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DFT Quantum Mechanical and Electrochemical Methods for evaluation of Corrosion Inhibition of Aryl-triazino-benzimidazole-2-thiones in Acid Media

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INTRODUCTION

The use of corrosion inhibitors is one of the most effective ways to reduce corrosion in acidic environments [1]. Corrosion inhibitors are chemicals which are reduced the corrosion rate to an acceptable level when they are added to the corrosive media [2]. Azoles are widely used as corrosion inhibitors to prevent corrosion of carbon steel in the hydrochloric acid solution [3-5]. Aryl-triazino-benzimidazole-2-thiones were synthesized *via* three-component reaction between benzoyl chlorides, ammonium thiocyanate, and 2-aminobenzimidazole [6]. In this paper, their inhibition behavior was evaluated by polarization and electrochemical impedance spectroscopy (EIS) in hydrochloric acid solutions. Their performance was also studied with DFT quantum method.

MATERIALS AND INSTRUMENTS

The reagents and solvents used in this study were obtained from Merck and used without further purification. For polarization experiments and electrochemical impedance, potentiostat/ Galvanostat, Zahner model MeX6, Germany, was used. Also, potentiodynamic polarization curves were obtained with a sweep rate of 1 mV/s in the potential range of ± 0.25 V vs. SCE related to open circuit potential at 298 K. EIS measurements were conducted on open circuit potential after 1 hour immersion in the frequency range of 100 KHz to 10 mHz with potential perturbation AC amplitude of 10 mV.

RESULTS AND DISCUSSION

Figure1 showed the steps of preparation of the compounds 3a-c. Polarization curves show that the addition of different concentrations of 3a to the solution reduces the anodic dissolution of the steel and delayed the cathodic reaction (Fig. 2).

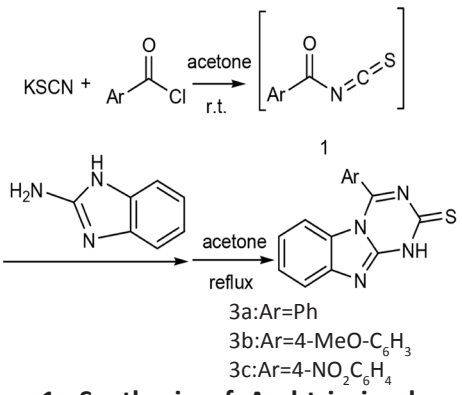

Figure 1: Synthesis of Aryl-triazino-benzimid-azole-2-thiones 3a-c.

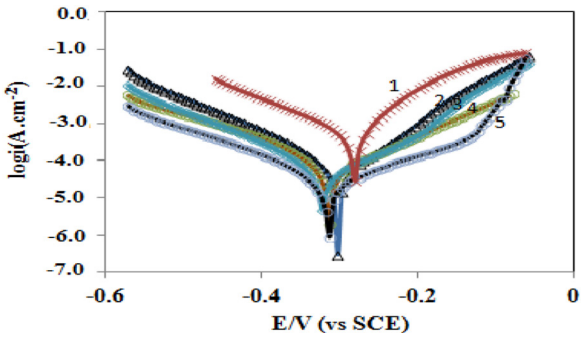

Figure 2: The polarization curves for carbon steel in 2 M HCl solution containing different concentrations of 3a:1) Blank 2) 3.0 × 10^{-5}, 3) 8.0 × 10^{-5}, 4) 2.0 × 10-4, 5) 3.0 × 10^{-4} M.

Also, the inhibition properties increase to more than 90% in the concentration of 3 × 10^{-4} M in 2 M HCl solution. The EIS plots for 3a are shown in Fig. 3.

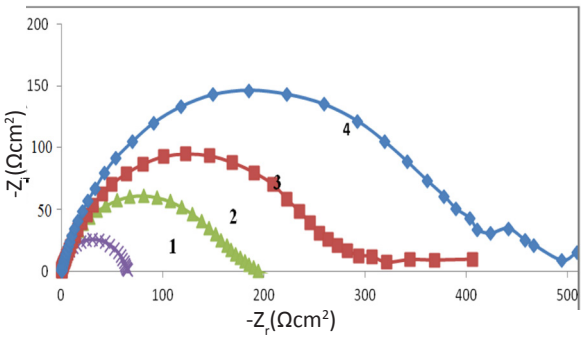

Figure 3: Nyquist plots for carbon steel in 2 M HCl solution containing different concentrations of 3a: 1) Blank 2) 3.0 × 10^{-5}, 3) 8.0 × 10^{-5}, 4) 1.5 × 10^{-4}, 5) 2.5 × 10^{-4} M.

The impedance curves analysis showed the curve of 3a at low concentrations (3.0 × 10^{-5}M) are almost half-circle, indicating that the corrosion process is under the control of the charge transfer and consistent of one time constant. At high concentration (2.5 × 10-4 M) of 3a, there are two capacity rings. The first loop is located in the high frequency range and is related to the time constant and the electrical double layer. In addition, the second loop at low frequencies is produced by the absorption of inhibitor 3a on the surface of the carbon steel.

The Results of EIS experiment show that a decrease in capacitance and an increase in resistance could be attributed to the decrease in local dielectric constant or an increase in the thickness of the electrical double layer, indicating that the molecular absorption occurs at the boundary between the surface of the metal and the solution, reducing the extent of acidic dissolution for the carbon steel.

QUANTUM DFT CALCULATIONS

Quantum DFT calculations have been performed to optimize the structure of 3a-c compounds using B3LYP/ 6-311G. Table 1 shows that EHOMO of 3b is smaller than the other two compounds. Because the E_{HOMO} of the compound 3b is less, its electron-donating is greater. Also, the tendency to electrons is increased by decreasing electronegativity of 3b. Hard molecules have a high HOMO-LUMO gap, and soft molecules have a small HOMO-LUMO gap, and the highest softness, has the highest inhibition efficiency. This is because a soft inhibitor is more reactive towards a metal surface than a hard molecule [7, 8].

CONCLUSIONS

The effect of aminobenzimidazole-2-tions 3a-c on the corrosion behavior of carbon steel in 2 M HCl solution has been described.

Table 1: Quantum DFT calculations For 3a-c.

Quantum parameter	3a	3b	3c
E_{HOMO} (eV)	-7.209	-6.032	-7.245
E_{LUMO} (eV)	-2.964	-2.722	-3.841
ΔE_{gap} (eV)	3.592	3.310	3.404
D (debye)	10.960	7.306	5.475
(I=-E_{HOMO} (eV	7.209	6.032	7.245
A=-E_{LUMO} (eV)	2.964	2.722	3.841
χ (eV)	5.086	4.377	5.543
η (eV)	2.123	1.655	1.702
S (eV)	0.2355	0.3021	0.2938

Their inhibition efficiency is more than 90% based on the polarization method at a concentration of 3×10^{-4} M. The electrochemical impedance results show that in concentrations less than 50 $mg.L^{-1}$ of inhibitor, bade-phase curves show a time constant and in concentrations of greater than 50 $mg.L^{-1}$, bade-phase curves show two time constants. Moreover, DFT quantum studies also show that all three compounds have electron-donor capability and corrosion prevention. Based on the results of quantum DFT studies, polarization and electrochemical impedance methods, the inhibition efficiency of the 3a-c are as follows: 3b>3c>3a

Finally, the presence of methoxy group in 3b enhances the possible interaction between the π-electrons with the vacant d-orbitals of iron atoms.

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