

Corrosion Inhibition by Cysteine - An Over View

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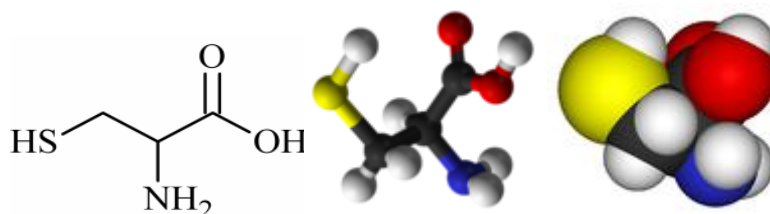
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Abstract: Interfacial behavior of Cysteine (Cys) as corrosion inhibitor to different metals in different solution has been studied by different techniques. Generally Cysteine has the ability to control corrosion of various metals such as carbon steel, zinc, tin and copper. It behaves as an inhibitor in acid medium, neutral medium and in desecrated carbonate solution. Various techniques like weight loss method, polarization study, electrochemical impedance Spectroscopy and AC impedance spectra have been used to evaluate the corrosion inhibition efficiency of Cysteine. All the results show Cysteine is the good corrosion inhibitor to different metal in different medium with or without additive known by all the reference.

Keywords: Cysteine, Weight loss method, polarization study, Electrochemical impedance Spectroscopy and AC impedance spectra.

1. INTRODUCTION

Corrosion control of metal is of technical, economical, environmental and aesthetical importance. The use of inhibitor is the best way to prevent metal and alloys from corrosion. It is well known that acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Acid solutions are extensively used, the most important of which are acid picking, industrial acid cleaning, acid-descaling and oil well acidizing. The commonly used acids are hydrochloric acid and sulphuric acid. Since acids are aggressive, inhibitors are usually used to minimize the corrosive attack on metallic materials. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent metal dissolution and acid consumption. Cysteine has the ability to control the corrosion of various metals. Generally Cysteine is a very interesting amino acid that contains amino group [–NH₂], carboxyl group [–COOH] and thiol group [–SH]. It can coordinate with metals through the nitrogen atom, oxygen atom of the carboxyl group and Sulphur atom of thiol group. They have used to prevent the corrosion of metals such as mild steel, aluminum and copper.



Scheme 1. Cysteine Structure

As far as the influence of pH is concerned, it can be said that at isoelectric point Cysteine are in the zwitterion form (Fig. 1a), in alkaline medium, they take the form of anion (Fig. 1b), whereas in acid medium, they are in the cation form (Fig. 1c).

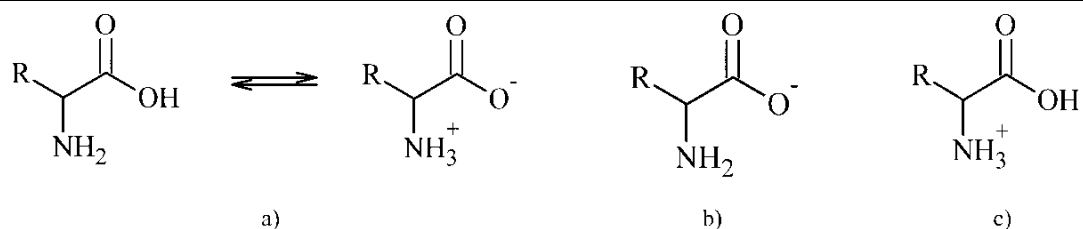


Figure 1. The form of amino acid depending on the pH value of the medium

2. DISSCUSION

2.1. Metals

Cysteine has been used to prevent the corrosion of a wide variety of metals. Cysteine has the ability to prevent the corrosion of carbon steel (mild steel) (1,2,3,6,8,12,14,19), Cu-Ni alloys (4,10), Bronze (5), Copper electrode (7,11,13,15,16,18), NST-44 carbon steel (17), Pb-Ca-Sn Alloy (9).

2.2. Medium

Cysteine has been used as inhibitor to prevent corrosion of metals in various environments acidic neutral and deaerated carbonate solutions. The mainly used acid is hydrochloric acid (1,3,11), and rarely used acids are sulphuric acid (4,6,9,13), sodium chloride (16, 17), Aqueous Chloride (10), sodium sulphate (18), phosphoric acid 15,12, and nitric acid (7),

2.3. Techniques

Even though several modern techniques are on the anvil, the mainly used methods in evaluation of inhibition efficiency of Cysteine in preventing corrosion of metals are weight loss method (7,9,11), electrochemical studies such as polarization and AC impedance spectra (1,2,3,4,7,8,9,10,11,12,13,14,15,16,17,18,19), and cyclic voltammetry. XPS has been used to analyze the film formed on carbon steel surface (5). SEM technique has been used to study the morphology of the corroded surface of zinc in acidic medium in the presence of luecine and methionine (9). Infrared spectroscopy been used to analyses the protective film formed on the metal surface.

2.4. Adsorption

The protective nature of Cysteine is attributed to its adsorption on the metal surface. Various adsorption isotherms have been proposed. The adsorption isotherms include Langmuir isotherms Flory- Huggins isotherm (6 ,9,14,) Freundlich isotherm (8),and Temkin Isotherm (6).

2.5. Langmuir adsorption isotherm

This type of isotherm is observed when iron immersed in HCl, in the presence of cysteine (9). Similar observation has been made when mild steel was immersed in HCl, in the presence of cysteine and N-acetylcystein, methionine and cystine(14).

2.6. Flory-Huggins isotherm

This type of isotherm is obeyed when mild steel is immersed in HCl, in the presence of decylamides of α -amino acid derivatives (6). Morad observed that Flory- Huggins isotherm is obeyed when mild steel was immersed in sulfamic acid in the presence of N-acetylcysteine (ACC), cysteine (RSH), S-benzylcysteine (BzC) cystine (RSSR) methionine (CH3SR).

2.7. Temkin isotherm

This type of isotherm is obeyed when mild steel is immersed in HCl in the presence of cysteine (6). The type of adsorption very much depends on the nature of metal, environment and Cysteine used.

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Table 1. Corrosion inhibition by Cysteine to different metal in different medium

S.No	METAL	MEDIUM	INHIBITOR	ADDITIVE	METHOD	FINDING	REFERENCE
1	Mild steel	1M HCl	Cysteine, serine amino butyric acid threonine, alanine valine, aromatic amino acid, phenylalanine, tryptophan and tyrosine	-	Polarization and electrochemical impedance spectroscopy method (EIS)	Cathodic inhibitor	1
2	Mild steel	Acid media	Cysteine	-	Electrochemical method	Good inhibitor	2
3	Mild steel	1M HCl	Cysteine Alanine, and S-methyl cysteine	-	Polarization, EIS, (EFM) technique and (ICP-AES)	Cathodic inhibitor and mixed type inhibitor	3
4	Cu-Ni alloy	0.5M H ₂ SO ₄	Cysteine	Nickel	Potentiodynamic polarization and EIS at open circuit potential	Cathodic inhibitor.	4
5	Bronze	0.2 g/L NaHCO ₃ +0.2 g/L Na ₂ SO ₄ aqueous solution (pH 5)	Two innoxious amino acids derivative DL alanine and DL cysteine	-	X-ray fluorescence spectrometry	Good inhibitors	5
6	Mild steel	5% sulfuric acid solution at 40°C	cysteine (RSSR) cysteine (RSH), S-benzylcysteine (BZC) N-acetylcysteine (ACC), methionine (CH ₃ SR)	-	Temkin isotherm, Flory-Huggins isotherm	Anodic inhibitors	6
7	Copper	Molar Nitric solution	Valine, Glycine Arginine, Lysine and Cysteine	-	Weight loss and electrochemical polarization measurements,	Good inhibitors	7
8	Mild steel	Acid solution	Glycine, alanine, valine, Histidine, glutamic acid and cysteine	Vanadium	Open circuit potential measurements, polarization technique	Cathodic inhibitors	8

					and EIS, Freundlich isotherm		
9	Pb-Ca-Sn alloy	Sulfuric acid solution	Cysteine, Methionine and Alanine	-	Potentiodynamic polarization and EIS, weight loss measurement and SEM.		9
10	Cu-Ni alloy	Aqueous chloride solutions	Glycine and cysteine	-	Polarization and impedance techniques	Anodic inhibitors	10
11	Copper	0.5M HCl solution	dl-alanine and dl-cysteine		Weight loss measurements, Potentiodynamic polarization and EIS.	Anodic inhibitors.	11
12	Mild steel	40% H ₃ PO ₄ solution	Cysteine (RSH), methionine(CH ₃ SR), cysteine (RSSR) and N-acetylcysteine(ACC)	-	Potentiostatic (EIS) techniques under anodic and cathodic polarization conditions	Mixed inhibitors	12
13	Copper	Sulfuric acid medium	Cysteine	-	Electrochemical methods	Good inhibitor	13
14	Mild steel	Phosphoric acid	Cysteine and N-acetylcysteine methionine and cysteine.	-	(EIS), Frumkin adsorption isotherm, Langmuir adsorption isotherm	Mixed inhibitors	14
15	Copper	8 M Phosphoric acid	Proline, cysteine, phenyl alanine, Histidine and glycine	-	Potentiodynamic polarization and rotation techniques,	Cathodic inhibitors	15
16	Copper	3% NaCl	Phenylalanine (Phe) and tryptophan (Trp)	-	Potentiodynamic polarization and (EIS)	Good inhibitors	16
17	Carbon steel	CO ₂ saturated NaCl solution at different pH level	L-Cysteine	-	Potentiodynamic and (EIS).	Protective film formed	17
18	Copper	0.5 M Na ₂ SO ₄ solution (pH 7 and pH 9)	Cysteine	-	Potentiodynamic polarization measurement	Anodic inhibitor.	18

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19	Mild steel	1 M HCl and 0.5 M H ₂ SO ₄	L-Cysteine	-	EIS and Molecular dynamics (MD) simulation.	Cathodic inhibitor	19
20	Mild steel	1 M HCl	N-Acetyl-L-Cysteine (NACYS), N-Acetyl-S-Benzyl-L-Cysteine (NASBCYS), and N-Acetyl-S-Hexyl-L-Cysteine (NASHCYS)	-	Weight loss and polarization measurement	Cathodic inhibitors.	20
21	Mild steel	1 M HCl solution	L-cysteine, L-Histidine, L-tryptophan and L-serine	-	Polarization, EIS and quantum chemical calculation and molecular dynamics simulation.	Good inhibitors	21
22	Iron	1.0 M HCl solution	Cysteine (Cys) and S-methyl cysteine (S-MCys), alanine (Ala),	-	Polarization and impedance measurements.	Anodic inhibitors	22
23	Mild steel	1M H ₂ SO ₄	Cystine and methionine	-	Polarization and Adsorption method	Cathodic inhibitors	23
24	Iron	Hydrochloric acid solutions	Hydroxyproline, cystine, and cysteine	-	Potentiodynamic polarization	Cathodic inhibitors	24
25	Tin plate	Citric acid	Cysteine arginine monohydrochloride, Lysine monohydrochloride and methionine	-	Potentiodynamic polarization technique	Mixed inhibitors	25
26	Zinc	HCl solution	Onion pulp (S-(1-propenyl)-L-cysteine sulfoxide)	-	Potentiodynamic polarization technique	Anodic inhibitor	26
27	Copper	0.6 M NaCl and 1.0 M HCl	Cysteine	-	Potentiodynamic polarization measurements and "EIS"	Good inhibitor	27
28	Bulk nanocrystalline ingot iron (BNII)	0.5 M H ₂ SO ₄ solution	Cysteine (cys)	-	EIS and Potentiodynamic polarization	Good inhibitor	28

	fabricated from conventional polycrystalline ingot iron (CPII)				techniques		
29	Copper	0.5M HCl solution	Cysteine with dodecylacid (DAC) and with dodecylamine (DAM)	-	Potentiodynamic polarization curves and EIS.	Anodic inhibitors	29
30	Bronze	0.2 g/L Na ₂ SO ₄ + 0.2 g/L NaHCO ₃ (pH=5)	Cysteine (Cys), glutamic acid (Glu), arginine (Arg), Histidine (His) and Methionine (Met)	-	Potential and EIS measurements	Cathodic inhibitors	30
31	Mild steel	5% Sulfamic acid solution	N-acetylcysteine (ACC),cysteine (RSH),S-benzylcysteine (BzC),cystine (RSSR),Methionine (CH ₃ SR).	-	Potentiodynamic polarization curves and EIS techniques	Good inhibitors	31
32	Copper	0.5 mol/L HCl	DL-cysteine	-	Electrochemical measurement	Good inhibitor	32
33	Vanadium	Aqueous solutions of different pH	Cysteine, glycine, alanine, valine, histidine, and glutamic acid	-	Open-circuit potential measurements, Polarization techniques and EIS	Anodic inhibitor and Cathodic inhibitor.	33

REFERENCE

- [1] Eddy N.O., Journal of Advanced Research, 2011, 2(1), 35-47.
- [2] Tkalenko D.A., Venkatesvaran G., Vishevskaya Yu.P., Keny S.J.,Byk M.V., Muthe K., rotection of Metals and Physical Chemistry of Surfaces, 2010, 46(5), 609-614.
- [3] Amin M.A, Khaled K.F., Mohsen Q., Arida H.A., Corrosion Science, 2010, 52(5), 1684-1695.
- [4] Saifi H., Bernard M.C., Joiret S., Rahmouni K., Takenouti H., Talhi B., Materials Chemistry and Physics, 2010, 120(2-3), 661-669.
- [5] Varvara S., Popa M., , Rustoiu G., Bostan R., Mureşan L., Studia Universitatis Babes-Bolyai Chemia, 2009, 2, 73-85.
- [6] Morad M.S., Journal of Applied Electrochemistry, 2008, 38(11), 1509-1518.
- [7] Barouni K., Bazzi L., Salghi R., Mihit M., Hammouti B., Albourine A., El Issami S., Materials Letters, 2008, 62(19), 3325-3327.
- [8] El-Rabee M.M., Helal N.H., El-Hafez Gh.M.A., Badawy W.A, Journal of Alloys and Compounds, 2008, 459(1-2), 466-471.
- [9] Kiani M.A., Mousavi M.F., Ghasemi S., Shamsipur M., Kazemi S.H., Corrosion Science, 2008, 50(4), 1035-1045.
- [10] Badawy W.A., Ismail K.M, Fathi A.M., Electrochimica Acta, 2006, 51(20), 4182-4189.

- [11] Zhang D.-Q., Gao L.-X., Zhou G.-D, Journal of Applied Electrochemistry, 2005, 35(11), 1081-1085.
- [12] Morad M.S., Journal of Applied Electrochemistry, 2005, 35(9), 889-895.
- [13] Matos J.B., Pereira L.P., Agostinho S.M.L., Barcia O.E., Cordeiro G.G.O., D'Elia E., Journal of Electroanalytical Chemistry, 2003, 570(1), 91-94.
- [14] Morad M.S.S., Hermas A.E.-H.A, Aal M.S.A., Journal of Chemical Technology and Biotechnology, 2002, 77(4), 486- 494.
- [15] Abdel-Fatah H.T.M., Anti-Corrosion Methods and Materials, 2012, 59(1), 23-31.
- [16] Liu P., Gao L., Zhang D., Journal of the Chinese Society of Corrosion and Protection, 2012, 32(2), 163-167,
- [17] Yayan Sunarya, Cynhthia L Radiman, Bunbun Bundjali, Sadijah Achmad, ICCS 2007, UGM, 21-26 May 2007
- [18] Marija B. Petrović, Milan B. Radovanović, Ana T. Simonović, Snežana M. Milić Milan M. Antonijević., Int. J. Electrochem. Sci., 2012,(7) 9043 – 9057
- [19] Hui Cang1., Zhenghao Fei2, Wenyan Shi1,3, Qi Xu1 Int. J. Electrochem. Sci., 2012,(7) 10121 - 10131
- [20] Fu, J.-j., Li, S.-n., Wang, Y., Liu, X.-d., Lu, L.-d. Journal of Materials Science ,2011, pp. 1-10
- [21] Fu, J.-J., Li, S.-N., Wang, Y., Cao, L.-H., Lu, L.-D. Journal of Materials Science, 2010, 45 (22), pp. 6255-6265
- [22] Amin, M.A., Khaled, K.F., Mohsen, Q., Arida, H.A. Corrosion Science,2010,52 (5), pp. 1684-1695
- [23] Abd-El-Nabey, B.A., Khalil, N., Mohamed, A. Surface Technology,1985, 24 (4), pp. 383-389
- [24] Hluchan, V., Wheeler, B.L., Hackerman, N. Werkstoffe und Korrosion, 1988,39 (11), pp. 512-517
- [25] Quraishi, M.A., Ansari, F.A., Jamal, D. Indian Journal of Chemical Technology,2004 11 (2), pp. 271-274
- [26] El-Etre, A.Y. Bulletin of Electrochemistry,2006 22 (2), pp. 75-80
- [27] Ismail, K.M. Electrochimica Acta,2007 52 (28), pp. 7811-7819
- [28] Oguzie, E.E., Wang, S.G., Li, Y., Wang, F.H. Journal of Solid State Electrochemistry,2008 12 (6), pp. 721-728
- [29] Zhang, D.-Q., Gao, L.-X., Cai, Q.-R., Lee, K.Y. Materials and Corrosion,2010 61 (1), pp. 16-21
- [30] Varvara, S., Popa, M., Muresan, L.M. Studia Universitatis Babes-Bolyai Chemia,2009 3, pp. 235-247
- [31] Morad, M.S. 2008 Journal of Applied Electrochemistry,2008 38 (11), pp. 1509-1518
- [32] Zhang, D., Feng, J., Gao, L. Journal of the Chinese Society of Corrosion and Protection,2008,28 (4), pp. 235-239
- [33] El-Rabee, M.M., Helal, N.H., El-Hafez, Gh.M.A., Badawy, W.A. Journal of Alloys and Compounds,2008, 459 (1-2), pp. 466-471.

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