International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.4, pp 1897-1901, April-June 2013

Corrosion Inhibition Of Mild Steel In Well Water: An Experimental And Theoretical Approach

S.Karthikeyan[1]*, P.A.Jeeva[2], S.Narayanan[2]

[1]Surface Engineering Research Lab, Centre for Nanobiotechnology, VIT University, Vellore-632014, India
[2]School of Mechanical and Building Sciences, VIT University, Vellore-632014, India

***Corres. author: skarthikeyanphd@yahoo.co.in**

Abstract: The Inhibition of mild steel corrosion in well water 1,3-diethyl thiourea (DETU) has been reported by weight loss, electrochemical polarization technique, impedance method and quantum mechanical measurement. It was found that the compound effectively reduces the steel corrosion in the salt water medium. The inhibition efficiency (IE) increases as the inhibitor concentration is increased. Quantum mechanical studies confirm the adsorption of protective layer of inhibitor on mild steel surface.
Keywords: Corrosion Inhibition, Mild Steel, Well Water, Experimental Approach, Theoretical Approach.

Introduction

Mild steel is widely used in many industries due to its admirable mechanical properties .When mild steel is exposed to well water in the form of pipelines, storage tanks, the attack on metal will be severe due to the presence of chlorides, sulphates, carbonates and bicarbonates of alkali metals in well water. Hence the use of inhibitor for the dissolution of mild steel is to be suggested. Thiourea and its derivatives have been reported as inhibitors for the corrosion of mild steel in acidic media [1-6]. The detailed study on literature indicates no significant investigations are available for the corrosion inhibition of mild steel in well water using 1,3-diethylthiourea. This paper discusses the influence of diethyl thiourea on the corrosion of mild steel in well water and the mode of inhibition of the compound has been explained by weight loss, gasometric, potentiodynamic polarization and impedance measurements. Quantum mechanical factors have been explained to understand the performance of the inhibitor through its effective adsorption on metal surface.

1, 3- diethyl thiourea (DETU) is an aromatic substance containing π-electrons and heteroatom's S, N & O. The molecule is planar (Melting point: 77^{o}C) and can block more surface area through its lone pair of electrons.

Experimental procedure

The inhibitor was preliminarily assessed by a weight loss method as described elsewhere [7]. The potentiodynamic polarization was performed at the scan rate of 1mV s^{-1} using EG&G Princeton Applied Research-6310. A platinum metal with 3 cm^2 surface area, Hg/Hg_2Cl_2/Satd KCl were used as counter and reference electrodes. Constant phase equivalent (CPE), Surface inhomogenites (n), relaxation time (τ) and charge transfer resistance values (R_t,) were obtained using AC impedance measurements with aid of the above instrument. Gaussian software was used to study the hardness, softness, Huckel molecular orbitals, Mullikan's charges and dipole moment responsible for identifying the mode of adsorption of atoms of DETU on the steel surface.

Results and Discussion

Weight loss and Gasometric measurements

The inhibition efficiencies measured from weight loss and gasometric experiments for various concentrations of 1,3-diethyl thiourea (DETU)for the corrosion of mild steel in well water is given in table 1. The inhibitor performed well in well water. The mode of action of inhibition could be explained as follows:

1. The hetero atoms of the inhibitor exert negative charges which facilitate the interaction with positive metallic surface[8].
2. The presence of two electron releasing ethyl groups in the molecule increase the electron density of the heteroatoms by +I effect improving the adsorption of the compound on mild steel.

The results of weight loss and gasometric studies agreed very well with each other.

Table 1. Values of inhibition efficiency for the corrosion of mild steel in the presence of different concentrations of DETU obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (ppm)	Inhibition efficiency (%)	
	Weight loss Studies	Gasometric measurements
Blank	---	---
50	63	62.7
100	73	73
150	92	91.6

Potentiodynamic polarization studies

Table 2 explains the corrosion kinetic factors like Tafel slopes (b_a and b_c) ,corrosion current (I_{corr}) and corrosion potential (E_{corr}) and inhibition efficiency measured from potentiodynamic polarization for mild steel in well water in the presence of various concentrations of inhibitor.

The presence of inhibitor brought down both Ecorr and Icorr values in well water. This is due to the formation of strong adsorption layer of DETU on the metal surface. Also both anodic and cathodic Tafel slopes have been shifted to ± 70 mV equally, confirming the mixed mode of action of the inhibitor.

Table 2: Corrosion kinetic parameters of steel in well water in the presence of different concentrations of DETU obtained from potentiodynamic polarization studies.

Concentration of inhibitors	R_t	C_{dl}	CPE	n	τ	IE (%)
Well water	38.2	59.6	38.126	---	0.0263	
40 mg/l	80.2	28.2	79.965	0.66	0.0261	52.68
80 mg/l	122.1	13.4	120.57	0.768	0.0187	77.51
120 mg/l	139.5	5.4	139.2	0.964	0.0087	90.93

Impedance measurements

The impedance values obtained in the presence and absence of various concentrations of DETU in well water is given figure 1. Perfect semicircles were observed in this study confirming the charge transfer reaction between metal and inhibitor. The compound enhances the charge transfer values indicating the inhibitive action of DETU. The usefulness of Constant phase equivalent(CPE) in Warburg impedance , $Z_{CPE} = 1/ C_{dl} [(-1/ \tau)^n]^{-1}$ and the surface uniformity (n) measured in this work establishing that in presence of DETU, the metal dissolution in well water can be minimized. The increase of concentrations of inhibitors increases the relaxation time (τ) indicating that the protective layer formed delays the attack of well water on metal surface. Also the Cdl values are lessened in presence of inhibitor. Similar observation has been made earlier by Harikumar[9] for the corrosion inhibition of mild steel by Cloxacillin drug.

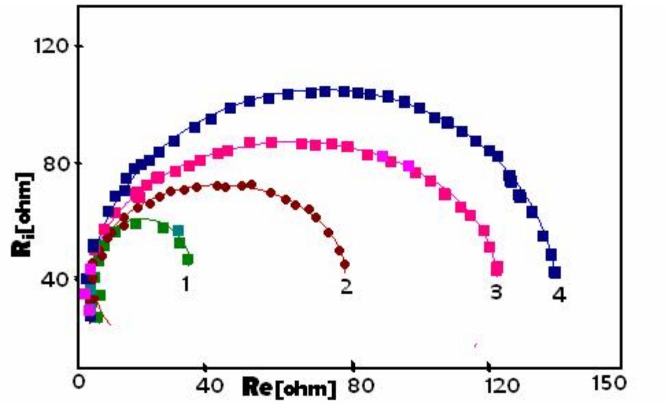

Figure 1.Impedance plots for the corrosion inhibition of steel in well water.
1. No EDTU; 2. 40 mg/l; 3. 80 mg/l; 4. 120 mg/l

Quantum mechanical studies

The measured quantum values like energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}),Ionization potentials (I), Hardness (η),softness (σ) energy gap (ΔE), dipole moment (μ), Total negative charges (TNC) of the inhibitor, electron affinity (A) and electronegativity (χ) are given in Table 3 and the optimized structure of the compound is given in figure 2(a). It can be observed from figure 2(b) and 2(c) that the existence of LUMO energy orbital's on and nitrogen, sulphur atoms of thiourea groups were stronger than HOMO concluding the presence of electronegative atoms in the inhibitor. The Mullikan's charges for atoms C1, S8, C14 signify that the adsorption will be better through these atoms than the other atoms of the compound which is a reason for the best localization of LUMO. In the case of thio compounds, if the values of ΔE > 8 eV and μ > 4 debye , they may be considered as effective corrosion inhibitors. The above measured parameters concluding that DETU retards the corrosion of mild steel in well water.

Table 3: Impedance parameters for the corrosion of mild steel with and without the presence of DETU

Con. DETU	E_{corr} (mV vs SCE)	I_{corr} (μA cm^{-2})	βa (mV dec^{-1})	βc (mV dec^{-1})	IE (%)	Ø
Well water	-896	360.14	193.0	185.2	-	-
40 mg/l	-874	130.53	180.6	162.0	63.75	0.63
80 mg/l	-865	96.47	176.2	141.4	73.21	0.73
120 mg/l	-787	30.69	120.2	115.5	91.47	0.91

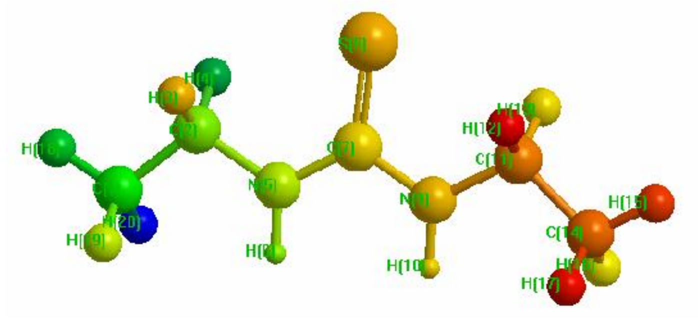

Figure 2.a. Optimized structure of DETU

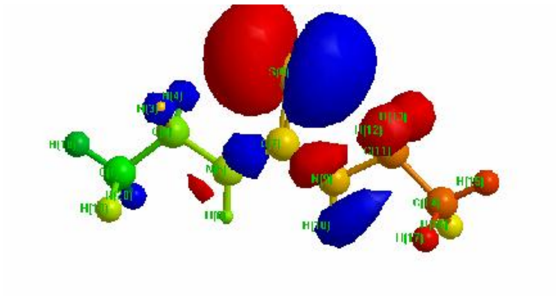

Figure 2(b) HOMO of DETU

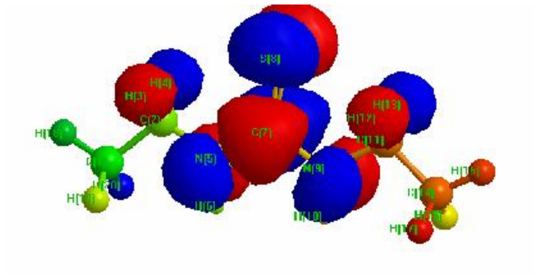

Figure 3. LUMO of DETU

Table 4.Mullikan's charges calculated from quantum mechanical studies

C	**-0.127**	**C(1)**
C	0.030	C(2)
N	0.071	N(5)
C	0.246	C(7)
S	**-0.677**	**S(8)**
N	0.069	N(9)
C	0.031	C(11)
C	**-0.129**	**C(14)**
H	0.038	H(18)
H	0.039	H(19)
H	0.039	H(20)
H	0.019	H(3)
H	0.019	H(4)
H	0.091	H(6)
H	0.089	H(10)
H	0.019	H(12)
H	0.019	H(13)
H	0.038	H(15)
H	0.039	H(16)
H	0.039	H(17)

Table 5. Quantum mechanical studies of corrosion of mild steel in well water:

Compound	**E_{HOMO}(eV)**	**E_{LUMO}(eV)**	**Δ E (eV)**	**μ(Debye)**	**TNC**	**η**	**χ**	**σ**
DETU	-8.13096	0.72911	8.86007	4.1	-0.311	4.43	3.7009	0.225

Conclusion

The corrosion inhibition of mild steel in well water by DETU has been thoroughly analyzed by weight loss, potentiodynamic polarization and impedance measurements. The polarization studies confirmed the mixed mode of action of inhibitor. The quantum mechanical studies established the better performance of the inhibitor through its vibrant adsorption on steel surface.

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