A Study Of Corrosion Inhibition Of Urea And Thiourea On Copper In 2M Nitric Acid

¹Kriti Tripathi, ²A.V. Trivedi

Career Point University, Aalaniya Kota, 325003 Rajasthan (India)

Abstract- The corrosion of copper in 2M nitric acid (HNO₃) at 30°C, 40°C, and 50°C have been done. Six time intervals, from one to six hours, were chosen for the present study. Rate of corrosion for all the temperature understudy shows significant corrosion of copper in 2M nitric acid ranging from 4.301×10^{-5} gram cm⁻² min⁻¹ to 7.751×10^{-5} gram cm⁻² min⁻¹. The results show a strong effect of HNO₃ at 2M concentration on copper corrosion. It has been observed that higher temperatures and longer exposure times leading to a considerable rise in corrosion rates. The effect of the addition of organic compounds containing an amino group and thio group such as urea and thiourea on the corrosion of copper in nitric acid was studied by weight loss methods. Results obtained from this study reveals that both urea and thiourea shows a remarkable corrosion inhibition effect with inhibition efficiency of 91.11% to 94.99%. However urea was found strong inhibitor than thiourea. Thus thiogroup reduced the inhibition efficiency.

Keywords: Copper; Nitric acid; Corrosion inhibition; Urea; Thiourea

INTRODUCTION

Copper has so many industrial applications because of their excellent corrosion resistance properties as well as their superior electrical and thermal conductivity [1,2]. It is a versatile and commonly used metal in many industrial applications. Copper can corrode in certain environm1ental conditions. Because of its possible effects on industrial processes and the durability of materials, nitric acid (HNO₃), which is notorious for being corrosive, has drawn Scientific attention when it comes to its interaction with copper. A key component of this study is the careful evaluation of corrosion rates over a range of temperatures and times. The corrosion rates, which are expressed in grams per square centimetre per minute (gram cm⁻² min⁻¹, are important markers of how much copper deterioration occurs when exposed to 2M nitric acid. The findings provide a clear picture of the increasing effect that higher temperatures and longer exposure periods increase copper corrosion. The most widely used corrosive solution contains nitric acid, so this medium has induced a great deal of research on copper corrosion [3-7]. One of the most important methods in the corrosion protection of copper is the use of organic inhibitors [1, 8-10]. Most of the excellent acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen [11-18]. The inhibiting action of these organic compounds is usually attributed to their interactions with the copper surface via their adsorption. Polar functional groups are regarded as the reaction centre that stabilizes the adsorption process [19]. In general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure, and the type of the electrolyte solution. This paper investigates the corrosion of copper in 2M nitric acid at three different temperatures: 30°C, 40°C, and 50°C. A detailed knowledge of the temporal evolution of corrosion rates is made possible by the investigations in six unique time intervals, which range from one to six hours. The aim of the present investigation was also to study the inhibitive action of urea and thiourea against the corrosion of copper by 2M nitric acid solution.

EXPERIMENTAL METHODS

In order to examine the behaviour of copper corrosion in 2M nitric acid (HNO₃) at different temperatures (30° C, 40° C, and 50° C) weight loss method was used. Inhibition efficiency of urea where also studied using weight loss method.

Preparation of the specimen sample: Experimental material consisted of specimens of high purity copper. A copper plate of $30 \text{ cm} \times 30$ cm of thickness 0.3 cm was purchased and cut down to pieces of 2×2 cm. To ensure that there were no surface impurities obstructing the corrosion process, every copper sample was thoroughly cleaned before being exposed.

Preparation of 2M nitric acid solution: The preparation of a 2M nitric acid solution was done with great care in order to replicate the harsh corrosive environment. In order to simulate circumstances that might be found in some industrial processes, 2M nitric acid solution was prepared using fuming nitric acid of AR grade purity of 15.88 M. A

concentration of 2M was selected to represent a fairly strong acidic state. To guarantee the precision of the concentration, high-purity nitric acid and distilled water were used to make the acid solution.

Experimental Configuration: The experimental configuration comprised of a regulated environmental chamber with the ability to sustain temperatures at 30, 40, and 50 degrees Celsius. The 2M nitric acid solution was taken, and copper specimens were dipped in it for one to six hours.

Measurement of Corrosion Rate: The copper specimens were carefully taken out of the nitric acid solution after each prearranged exposure period. After the specimens were cleaned of the corrosion products, the mass loss that was ascribed to corrosion was measured once more. Next, by dividing the mass loss by the product of the exposed surface area and the exposure period, the corrosion rates were computed by the following equation:

Corrosion Rate
$$= \frac{\Delta \mathbf{W}}{At}$$

Where,

 ΔW = difference between initial and final weight A= area of cross section t = time taken for corrosion

Measurement of % Inhibition: % Inhibition measured by the following equation:

$$\% IE = \left(\frac{CR Blank - CR Inh.}{CR Blank}\right) \times 100$$

Where, CR blank and CR inh. are the corrosion rates in the absence and presence of the different inhibitors at different concentration.

RESULTS AND DISCUSSION

Results of the present study have been given in following table 1 to 5 and discussed accordingly. **Table 1- Corrosion of Copper in 2M HNO₃ at 30°C**

S.No.	Time (Minute)	Initial Weight (W1)	Final Weight (W ₂)	ΔW (W1-W2)	Rate of corrosion $\times 10^{-5}$ gm cm ⁻² min ⁻¹
1	60	10.169	10.153	0.016	4.301
2	120	10.36	10.335	0033	4.435
3	180	10.019	9.954	0.065	5.824
4	240	10.104	10.005	0.099	6.653
5	300	10.405	10.271	0.134	7.024
6	360	10.114	9.941	0.173	7.751

Table 2 Corrosion of Copper in 2M HNO3 at 40°C

S.No.	Time (Minute)	Initial Weight (W ₁)	Final Weight (W ₂)	ΔW (W1-W2)	Rate of corrosion × 10 ⁻⁵ gm cm ⁻² min ⁻¹
1	60	10.155	10.086	0.069	18.548
2	120	10.029	9.824	0.205	27.553
3	180	10.022	9.948	0.374	33.512
4	240	9.956	9.281	0.675	46.616
5	300	8.811	7.906	0.905	48.677
6	360	8.444	7.343	1.101	49.327

S.No.	Time (Minute)	Initial Weight (W ₁)	Final Weight (W ₂)	$\begin{array}{c} \Delta \mathbf{W} \\ (\mathbf{W}_1 \textbf{-} \mathbf{W}_2) \end{array}$	Rate of corrosion × 10 ⁻⁵ gm cm ⁻² min ⁻¹
1	60	10.086	9.995	0.091	33.852
2	120	10.335	10.029	0.306	41.129
3	180	9.948	9.551	0.397	53.360
4	240	9.281	8.325	0.956	64.247
5	300	10.238	9.019	1.219	65.537
6	360	9.941	8.444	1.497	67.069

Table 3 Corrosion of copper in 2M HNO3 at $50^{\circ}C$

Table 4- Corrosion inhibition of urea on copper in 2M HNO₃ at 30°C (Corrosion Time 4 hour)

S. No.	Concentration of Urea (Mole)	Initial Weight (W1)	Final Weight (W ₂)	Δ W (W ₁ - W ₂)	Corrosion Rate CR × 10 ⁻⁵ gm cm ⁻² min ⁻¹	% Inhibition (IE%)
1	0.0 M Urea	10.104	9.985	0.119	7.99	0
2	0.2 M Urea	10.139	10.134	0.005	0.35	95.61
3	0.4 M Urea	10.059	10.055	0.004	0.28	96.49
4	0.6 M Urea	9.929	9.926	0.003	0.21	97.37
5	0.8 M Urea	10.153	10.152	0.001	0.14	98.24

Table.5: Corrosion inhibition of thiourea on copper in 2M HNO₃ at 30°C (Corrosion Time 4 hour)

S. No.	Concentration of Thiourea (Mole)	Initial Weight (W ₁)	Final Weight (W2)	∆W (W₁-W₂)	Corrosion Rate CR × 10 ⁻⁵ gm cm ⁻² min ⁻¹	% Inhibition (IE %)
1	0.0 M	10.104	9.985	0.119	7.99	0
2	0.2 M	10.011	9.906	0.105	0.71	91.11
3	0.4 M	10.648	9.726	0.922	0.62	92.24
4	0.6 M	10.409	9.606	0.803	0.54	93.24
5	0.8 M	10.115	10.109	0.006	0.4	94.99

DISCUSSION

The results of the present study have been given in above table 1 to 5. It is clear from the tables 1, 2 and 3 that 2M nitric acid corrode copper significantly with rate of corrosion ranging from 4.301×10^{-5} gm cm⁻² min⁻¹ to 7.751×10^{-5} gm cm⁻² min⁻¹. Minimum rate of corrosion was observed at 30°C temperature in 1 hour exposure time and the maximum rate of corrosion was observed at 50°C temperature in 6 hours exposure time period. It is very clear from table 1 to 3 that corrosion rate increases with exposure time and temperature.

Corrosion Inhibition effect

Corrosion inhibition of urea and thiourea have been given in table 4 and 5. It is clear from table 4 that urea significantly inhibit rate of corrosion with maximum % inhibition of 98.24%. Similarly thiourea also shows significant inhibition at a maximum of 94.99 %. It is clear from the inhibition data that thio group is reduces inhibition efficiency and urea is found more strong inhibitor than thiourea.

CONCLUSION

The collected data, as presented in the abstract, show a direct relationship between the rates of copper corrosion in 2M nitric acid and temperature and exposure time. The trends that have been discovered offer significant understanding of the fundamental mechanisms that control the corrosion process. They also highlight the complex interaction between temperature-dependent kinetics and acid concentration. The experimental approach employed provides a strong basis for comprehending the complex corrosion behaviour of copper in nitric acid. Insights from this research contribute to the field of corrosion science and materials engineering in general as well as to the specific understanding of copper corrosion. These insights can be used to develop corrosion-resistant materials and practical preventative techniques for industrial applications.

REFRENCES:

1. K.tripathi and A.V.Trived, A review on metal corrosion inhibitors, Int. jr. novel res. dev., 7(2022)156

2. H. Leidheiser, (1979) "Aqueous Corrosion" in The Corrosion of Copper, Tin and Their Alloys, Robert E. Krieger Publishing Company, Huntington, NY, pp. 71 – 126.

3. U.R. Evans, Behaviour of metals in nitric acid, Trans. Farad. Soc. 40 (1944) 120.

4. C.N. Hinshelwood, Presidential address. Some observations on present day chemical kinetics, J. Chem. Soc. (1947) 694.

5. E.A. Travincek, J.H. Weber, Continuous dissolution of copper by nitric ACID, J. Phys. Chem. 65 (1961) 235.

6. Rasheed Arain, A.M. Shams El Din, A thermometric study of the kinetics of acid dissolution of four copper alloys used in desalination plants, Thermochim. Acta 89 (1985) 171.

M. Sato, R. Aogaki, Electrochemical Methods in Corrosion Research VI, Mater. Sci. Forum 289–292 (1998) 459.
D.-Q. Zhang, L.-X. Gao, G.-D. Zhou, Inhibition of copper corrosion by bis-(1-benzotriazolymethylene)-(2,5-thiadiazoly)-disulfide in chloride media, J. Appl. Surf. Sci. 225 (2004)287.

9. D.-Q. Zhang, L.-X. Gao, G.-D. Zhou, Inhibition of copper corrosion in aerated hydrochloric acid solution by heterocyclic compounds containing a mercapto group, Corros. Sci. 46 (2004) 3031.

10. D.-Q. Zhang, L.-X. Gao, G.-D. Zhou, Synergistic effect of 2-mercapto benzimidazole and KI on copper corrosion inhibition in aerated sulfuric acid solution, J. Appl. Electrochem. 33 (2003) 361.

11. A.G. Christy, A. Lowe, V. Otieno-Alego, M. Stoll, R.D. Webster, Voltammetric and Raman microspectroscopic studies on artificial copper pits grown in simulated potable water ,J.Appl. Electrochem. 34 (2004) 225.

12. H. Otmacic, J. Telegdi, K. Papp, E. StupnisekLisac, Protective Properties of An Inhibitor Layer Formed on Copper in Neutral Chloride Solution ,J. Appl. Electrochem.34 (2004) 545.

13. H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, D. Li, Inhibition of copper corrosion by several Schiff bases in aerated halide solutions, J. Appl. Electrochem.32 (2002) 65.

14. F. Zucchi, G. Trabanelli, M. Fonsati, Tetrazole derivatives as corrosion inhibitors for copper in chloride solutions, Corros. Sci. 38 (1996) 2019.

15.Wang, S. Chen, S. Zhao, Inhibition Effect of ACTreated, Mixed Self-Assembled Film of Phenylthiourea and 1-Dodecanethiol on Copper Corrosion, J. Electrochem. Soc. 151 (2004) B11.

16. M. Kendig, S. Jeanjaquet, Cr(VI) and Ce(III) Inhibition of Oxygen Reduction on Copper, J. Electrochem. Soc. 149 (2002) B47.

17. H.Y. Ma, C. Yang, B.S. Yin, G.Y. Li, S.H. Chen, J.L. Luo, Electrochemical characterization of copper surface modified by n-alkanethiols in chloride-containing solutions, J. Appl. Surf. Sci. 218 (2003) 143.

18. G.K. Gomma, M.H. Wahdan, Effect of temperature on the acidic dissolution of copper in the presence of amino acids Mater. Chem. Phys. 39 (1994) 142.

19. K.F. Khaled, N. Hackerman, Ortho-substituted anilines to inhibit copper corrosion in aerated 0.5 M hydrochloric acid, Electrochem. Acta 49 (2004) 485.