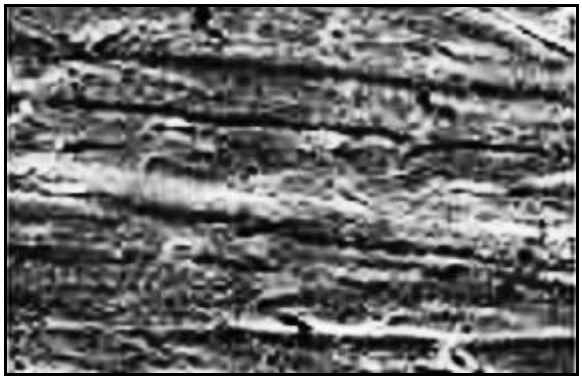

Figure 7.The SEM micrograph for mild steel in 1.0 M HCl at 30 °C for 5 h as immersion time.

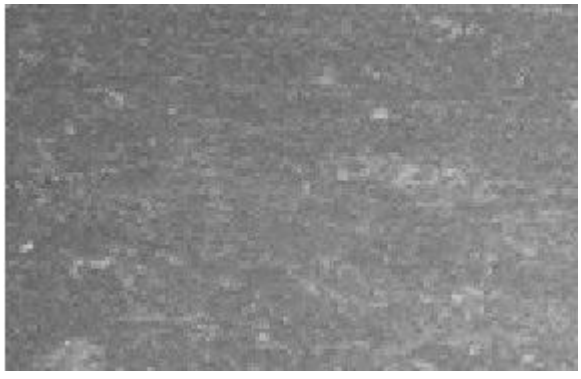

Figure 8.The SEM micrograph for mild steel in 1.0 M HCl with 0.5 mM of 3-acetamidocoumarin at 30 °C for 5 h as immersion time.

Postulated mechanism

3-Acetamidocoumarin is adsorbed on the MS surface to produce a thin film as a completely protective potentiality and/or coordination bonds through the reaction of 3-acetamidocoumarin as an inhibitor and MS as a metal. The adsorption mechanism of 3-acetamidocoumarin could conduct through one of three channels. The first channel, is the charge of 3-acetamidocoumarin molecules and electrostatically attract o the metal. Second channel, represented by the interaction of unshared electrons of oxygen and/or nitrogen atoms with the metal. Third Channel is the interaction of π-electrons of double bond of 3-acetamidocoumarinand the metal surface. 3-Acetamidocoumarin may protect the metal surface via blocking cathodic and/or anodic to produce metal complex. Inhibition efficiencies of 3-acetamidocoumarinof the corrosion of mild steel in corrosive solution may be demonstrated based on the adsorption sites, charge, size of molecules, interaction with metal and ability of metal complex. The π electrons for the double bond and free electrons on the oxygen and nitrogen atoms form chemical bonds with the metal surface as shown in Figure 9.

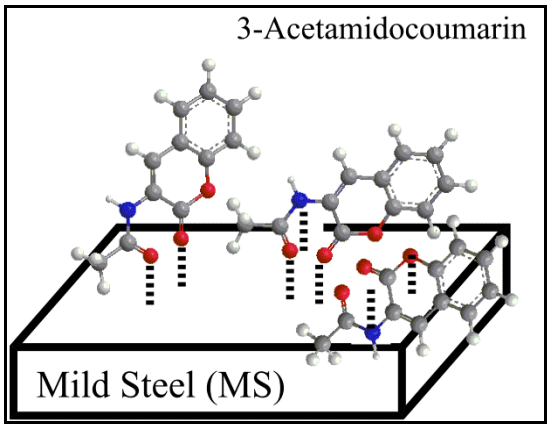

Figure 9. The postulated inhibition mechanism for 3-acetamidocoumarin

Adsorption Isotherm

Generally adsorption rely, on the nature of the metal surface, electronic properties of the metal, adsorption of solvents and ionic species, on the electrochemical potential at solution interface. The adsorption mechanism of inhibitors molecules on MS surface could be demonstrated based on the investigation of adsorption isotherm and behavior of the inhibitor. The generality frequently utilized adsorption isotherms are the Langmuir, Temkin, Frumkin, and Freundluich isotherms[31]. Corrosion inhibition of inhibitors on MS corrosive solution could be explained according to a molecular adsorption technique. The adsorption method is affected by the molecular structure of inhibitor with distribution of charge on molecules in addition to nature of the MS surface and the corrosive media[32].The significance of surface coverage (θ) for the various concentrations of 3-acetamidocoumarin had been utilized to show the worth adsorption isotherm to determine the adsorption process. To estimate θ, it was supposed[33-38] that the IE (%) was appropriate generally to the blocking impact of the adsorbed species as in Equation (3) applies:

$$\theta = IE\%/100 \qquad (3)$$

In this investigation, θ was estimated from the equation 3, utilizing the IE that estimated from the weight loss method. The plots of C_{inh}/θvs C_{inh}yield a straight line, referencing that 3-acetamidocoumarin obeys the Langmuir adsorption isotherm, as inthe Equation (4):

$$C_{inh}/\theta = 1/k_{ads} + C_{inh} \qquad (4)$$

where$C_{inh}$is 3-acetamidocoumarin concentration and $k_{ads}$is the adsorption constant gained from the intercept of the straight line.

k_{ads}iscorrelating with the standard free energy of adsorption ΔG^{o}_{ads}.

ΔG^{o}_{ads}isassumed by means of Equation (5):

$$\Delta G^{o}_{ads} = -RTln[k_{ads}] \qquad (5)$$

where the value of 55.5 demonstrate the molar concentration of water in solution obvious in units of M. R is the universal gas constant and T is the absolute temperature.

The value of *Kads* and ΔG^{o}_{ads} wareestimated based on Figure 10 and the estimated $\Delta G^{o}_{ads}$was−26.13 kJ/mol. The negative charge of ΔG^{o}_{ads}indicate spontaneously adsorption of the 3-acetamidocoumarin on MS surface and a strong interactionsof 3-acetamidocoumarin molecules and the MS surface. Usually, a value of ΔG^{o}_{ads} nearly −20 kJ/mol is consistent with physical adsorption, but value of ΔG^{o}_{ads}nearly −40 kJ/mol is chemical adsorption occurring viatransfer of unpaired electrons from 3-acetamidocoumarin to MS.

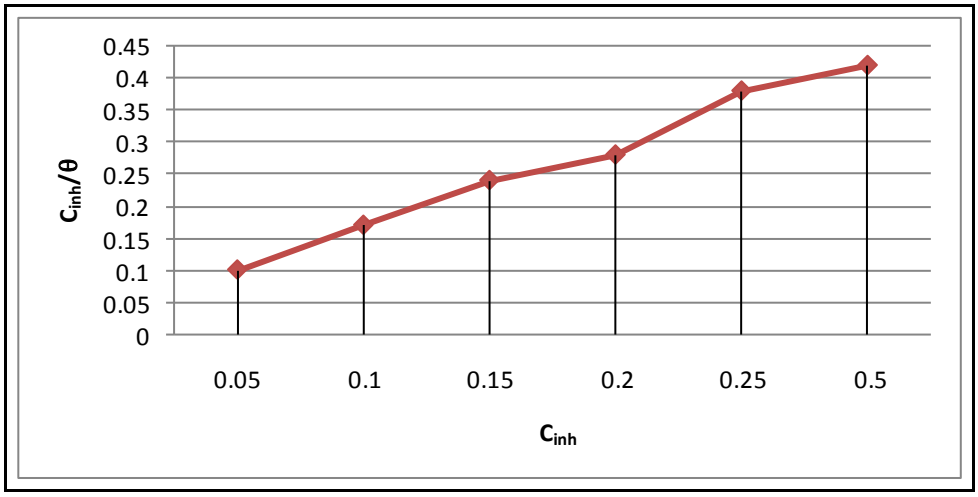

Figure 10.Adsorption isotherm for mild steel in 1.0 M HCl with different concentrations of the corrosion inhibitor.

Conclusions

The investigation results implied that 3-acetamidocoumarin was a perfect corrosion inhibitor for mild steel in corrosive solution in a conditional concentration. Inhibition efficiency of 3-acetamidocoumarin at the maximum concentration was up to 86.1%reducing with a higher temperature degrees. 3-acetamidocoumarin is adsorbed by mild steel surface that obey Langmuir/isotherm. 3-acetamidocoumarin is demonstrate as an effective inhibitor having perfect, inhibitive characteristics because of oxygen and nitrogen atoms. SEM analysis confirmed the forming of a barrier layer from 3-acetamidocoumarin on the mild steel surface. The anti-corrosion investigation of 3-acetamidocoumarin obviously demonstrated its controlling protection of MS in corrosive solution.

Competing Interests: The authors have declared that no competing interests exist.

Acknowledgments

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Author Contributions

Conceived and designed the experiments: AAA. andAIA; Performed the experiments: AIA and AQS. Analyzed the data: AAA. Contributed reagents/materials/analysis tools: AAA and KSR.Wrote the paper: AAA and KSR.

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