Art-2

J. Surface Sci. Technol., Vol 28, No. 3-4, pp. 101-110, 2012

The Inhibitive Action of Tolyl-3,3 Dimethyl Thiourea on the Corrosion of Mild Steel in Brine Water

S. KARTHIKEYAN[1*], XIANGUO HU[2], P. A. JEEVA[3], S. HARIKUMAR[1] and S. NARAYANAN[3]

[1]*Centre for Nanobiotechnology, VIT University, Vellore-632 014, India*
[2]*Institute of Tribology, Hefei University of Technology, Hefei, Anhui-230 009, P.R. China*
[3]*School of Mechanical & Building Sciences, VIT University, Vellore-632 014, India*

Abstract — The inhibitive action of Tolyl-3,3 dimethyl thiourea (TDMTU) on corrosion of mild steel in brine water (5% NaCl) has been studied using weight loss, gasometric measurements, potentiodynamic polarization and impedance studies. The studies clearly indicated that TDMTU acted as cathodic inhibitor. The adsorption of the compound on mild steel surface obeyed Temkin's adsorption isotherm. Diffused reflectance spectra and SEM images confirmed the formation of adsorbed film of inhibitor on metal.

Keywords : *Corrosion inhibitor, Thio compounds, Impedance measurements, Adsorption.*

INTRODUCTION

Mild steel is an important category of materials due to their wide range of industrial applications. It is used in many industries due to its excellent mechanical properties. These are used in industries as pipelines for petroleum industries, storage tanks, shipment vessels and chemical batteries [1] in seashore. Due to their high corrosive nature, salt water may cause damage to the steel components. Various methods are used to decrease the corrosion of steel in salt water. Among them, the use of inhibitors is most commonly suggested [2–3]. Several substituted thioureas have been investigated as corrosion inhibitors [4]. Most of the effective organic inhibitors have heteroatom such as O, N, S containing multiple bonds in their molecules through

*Corresponding Author. E-mail : skarthikeyanphd@yahoo.co.in

which they can adsorb on the metal surface [5–8]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair of electrons determines the adsorption of these molecules on the metal surface. The present paper describes a study of corrosion protection action of Tolyl-3,3 dimethyl thiourea on corrosion of mild steel in brine water using weight loss, gasometric measurements and various electrochemical techniques.

Tolyl-3,3 dimethyl thiourea (TDMTU) is an organic compound with π-electrons and heteroatom's S, N & O. The molecule is big enough (Melting point : 135) and sufficiently planar to block more surface area due to adsorption on mild steel. These factors favour the interaction of TDMTU with the metal. As far as we know no concrete report has been published so for TDMTU in brine water with use of potentiodynamic polarization, impedance measurements and diffuse reflectance spectra. The structure of the TDMTU is shown in the Fig. 1. Different concentrations of inhibitor were prepared and their inhibition efficiencies in 5% salt water were investigated.

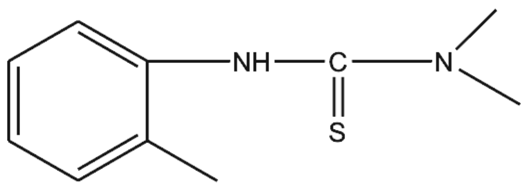

Fig. 1. Structure of Tolyl-3,3 dimethyl thiourea.

EXPERIMENTAL

Mild steel specimens of compositions, C = 0.08%, P = 0.07%, Si = O%, S = O%, Mn = 0.41% and Fe remainder, and of size 4 × 1 × 0.020 cm were used for weight loss and gasometric studies. The weight loss study was carried out at room temperature for three hours in 5% NaCl. The inhibition efficiency (IE %) was determined by the following equation, I.E (%) $= (W_0 - W_i / W_0) \times 100$

Where W_0 & W_i are the weight loss values in the absence and presence of the inhibitor. A mild steel cylindrical rod of the same composition as above and embedded in araldite resin with an exposed area of 0.283 cm^2 was used for potentiodynamic polarisation and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier [9]. Both cathodic and anodic polarisation curves were recorded in brine water

(5% NaCl) potentiodynamically (1 mA s^{-1}) using corrosion measurement system BAS Model : 100 A computerised electrochemical analyzer (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil and Hg/Hg_2Cl_2/5%NaCl were used as auxiliary and reference electrodes respectively. Double layer capacitance (Cdl) and charge transfer resistance values (R_{ct},) were measured using AC impedance measurements [10–18]. The surfaces of corroded and corrosion inhibited mild steel specimens were examined by diffuse reflectance studies in the region 200 – 700 nm using U-3400 spectrometer (UV-VIS-NIR Spectrometer, Hitachi, Japan).

RESULTS AND DISCUSSION

Weight loss and Gasometric measurements

Table 1 gives the values of inhibition efficiency for different concentrations of Tolyl-3,3 dimethyl thiourea for the corrosion of mild steel in brine water obtained from

TABLE 1.

Values of inhibition efficiency for the corrosion of mild steel in brine water in the presence of different concentrations of Tolyl-3,3 dimethyl thiourea obtained from weight loss and gasometric measurements.

Concentration of	Inhibition efficiency (%)	
Inhibitor (ppm)	Weight loss Studies	Gasometric measurements
Blank	–	–
50	75	74.7
100	86	86
150	93	92.8

weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of mild steel effectively in salt water. The presence of tolyl and two $-CH_3$ groups in the molecule which shows inductive (+I) effect may increase the electron density on the sulfur atom that leads to better performance than the unsubstituted thiourea.

A good conformity between the values of inhibition efficiency obtained by weight loss and gasometric methods is found.

Potentiodynamic polarization studies

The corrosion kinetic parameters such as Tafel slopes (b_a and b_c, corrosion current (I_{corr}) and corrosion potential (E_{corr}) and inhibition efficiency obtained from potentiodynamic polarization curves for mild steel in brine water containing different concentrations of inhibitor are given in Table 2.

TABLE 2.

Corrosion kinetic parameters of mild steel in brine water in the presence of different concentrations of TDMTU obtained from potentiodynamic polarization studies.

Con. TDMTU	E_{corr} (mV vs SCE)	I_{corr} (μA cm^{-2})	b_a (mV dec^{-1})	b_c (mV dec^{-1})	IE (%)	θ
Blank	–379.12	559.57	82.0	135.3	–	–
50 PPM	–336.28	150.37	68.2	129.0	75.04	0.75
100 PPM	–370.82	89.67	66.5	113.2	86.05	0.86
150 PPM	–395.43	47.45	61.0	106.0	92.47	0.92

The values of b_a, b_c and I_{corr} are very much similar to those reported earlier [11–13]. Further it is ascertained that increasing concentrations of TDMTU enhances the values of both b_a and b_c, but the values of b_c are enhanced to greater extent. So the inhibition of corrosion of mild steel in salt water is under cathodic control. Values of E_{corr} is shifted to less negative values in the presence of different concentrations of compound. This can be ascribed to the formation of closely adherent adsorbed film on the metal surface. The results of potentiodynamic polarization for the corrosion of mild steel in brine water are given in Fig. 2.

Impedance measurements

Corrosion inhibition of mild steel in brine water solution with and without inhibitor was investigated by electrochemical impedance spectroscopy measurements and it is shown in Fig. 3 and the results are presented in Table 3. At all concentrations range of TDMTU, large capacitive circle at higher frequency range followed by small capacitive loops at lower frequency range. The diameter of the circles increased with increase in inhibitor concentration. The higher frequency capacitive loop is due to the adsorption of inhibitor molecule [14–18]· Also the values of R_{ct} are found to increase with increase in concentrations of compound in brine water solution whereas values of C_{dl} are reduced considerably. This can be ascribed to the strong adsorption

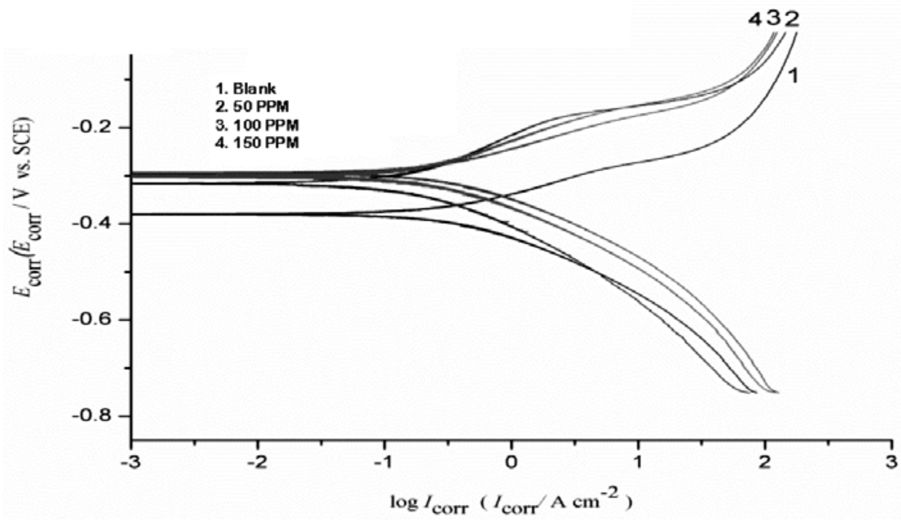

Fig. 2. Potentiodynamic polarization plot for mild steel in brine water with different concentrations of inhibitor.

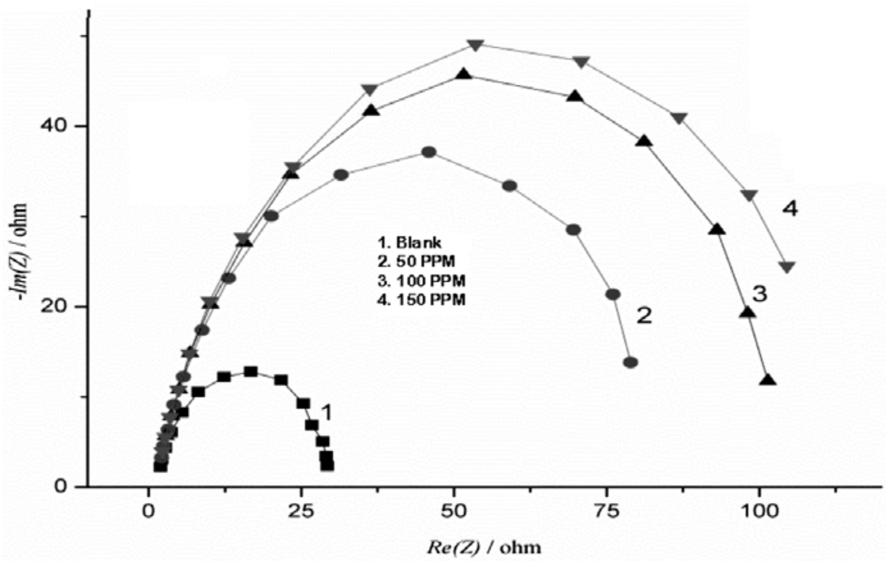

Fig. 3. Impedance curves for the corrosion of mild steel in brine water in the presence and absence of TDMTU.

TABLE 3.

Impedance values for the corrosion of mild steel in brine water in the presence of different concentrations of Tolyl-3,3 dimethyl thiourea

Concentration of Inhibitor (ppm)	brine watersolution	
	Charge Transfer resistance (R_{ct}) Ohm.cm^2	Double layer capacitance (C_{dl}) μF.cm^{-2}
Blank	30	172
50	79	110
100	105	88
150	112	72

of the compound on the metal surface. Similar observation was reported by Harikumar [13] and others [14–18] for the corrosion inhibition of mild steel in acidic media by Ampicilin drug and thio compounds.

Diffused Reflectance Studies

The formation of thin film on the surface of mild steel is ascertained by UV reflectance studies carried out using spectrophotometer in different concentrations of inhibitor with different mild steel specimens. The reflectance curves for polished specimen, specimen dipped in salt water and different concentrations of inhibitor are shown in the Fig. 4. The percentage of reflectance is maximum for polished mild steel and it gradually decreases for the specimen dipped in brine water solution. This observation reveals that the change in surface characteristic is due to the corrosion of mild steel in salt water. When compared with uninhibited solution, the reflectance percentage increased as the concentration of the inhibitor increased. This can be ascribed to the increase in film thickness formed on mild steel surface [19].

SEM studies

SEM images portrayed for mild steel surface immersed in brine water for 3 hrs in the absence and presence of 150 ppm of TDMTU are shown in Figs. 5 & 6. The specimen surface (Fig. 5) was extremely damaged in the absence of the inhibitor. Fig. 6 reveals that a good protective adsorbed film is formed on the specimen's surface, which suppresses the rate of corrosion.

A plot of surface coverage (ϕ) versus log C gives a straight line showing that the adsorption of TDMTU on the mild steel surface from brine water obeys Temkin's adsorption isotherm (Fig. 7).

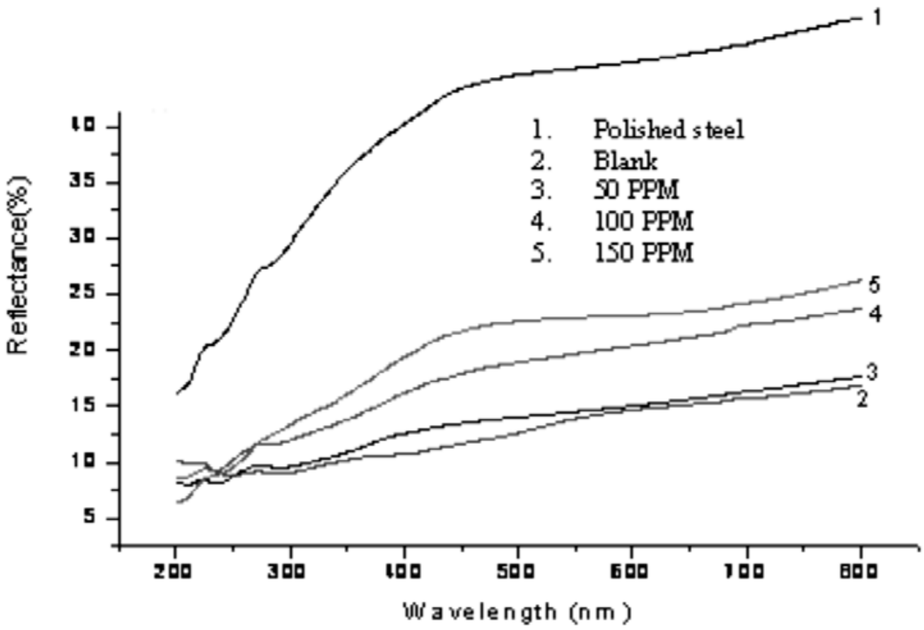

Fig. 4. UV Reflectance curves for Mild Steel in salt water with different concentrations of inhibitor.

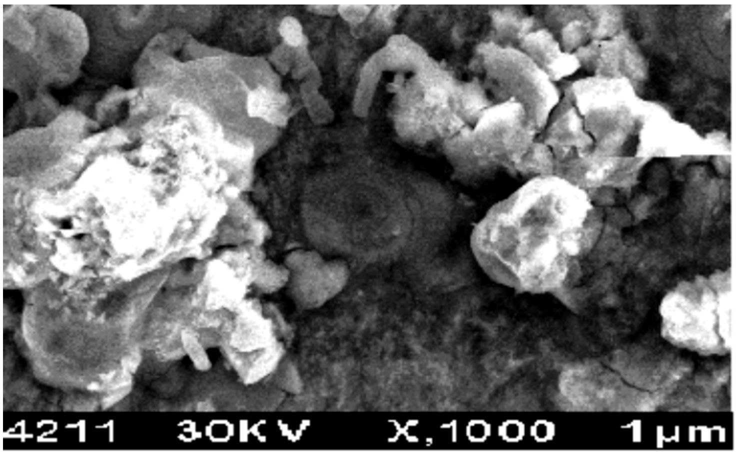

Fig. 5. SEM images of mild steel in brine water.

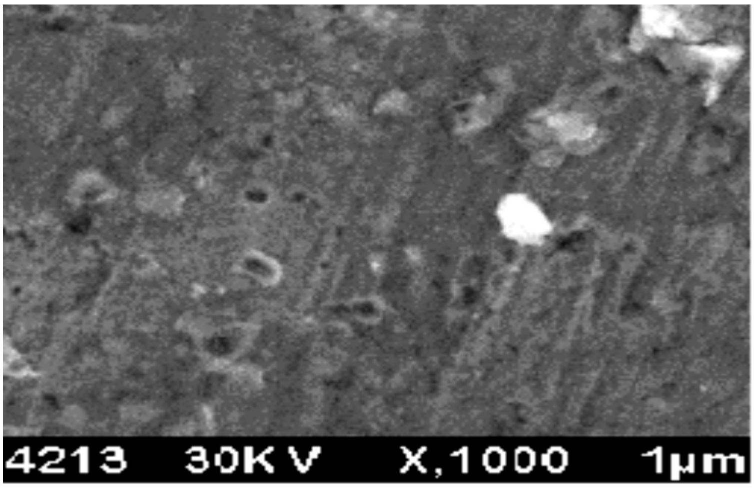

Fig. 6. SEM images of mild steel in the presence of TDMTU (150 ppm).

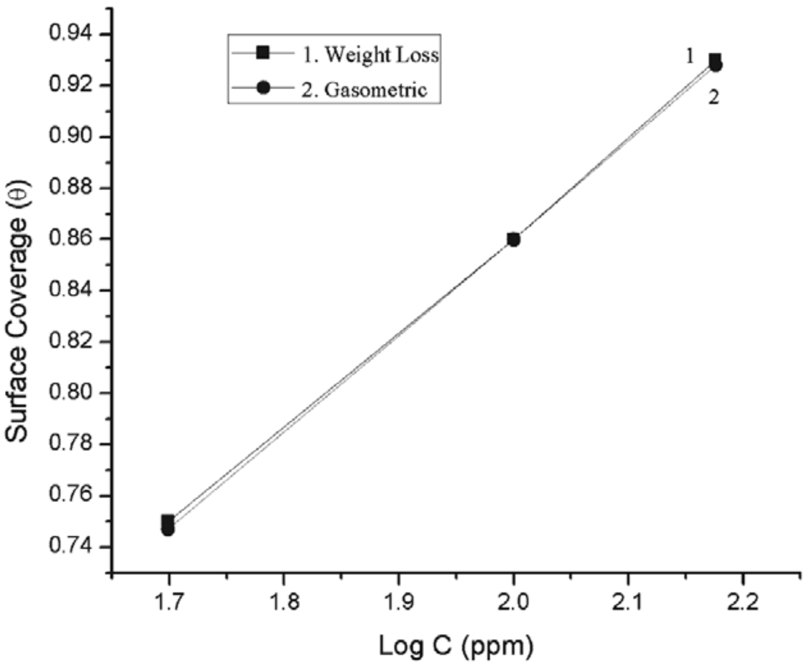

Fig. 7. Temkin's adsorption isotherm for TDMTU in brine water.

CONCLUSIONS

1. Tolyl-3,3 dimethyl thiourea inhibits the corrosion of mild steel effectively in brine water.
2. The inhibition of corrosion of mild steel in salt water, by the compound is under cathodic control.
3. R_{ct} and C_{dl} values obtained from impedance measurements confirm the better performance of the compound.
4. The adsorption of the compound on mild steel surface obeys Temkin's adsorption isotherm.
5. UV–reflectance studies reveal the mere adsorption of the inhibitor on the mild steel surface accounted for the corrosion inhibition of steel in brine water.

REFERENCES

1. Singh, I., Inhibition of Steel Corrosion by Thiourea Derivatives (1993) Corrosion, 49(6), pp. 473–478.
2. Agrawal, R., Namboodhri, T. K. G. Inhibition of sulphuric acid corrosion of 410 stainless steel by thioureas (1990) Corr. Sci., 30(1), pp. 37–52.
3. Sekine, I. A., Masuko, A., Senoo, K. Corrosion of AISI 316 stainless steel in formic acid and acetic acids (1987) Corrosion, 43 (9), pp. 553–560.
4. Quraishi, M. A., Ansari, F. A., Jamal, D. Thiourea derivatives as corrosion inhibitors for mild steel in formic acid (2003) Materials Chemistry and Physics, 77(3), pp. 687–690(4).
5. Quraishi, M. A., Khan, M. A. W, Ajmal, M. Influence of some thiazole derivatives on the corrosion of mild steel in hydrochloric acid (1996) Anti-Corros. Methods Mater., 43(5), pp. 5–8.
6. Murlidharan, S. Iyer, S. V. K. Influence of *N*-heterocyclics on corrosion inhibition and hydrogen permeation through mild steel in acidic solutions (1997) Anti-Corros. Methods Mater., 44, pp. 100–109.
7. Al-Andis, N., Khamis, E., Al-Mayouf, H., Aboul b Enicm. Electrochemical studies of two corrosion inhibitors for iron in HCl (1995) Corros. Prev. Control, 42(1), 13–20.
8. Hammouti, B., Aouniti, M., Taleb, Brighli M., Kertit S. L-Methionine methyl ester hydrochloride as corrosion inhibitor of iron in 1M HCl (1995) Corrosion, 51, pp. 441–448.

9. Muralidharan, S., Madhavan, K., Karthikeyan, S., Iyer, S. V. K. Influence of anions on corrosion inhibition and hydrogen permeation through mild steel in acidic solutions in the presence of p-tolyl thiourea (2002) Ind. J. Chem. Tech., 9, pp. 68–77.

10. Devanathan, M. A., Tilak, B., The Structure of the Electrical Double Layer at the Metal-Solution Interface (1965) Chem. Revs., 65, pp. 635–643.

11. Soriaga, M. P., Surface coordination chemistry of monometallic and bimetallic Electrocatalysts (1990) Chem. Revs., 90, pp. 77–87.

12. Reeta Agarwal, Namboodri, T. K. G., The inhibition of sulphuric acid corrosion of 410 stainless steel by thioureas (1990) Corros. Sci., 30, pp. 37–52.

13. Madhavan, K. PhD Thesis, Mechanism of Corrosion and its inhibition, Alagappa University, India, June, 1996.

14. Hari Kumar, S. and Karthikeyan, S., The influence of ampicill in on the corrosion inhibition of mild steel in 1n hydrochloric acid solution (2012) International Journal of Current Research and Review, 4, pp. 96–104.

15. Lane, T. J., Yamaguchi, A., Quac hano, J. V., Ryan, R. A., Muzhushi, A., Infrared Studies of Methylthiourea and its Metal Complexes (1959) J. Am. Chem. Soc., 81, 3824–3831.

16. Gu Hough, Zhou Zhongbai, Tao Yingachu and Yao Luaw, Study on the effect of thiourea and its derivatives on hydrogen permeation rate in steel in hydrochloric acid solution, Chemical abstracts, 98, 38540 n.

17. Trabanelli, G., Zucchui F. Revon, Sulphur containing organic compounds as corrosion inhibitors (1973) Corrosion and coatings, 1, pp. 47–54.

18. Lahiri, A. K., Banerjee, N. G, Dissolution of steel and absorption of hydrogen by steel during acid picking in presence of inhibitor (1963) NML Tech. Journal, 5 (2), 33–37.

19. Hari Kumar, S. and Karthikeyan, S. Inhibition of mild steel corrosion in hydrochloric acid solution by cloxacillin drug (2012) J. Mater. Environ. Sci., 3 (5), 925–934.