Journal of Molecular Structure 1076 (2014) 658-663

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Experimental and theoretical study of [N-substituted] p-aminoazobenzene derivatives as corrosion inhibitors for mild steel in sulfuric acid solution

Mehdi Salih Shihab*, Hanan Hussien Al-Doori

Al-Nahrain University, College of Science, Department of Chemistry, Al-Jadrya, Baghdad, Iraq

HIGHLIGHTS

- [N-substituted] p-aminoazobenzene derivatives were prepared as corrosion inhibitors.
- Corrosion inhibitors were tested for mild steel in 1 M H₂SO₄ solution.
- Weight loss measurements achieved in absence and presence of inhibitors.
- Theoretical approach was studied adsorption process of corrosion inhibitors.

G R A P H I C A L A B S T R A C T

In this work, [N-substituted] p-aminoazobenzene derivatives were prepared and investigated as corrosion inhibitor for mild steel in 1 M H_2SO_4 solution by weight loss measurements. Semiempirical molecular orbital calculations were carried out for prepared compounds as molecular models and gave useful information to explain the interaction between the surface of metal and the organic molecules as corrosion inhibitors.



ARTICLE INFO

Article history: Received 24 February 2014 Received in revised form 7 August 2014 Accepted 7 August 2014 Available online 27 August 2014

Keywords: Corrosion inhibitor Inhibition efficiencies Physisorption

ABSTRACT

[N-substituted] p-aminoazobenzene derivatives (1), (2), (3), (4) and (5) were prepared and investigated as corrosion inhibitors for mild steel in 1 M H₂SO₄ solution by weight loss measurements. It has been observed that the corrosion rate decreases, inhibition efficiencies increase and surface coverage degree increases with increasing inhibitor concentration. Inhibition efficiencies for prepared compounds were ordered: (1)>(2)>(5)>(4)>(3) with the highest inhibiting efficiency of 63% for 10⁻³ M. The values of ΔG_{ads}^{0} are showing physisorption effect for all prepared compounds. Semiempirical molecular orbital calculations for (1), (2), (3), (4) and (5) could be used as a useful tool to obtain information for explaining the nature of interaction between the metal surface and the organic molecule as a corrosion inhibitor. © 2014 Elsevier B.V. All rights reserved.

Introduction

Corrosion is the destructive attacks of metals from its environment. Corrosion of metals is a major industrial problem that has attracted many investigators [1]. Use of corrosion inhibitors is one of the most practical methods for protection against metallic

* Corresponding author. *E-mail address:* mehdi_shihab@yahoo.com (M.S. Shihab).





CrossMark

corrosion, especially in acidic media [2,3]. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms [4–6]. Organic molecules of this type may adsorb on the metal surface and form coordination between their N-electron pair and/or π electron cloud and the metal surface, thereby reducing the corrosion in acidic solutions [7–9]. In recent years, attention has been focused on the investigation of organic dyes as potential inhibitors for the metals in corrosive environment [10–17].

In the present work, some Azo dyes of corrosion inhibitors, namely [N-substituted] p-aminoazobenzene were prepared. The aim of this work was to investigate the efficiency of these organic compounds as a corrosion inhibitor for mild steel in a solution of 1 M sulfuric acid.

Experimental testing

Materials

The sheet of mild steel used had the composition percentages (0.002% P, 0.288% Mn, 0.03% C, 0.0154% S, 0.0199% Cr, 0.002% Mo, 0.065% Cu, 0.0005% V, and the remainder iron). The mild steel sheet was mechanically press-cut into disc shape with a diameter (2.5 cm) and thickness (0.05 cm). These disc shapes were polished with emery papers ranging from 110 to 410 grades to get a highly smooth surface. However, surface treatments of the mild steel involved degreasing in absolute ethanol and drying in acetone. The treated specimens were then stored in a moisture-free desiccator before their use in corrosion studies.

Azo dyes inhibitors, namely: N, N-dimethyl-4-((E)-(4-((E)-phenyldiazenyl) phenylimino) methyl) aniline (1), (E)-N-(4-bromobenzylidene)-4-((E)-phenyldiazenyl)aniline (2), (E)-N-(4-nitrobenzylidene)-4-((E)-phenyldiazenyl)aniline (3), (E)-N-(furan-2-ylmethylene)-4-((E)-phenyldiazenyl)aniline (3), (E)-N-(furan-2-ylmethylene)-4-((E)-phenyldiazenyl)aniline (4), and N-((1E,4E)-1,5-diphenylpenta-1, 4-dien-3-ylidene)-4-((E)-phenyldiazenyl)aniline (5) were synthesized as follows:



Scheme 1. The molecular structure of suggested inhibitors.

First, the preparation of azo aniline was carried out by coupling reaction between the diazonium salt and aniline [18]. Then, a mixture of p-aminoazobenzene (1 g, 0.01 mol), abs. ethanol (20 ml) and appropriate aromatic aldehyde or ketone (0.01 mol) with a few drops of glacial acetic acid was refluxed for 8 h. After cooling to room temperature, the precipitate was filtered and dried. The product was crystallized from ethanol [19]. All prepared compounds were identified from melting point, FTIR (KBr disc) and ¹H NMR (DMSO-d₆) techniques. The molecular formula of suggested inhibitors is shown in Scheme 1.

Inhibitor concentrations of 1×10^{-3} to 5×10^{-5} M were prepared in 1 M H₂SO₄ solution at 30 °C. Solutions of 1 M H₂SO₄ were prepared by dilution of analytical grade 98% H₂SO₄ with distilled water.

Weight loss method

Mild steel specimens were initially weighed using an electronic balance. After that the specimens were suspended and completely immersed in 250 ml beaker containing 1 M sulfuric acid in the presence and absence of inhibitors. The specimens were removed after 8 h exposure period at 30 °C, washed with water to remove any corrosion products and finally washed with acetone. Then, they were dried and reweighed. Mass loss measurements were performed per ASTM standard test method described previously [20,21]. The tests were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss is reported in 1–2% data errors. Weight loss allowed calculation of the mean corrosion rate in (mg cm⁻² h⁻¹). The corrosion rate of mild steel was determined using the relationship [22]:

$$W = \frac{\Delta M}{St} \tag{1}$$

where Δm is the mass loss, *S* the area and *t* is the immersion period.

Table 1

Corrosion rate, inhibition efficiency, surface coverage (θ) and standard free energy of adsorption for mild steel in 1 M H₂SO₄ by using weight loss measurements.

	Inhibitor concentration (M)	1 M H ₂ SO ₄					
		Δ <i>M</i> (g)	Corrosion rate $(mg cm^{-2} h^{-1})$	IE (%)	θ	$\Delta G_{\rm ads}^{\rm o}$ (kJ/mol)	
	Uninhibited	0.113	2.88	-	-	-36.08	
	(1)					$(R^2 = 0.997)$	
	0.00005	0.0614	1.56	45.8	0.458		
	0.0001	0.0575	1.47	49.00	0.490		
	0.0005	0.0491	1.25	56.6	0.566		
	0.001	0.0415	1.06	63.2	0.632		
	(2)					-34.90	
	0.00005	0.0681	1.74	39.6	0.396	$(R^2 = 0.995)$	
	0.0001	0.0563	1.43	50.3	0.503		
	0.0005	0.0519	1.32	54.2	0.542		
	0.001	0.0419	1.07	62.9	0.629		
	(3)					-35.08	
	0.00005	0.0792	2.02	29.9	0.299	$(R^2 = 0.998)$	
	0.0001	0.0607	1.55	46.2	0.461		
	0.0005	0.0542	1.38	52.1	0.521		
	0.001	0.0475	1.21	58.0	0.580		
	(4)					-35.58	
	0.00005	0.0676	1.72	40.3	0.403	$(R^2 = 0.991)$	
	0.0001	0.0603	1.54	46.5	0.465		
	0.0005	0.0551	1.40	51.4	0.514		
	0.001	0.0443	1.13	60.8	0.608		
	(5)					-38.64	
	0.00005	0.0564	1.44	50.0	0.500	$(R^2 = 0.995)$	
	0.0001	0.0496	1.26	56.2	0.562	· · ·	
	0.0005	0.0475	1.21	58.0	0.580		
	0.001	0.0427	1.09	62.2	0.622		

Table 2	
Calculated quantum chemical parar	neters of suggested inhibitors by using PM3 method.

Inhibitor	HOMO (eV)	LUMO (eV)	$\Delta E \left(E_{ m HOMO} - E_{ m LUMO} ight) (m eV)$	μ (Debye)	Planarity
(1)	-9.0140	-1.2485	-7.7655	2.09	Planar
(2)	-8.3462	-1.0692	-7.2769	1.87	Planar
(3)	-9.3099	-1.7047	-7.6051	6.76	Planar
(4)	-8.8004	-1.1838	-7.6166	1.58	Planar
(5)	-8.5258	-1.3765	-7.1493	1.92	Semi-planar



Fig. 1. Effect of inhibitor concentration on the efficiencies of mild steel obtained at 30 °C in 1 M H_2SO_4 containing different concentrations of suggested inhibitors.

The percentage inhibition efficiency (IE (%)) was calculated using the relationship [23]:

$$IE(\%) = \frac{W_{corr} - W_{corr(inh)}}{W_{corr}} \times 100$$
(2)

where W_{corr} and $W_{\text{corr}(inh)}$ are the corrosion rates of mild steel in the absence and presence of inhibitor, respectively.

Theoretical calculations

The correlation between theoretically calculated properties and experimentally determined inhibition efficiencies has been studied successfully for uniform corrosion [24–27]. The purpose of this work was to provide information about the electronic structure of several organic inhibitors by quantum chemical calculations and to investigate the relationship between molecular structure and inhibition efficiency.

All the calculations were performed using the semi-empirical calculations with PM3 method [28]. For this purpose the Hyperchem Program [29] with complete geometry optimization was used. This computational method has been proven to yield satisfactory results [26,27]. The easiest way to compare the inhibition efficiencies of prepared compounds (1), (2), (3), (4) and (5) was to analyze the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The optimized molecular structures calculated energies E_{HOMO} , E_{LUMO} , energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) and other indices are given in Table 2.

Results and discussion

The results of corrosion rate and inhibition efficiency that were obtained from weight loss measurements at different concentrations of suggested inhibitors (1), (2), (3), (4) and (5) after 8 h. immersion at 30 °C are depicted in Fig. 1 and summarized in Table 1. These values indicate that the mild steel corrosion was



Fig. 2. More energetically stable conformations of suggested inhibitors (1), (2), (3), (4) and (5) with PM3 method.



Fig. 3. The frontier molecular orbital density distributions (HOMO and LUMO) for suggested inhibitors (1), (2), (3), (4) and (5) by using PM3 method.

reduced by the presence of suggested inhibitors in $1 \text{ M H}_2\text{SO}_4$ at all concentrations that were used in the current study. However, there is remarkable decrease in the weight of mild steel specimen after 8 h without using an inhibitor. This could be explained by adsorption of organic compounds on the mild steel surface which makes an impediment to the corrosive environment.

The increase in efficiency of inhibition in concentration indicates that more inhibitor molecules are adsorbed on the metal surface at higher concentration, leading to greater surface coverage.

An inspection of the values of IE (%) in Table 1 indicates that the protection efficiency increases with increasing the concentration of suggested inhibitors, with higher inhibition efficiencies achieved at 10^{-3} M. Thus, the comparative study revealed that the order of higher inhibition efficiency was as follows:

(1) > (2) > (5) > (4) > (3). This order could be explained by the effect of molecular structure of organic inhibitors on inhibition efficiency, as well as adsorption process.

Basic information can be provided from the adsorption isotherms to explain the interaction between the organic compounds and metal surfaces. Specifically, the degree of surface coverage values (θ) at different inhibitor concentrations in 1 M H₂SO₄ was achieved from weight loss measurements (θ = IE (%)/100) (see Table 1) at 30 °C and tested with Langmuir isotherm relationship [30]:

$$C/\theta = 1/K_{ads} + C \tag{3}$$

where K_{ads} is the equilibrium constant of the adsorption process.

According to the Langmuir isotherm, K_{ads} values can be calculated from the intercepts of the straight line of plotting C/θ versus C. K_{ads} is related to the standard free energy of adsorption, ΔG_{ads}^{o} , with the following equation:

$$K_{\rm ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{\rm ads}^0}{RT}\right) \tag{4}$$

The value 55.5 is the molar concentration of water in the solution in M unit.

In Table 1, the values of standard free energy of adsorption are negative to indicate that the processes of adsorption of all suggested inhibitors (1), (2), (3), (4) and (5) were spontaneous processes on the mild steel surface after 8 h immersion at 30 °C and that's given sense for remarkable interaction between suggested inhibitors and metal surface. Here, adsorbed molecule moves closer to the surface of metal making electrons and start to overlap with that of the surface atoms which causes physisorption for suggested inhibitors [31–34].

It is generally accepted that the adsorption of an organic inhibitor on a metal surface in acidic media usually involves the formation of a metal–inhibitor complex by combining an inhibitor with freshly generated Fe^{2+} ions on the steel surface [35]:

$$Fe + 2H^+ \rightarrow Fe^{+2} + H_2 \tag{5}$$

$$Fe^{+2} + Inh_{(ads)} \rightarrow [Fe - Inh]^{+2}_{(ads)}](Metal-inhibitor complex)$$
 (6)

Therefore, formation of a metal-inhibitor complex could work as a protective layer for the anodic cell to reduce formation of Fe^{+2} sites. As such, it could be suggested that at low concentrations of suggested inhibitors, the probability of forming a compact metal-inhibitor complex is low. The adsorption mechanism for giving inhibitors depends on the adsorption behavior of organic molecules containing N atom. The presence of more than one functional group has been reported to often lead to changes in the electron density of a molecule, which could influence its adsorption behavior [36]. The suggested inhibitor could adsorb to the corroding steel surface via the compact metal–inhibitor complex of anodic sites and thus reduces the Fe electro-dissolution. To study the relationship between molecular structure and inhibiting effect of the suggested inhibitors, molecular orbitals of semi-empirical calculations with PM3 method were used. All the theoretical quantum calculations were performed for suggested inhibitors (1), (2), (3), (4) and (5) using more energetically stable conformations in the gas phase at 25 °C (see Fig. 2).

The calculated quantum chemical parameters of suggested inhibitors are reported in Table 2.

The PM3 HOMO and LUMO isosurfaces for suggested inhibitors (1), (2), (3), (4) and (5) are shown in Fig. 3. Depending on the presence of N atoms in suggesting inhibitors, the repartition density of the HOMO and LUMO is preferentially localized on N of (C=N) and (N=N) groups of all molecules. Table 2 also shows different dipole moments for suggested inhibitors (1), (2), (3), (4) and (5). The values of dipole moment can be attributed to the non-uniform distributions of positive and negative charges on the various atoms, which could be related to improving the dipole-dipole interaction of organic molecules and mild steel surface. Electrostatic potential maps for suggested inhibitors (1), (2), (3), (4) and (5) are depicted in Fig. 4. The figure shows the non uniform distribution of electron density and concentration of negative charges on N (C=N), (N=N) for all molecules, which reflect the different values of the calculated dipole moment (see Table 2). From what was described earlier, different experimental and theoretical results due to different molecular structures were obtained, which influenced the inhibiting effect of the suggested inhibitors. There are steric and



Fig. 4. Electrostatic potential maps for suggested inhibitors (1), (2), (3), (4) and (5) by using PM3 method.

electronic effects to understand the role of molecular structure on inhibiting effect. Inhibitive effect of the suggested inhibitors depends on N (C=N), (N=N) for all molecules. Semi-planarity of (5) (see Table 2) improved the E% (see Table 1) to make N atom closer to the surface of metal and that in turn improved the physisorption at high concentrations. But the planar molecules are still preferred for improving the inhibiting effect [37] (1), (2), (3) and (4) (see Table 2).

Finally, we demonstrate the orders below:

- -(1)>(2)>(5)>(4)>(3) (Related to IE(%)(at 0.001 M), see Table 1)
- (5)>(1)>(4)>(3)>(2) (Related to ΔG_{ads}^{o} , see Table 1)
- (5) > (2) > (3) > (4) > (1) (Related to ΔE (energy gap), see Table 2).

For the orders above, the more interesting suggested inhibitor is (5), which showed physisorption with $\Delta G_{ads}^{\circ} = -38.64$ kJ/mol, and it is confirmed from the closed values of IE (%) (\approx 50–62 for different concentrations, see Table 1) compared with the others. In spite of low concentration (10⁻⁵ M) of (5), the values of IE (%) are very high compared with the values of IE (%) of (1), (2), (3) and (4). It is believed that the CH=CH groups play an important role in the molecular structure of (5). In addition, the regular distribution of the electron density on the surface of organic molecule improves the interaction between the organic molecule and metal surfaces.

Conclusions

The prepared [N-substituted] p-aminoazobenzene derivatives (1), (2), (3), (4) and (5) were used successfully as corrosion inhibitors on the mild steel surface in 1 M H_2SO_4 solution at 30 °C. The results of inhibitive efficiency showed interesting inhibiting effects of suggested inhibitors. The values free energy of adsorption revealed physisorption effect for (1), (2), (3), (4) and (5). Molecular models for prepared compounds (1), (2), (3), (4) and (5) were achieved by using semiempirical molecular orbital calculations and gave useful information to explain the interaction between the surface of metal and the organic molecules.

Acknowledgments

The authors would like to thank the Department of Chemistry at Al-Nahrain University for their help and cooperation throughout this research.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.08. 038.

References

- [1] O.K. Abiola, N.C. Oforka, J. Corros. Sci. Eng. 3 (2002) 117-124.
- [2] J.K. Stanly, P. Geetha, Corros. Sci. 52 (2010) 224–228.
- [3] C.C. Nathan, Organic Inhibitors, NACE, Houston, TX, 1977.
- [4] E.E. Ebenso, U.J. Ekpe, B.I. Ita, O.E. Offiong, U. Ibok, Mater. Chem. Phys. 60 (1999) 79–90.
 [5] M.A. Quraishi, M.A.W. Khan, M. Ajmal, S. Muralidharan, S.V. Iyer, Anti. Corros.
- Math. Mater. 43 (1996) 5–8.
- [6] K.F. Khaled, K. Babic-Samardzija, N.J. Hackerman, Appl. Electrochem. 34 (2004) 697-704.
- [7] K.M. Ismail, Electrochim. Acta 52 (2007) 7811-7819.
- [8] M. Benabdellah, R. Touzani, A. Aouniti, A. Dafali, S. EKadiri, B. Hammouti, M. Benkaddour, Mater. Chem. Phys. 105 (2007) 373–379.
- [9] N. Soltani, M. Behpour, S.M. Ghoreishi, H. Naeimi, Corros. Sci. 52 (2010) 1351– 1361.
- [10] E.E. Oguzie, E.E. Ebenso, Pigment Resin Technol. 35 (2006) 30-35.
- [11] E.E. Ebenso, E.E. Oguzie, Mater. Lett. 59 (2005) 2163-2165.
- [12] E.E. Ebenso, Niger. J. Chem. Res. 6 (2001) 8-12.
- [13] E.E. Ebenso, Bull. Electrochem. 19 (2003) 209-216.
- [14] E.E. Ebenso, Bull. Electrochem. 12 (2004) 551–559.
- [15] L. Tang, G. Mu, G. Liu, Corros. Sci. 45 (2003) 2251-2262.
- [16] L. Tang, X. Li, G. Mu, G. Liu, Appl. Surf. Sci. 252 (2006) 6394-6401.
- [17] H.A. Sorkhabi, B. Masoumi, P. Ejbari, E. Asghari, J. Appl. Electrochem. 39 (2009) 1497-1501.
- [18] B.S. Furniss, A.J. Hannford, P.W.G. Smith, A.R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, 5th ed., Longman Scientific and Technical, 1989.
- [19] R.M. Issa, A.M. Khedr, H. Rizk, J. Chin. Chem. Soc. 55 (2008) 875–884.
- [20] ASTM G 3–72, Standard practice for laboratory immersion corrosion testing of metals||, West Conshohocken, PA; ASTM, 1990.
- [21] M. Ajmal, A.S. Mideen, M.A. Quraishi, Corros. Sci. 36 (1994) 79-84.
- [22] M. Scendo, M. Hepel, Corros. Sci. 49 (2007) 3381-3407.
- [23] M. Scendo, Corros. Sci. 49 (2007) 3953–3968.
- [24] G. Bereket, C. Ogretir, A. Yurt, J. Mol. Struct. (THEOCHEM) 571 (2001) 139-145.
- [25] G. Bereket, E. Hur, C. Ogretir, J. Mol. Struct. (THEOCHEM) 578 (2002) 79-88.
- [26] N.O. Eddy, B. IIta, E.E. Ebenso, Int. J. Electrochem. Sci. 6 (2011) 2101–2121.
- [27] S.M. Quraishi, M.A. Quraishi, R. Quraishi, Open Corros. J. 2 (2009) 83-87.
- [28] J.P.J. Stewart, Method. J. Comput. Chem. 10 (1989) 209–220.
- [29] HyperChem 2002, version 7.5; Hypercube Inc.: Gainesville, FL, USA.
- [30] R. Agrawal, T.K.G. Namboodhiri, Corros. Sci. 30 (1990) 37-52.
- [31] N.I. Kairi, J. Kassim, J. Electrochem. Sci. 8 (2013) 7138-7155.
- [32] A.K. Maayta, N.A.F. Al-Rawashdeh, Corros. Sci. 46 (2004) 1129-1140.
- [33] A.I. Onen, B.T. Nwufo, E.E. Ebenso, R.M. Hlophe, Int. J. Electrochem. Sci. 5 (2010) 1563–1573.
- [34] T. Umasankareswari, T. Jeyaraj, J. Chem. Pharm. Res. 4 (2012) 3414–3419.
- [35] E.E. Oguzie, Y. Li, F.H. Wang, J. Colloid Interf. Sci. 310 (2007) 90–98.
- [36] N. Hackerman, E.L. Cook, J. Electrochem, Soc. 97 (1950) 1–9.
- [37] P. Udhayakala, T.V. Rajendiran, S. Gunasekaran, J. Comput. Methods Mol. Des. 2 (2012) 1–15.