Corrosion inhibition for mild steel in 1 M HCl solution using TriCholoroEthelene

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Abstract- TriCholoroEthelene (TCE)was investigated for corrosion inhibition of mild steel in 1 M HCl medium at room temperature. Gravimetric technique was used to study the corrosion behavior in the absence and presence of different concentrations of TCE. The result obtained showed that TCE is a good inhibitor for mild steel in 1 M HCl solution. The corrosion rate and inhibition efficiency were calculated. The inhibition efficiency calculated showed a great percentage result with optimum value of 90.37 %. TCE was adsorbed on the mild steel surface in accordance with Langmuir, Frumkim, and Floru-Huggins adsorption isotherm models. The negative adsorption energy ΔG_{ads} obtained inferred that the adsorption rates were spontaneous and the interaction between the inhibitive molecules was found to be repulsive.

Keywords – TCE, corrosion rate, inhibition efficiency, adsorption isotherm.

I. INTRODUCTION

Today in industry we are trying to reduce the maintenance cost of materials used. Among all the material iron metal and alloys has most promising features for being used in engineering applications due to its remarkable mechanical properties, effective cost and high strength [1]. The protection of metal and alloys from corroson reduce the waste of resources and money during the industrial applications. Process of corrosion depend upon aggressiveness of the medium and reactivity of the material. In many industries (especially chemical industry) mineral acids are frequently used in various applications which cause loss of functional properties of the metals, in form of corrosion, due to violent reaction of acid with metals [2]. Corrosion can be minimized using suitable preventive measures, and several techniques have been developed to control corrosion. Corrosion inhibition of steel in acid solutions has become one of the most urgent and severe challenges in acid pickling process . Efficiency of inhibitors depends upon its molecular structure, electron density, distribution of charges, aromaticity and its molecular size . In many cases organic inhibitors (chemically synthesized) were found very efficient but its toxicity and synthesis cost motivated people to develop environment friendly and cheap inhibitors .Use of inhibitors is one of the best methods of protecting metals against corrosion. Most of the efficient acid inhibitors are organic compounds containing nitrogen, sulphur and/or oxygen atoms in their molecule. Efficiency of inhibitors depends upon its molecular structure, electron density, distribution of charges, aromaticity and its molecular size . In many cases organic inhibitors (chemically synthesized) were found very efficient but its toxicity and synthesis cost motivated people to develop environment friendly and cheap inhibitors .

In this work we report trichloro ethelene[C_2HCl_3], for corrosion inhibition of steel in hydrochloric acid solution. Aqueous solution of TCE contain lone pairs and π electron density] which are very effective for mild steel in acidic medium. Reasons for selecting TCE for corrosion study are low cost, easy availability.

II. MATERIALS AND METHODS

Mild steel preparation

The mild steel used in the studies was analyzed using optical emission spectrometry and consists (in % weight): C(0.0285), Si(0.0096), P(0.0096), Mn(0.1965), Ni(0.0153), Cr(0.0124), Mo(0.0027), Cu(0.0137), Sn(0.043), W(0.0052), Zn(0.031), As(0.0037), Ru(0.0028), and Fe(99.657%). The metal sheet was cut into coupon with the following dimensions of 5 x 5 x 0.5cm and used for corrosion studies.

Gravimetric technique

Gravimetric technique used was according to the description by (ASTM G1-72, 1990). All reagents used were BDH grade. Prior to measurement, each coupon was degreased in ethanol, the surface smoothened using sic emery paper (of grades 400, 600, 800 and 1000) and then double washed with distilled water and air dried after dipping in acetone. The coupons were weighed using NJW-300 analytical electronic digital weighing balance (capacity of 300x0.01g,sensitivityof 0.0001). The specimen were immersed in 250 ml beaker containing 240 ml of 1 M HCl solution of different TCE Inhibition concentration ranging from 10^{-2} to10^{-5} concentrations of the inhibitor at room temperature (290K). The set up were exposed for a period of 2 days after which the specimen were taken out,washed, dried and weighed accurately. Triplicate experiments were performed in each case and the mean value reported.

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III. RESULTS AND DISCUSSION

The mass losses of mild steel coupon in 1 M HCl solution, with or without different concentrations of the investigated inhibitor, were recorded after 2 days of immersion at room temperature. The corrosion rate of mild steel was calculated using the Equation 1.

$$CR = \frac{\Delta W}{At\rho} \qquad (1)$$

Where ΔW is the weight lost (in grams), A is the surface area of the coupon (in cm^2), ρ is the density (in g/cm^3), t is the period of exposure (in hours)

Table 1:Weight loss values and calculated corrosion rate for mild steel corrosion in 1M HCl in the presence and absence of different concentrations of inhibitors.

S.No	Conc. Of TCE	ΔW	C.R.×10^{-4}
1	10^{-2}	0.96	0.98
2	10^{-3}	1.42	1.30
3	10^{-4}	1.90	1.75
4	10^{-5}	2.39	2.44
5	Blank	2.93	2.70

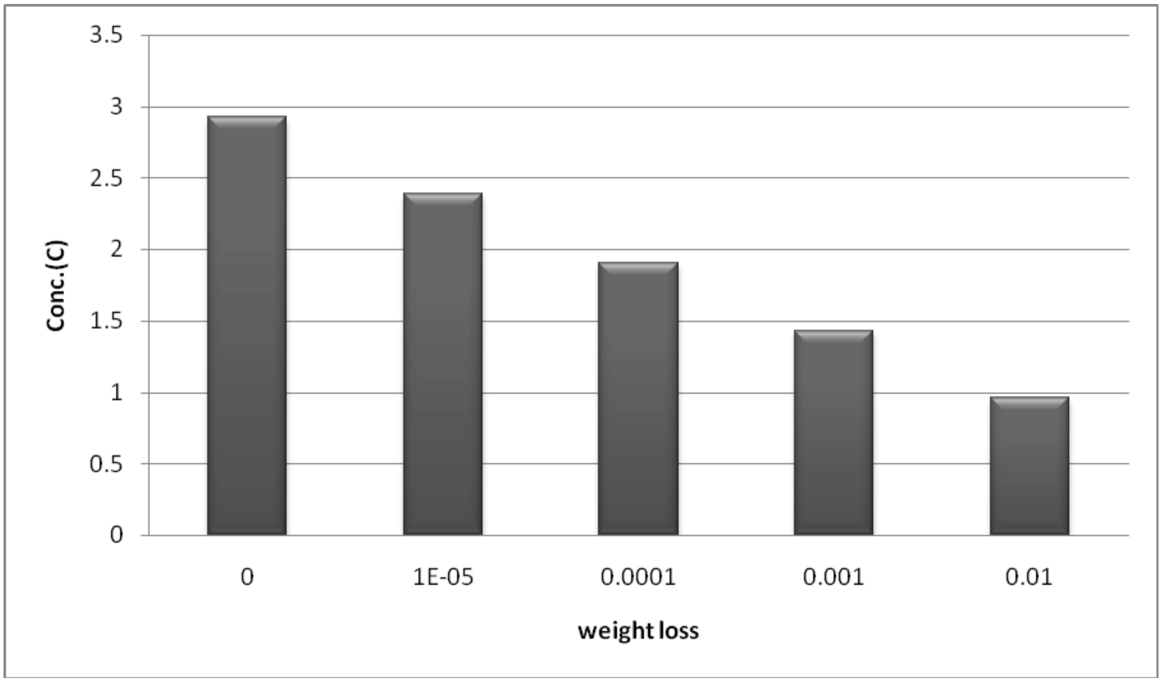

Figure 1. Mass loss for mild steel in the different concentration of TCE at 290k exposure for 2 days.

The inhibition efficiency and surface coverage were calculated from the mass loss data according to the Equations 2 and 3, respectively. Figure 1 shows the inhibition efficiency in different concentration of the TCE and it could be seen that the %IE increases linearly with the inhibitor concentration.

$$\theta = 1 - \frac{\rho inh}{\rho blank} \quad (2)$$

$$\%IE = \theta \times 100 \quad (3)$$

Where ρ_{inh} and ρ_{blank} are the corrosion rates in the absence and presence of inhibitor, respectively. It can be observed that the inhibition efficiency increased and the corrosion rate decreased as the inhibitor concentration increased. The maximum value of inhibition efficiency
was 90.37%**.** It could be considered thatTEC. As inhibitor of mild steel to 1 M HCl solution given the high level of the inhibition efficiency.

Table 2: Calculated values of inhibitor efficiency and surface coverage of mild steel in 0.1M HCl solution in absence and presence of different concentrations of inhibitors.

S.No	Conc. Of TCE	P	θ
1	10^{-2}	63.70	0.63
2	10^{-3}	51.85	0.51
3	10^{-4}	35.18	0.35
4	10^{-5}	9.62	0.09
5	Blank	-----	------

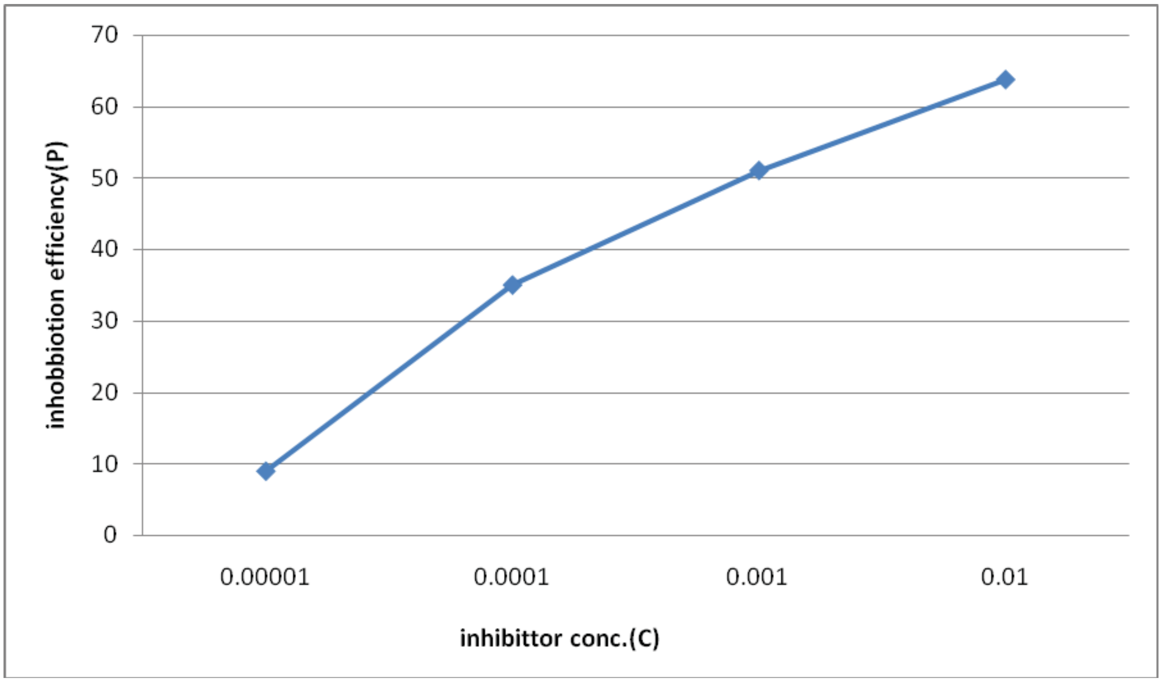

Figure 2. Inhibition efficiency of *TCE* for mild steel in 1 M HCl solution.

Adsorption mechanism

The inhibition of metal corrosion by organic compounds is attributed to either the adsorption of inhibitor molecule or the formation of a layer of insoluble complex of the metal on the surface which acts as a barrier between the metal surface and the corrosive medium.

Since no insoluble material was observed on the metal surface, the inhibitive action of TCE molecule may be due to its adsorption on the metal surface. The adsorption of TCE on the corroding mild steel surface creates a barrier that isolates the metal from the corrodent. Thus inhibition efficiency increases with an increase in the metal fraction occupied by the TCE molecule.

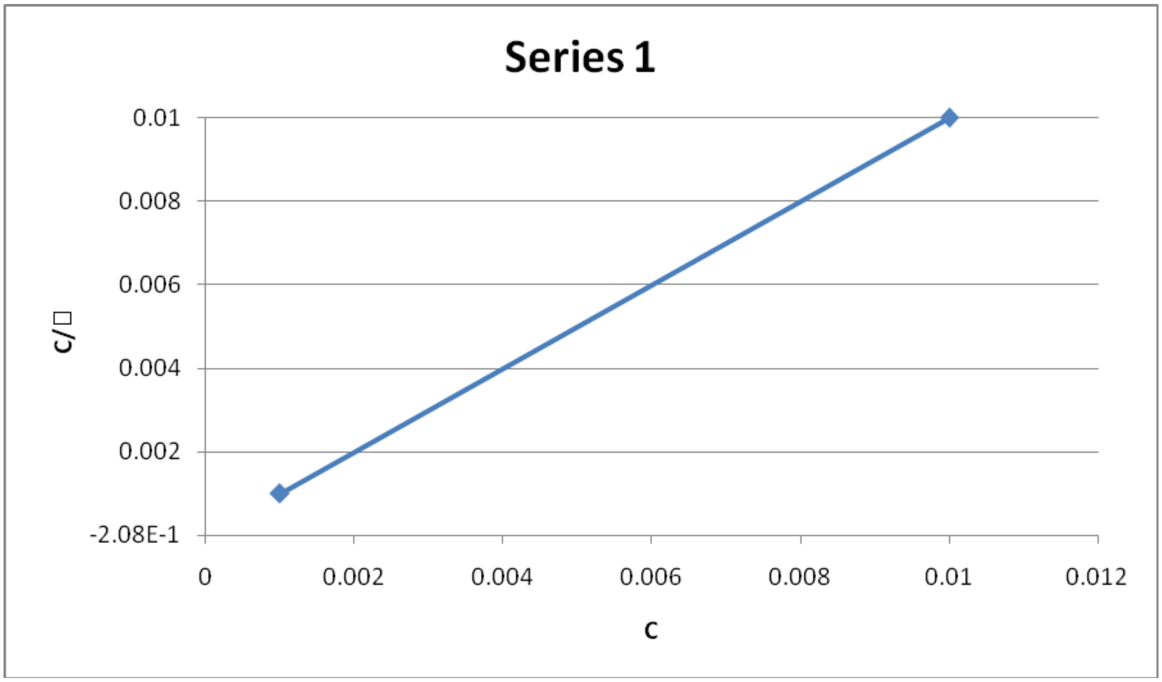

Figure 3. Langmuir adsorption isotherm for TCE on mild steel in 1 M HCl.

The relationship between inhibition efficiency and the bulk concentration of the inhibitor at constant temperature, which is known as isotherm, it gives an insight into the adsorption process.Several dsorption isotherms were attempted to fit surface coverage values to classical isotherms of Langmuir, Temkin, Frumkin, Flory-Huggins.The value of the correlation (R^2) was used to determine the best fit isotherm which was obtained for Langmuir, Frumkin isotherms and Flory- Huggins. The Langmuir isotherm, which is presented in Equation 4 is most often used to calculate the equilibrium constant k , which is the relationship between surface coverage and the inhibitor concentration.

$$\frac{c}{\theta} = \frac{1}{k} + c \qquad (4)$$

Where C is the inhibitor concentration, θ is the surface coverage. Figure 3 shows that a plot of c/ θ versus c yields a straight line .The plot obeys Langmuir adsorption isotherm as the plot has linearity and good correlation coefficient. The R^2 values are very close to unity, indicating strong adherence to Langmuir adsorption isotherm . The adsorption Gibb's free energy was calculated using Equation 5

$$\Delta G = RTIn\ln(55.5k) \qquad (5)$$

Where R is the gas constant (8.314 kJ/mol); and T is the absolute temperature (K). The constant value of 55.5 is the concentration of water in solution in mol/L. The value of ΔG_{ads} for the inhibitor on the surface of mild steel is given -22.81 kJ/mol since ΔG_{ads} is below 40 kJ/mol, it corroborates that the adsorption process is physisorption. The negative value of ΔG_{ads} indicated spontaneous adsorption of the inhibitor on the mild steel surface.

Considering the Frumkin isotherm commonly used to quantify the interactions occurring between corrosion inhibitor and a metal surface.

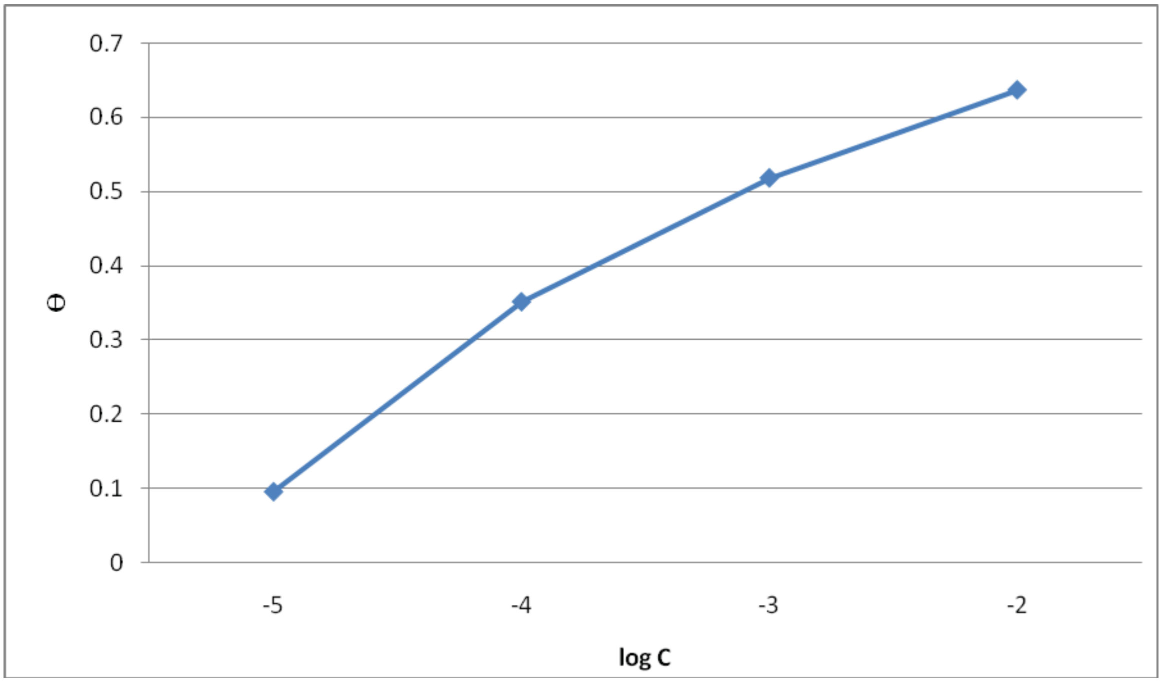

Figure 4. Frumkim adsorption isotherm TCE on mild steel in
1 M HCl.

$$\exp(-f\theta) = c\left[\frac{1}{55.5}\exp\left(\frac{-\Delta G}{RT}\right)\right] \qquad (6)$$

Where Θ is the degree of surface coverage, *f* is the interaction term parameter (if $f > 0$, there is a lateral attraction, if $f < 0$, there is a lateral repulsion between the adsorbing molecules), c (in moles/L) is the inhibitor concentration, is the standard free energy of adsorption (kJ/mol). The Frumkin adsorption isotherm is a general expression since the limiting case for which $f = 0$ is representative of an interaction free behavior between adsorbed species and defines the Langmuir isotherm. Equation 6 can be rearranged to give Equation 7 .

$$LogC = \log\left(\frac{\theta}{1-\theta}\right) + A\theta + B \qquad (7)$$

Where $A = -f/2.3$ and $B = (\Delta G^0_{ads} /2.3RT) + \log 55.5$ and has the meaning of equilibrium constant of the adsorption process. Equation 7 was used to plot the Frumkin isotherm (Θ against Log C) shown in Figure 4. The existence of adsorption interactions between adsorbed TCE molecule and the metal surface is thus confirmed since most of the experimental data fit nicely into the Frumkin isotherm plot, the slight *S*-shape.The adsorption parameters *B, f* and ΔG^0_{ads} obtained were 1.75 M^{-1}, -9.79 and -22.81 kJ/mol, respectively using two values of C (10^{-5} – 10^{-2} moles/L) and the corresponding Θ. The negative value of *f* indicates that the adsorption of the tested compound is accompanied by mutual repulsion of the inhibitor molecules .

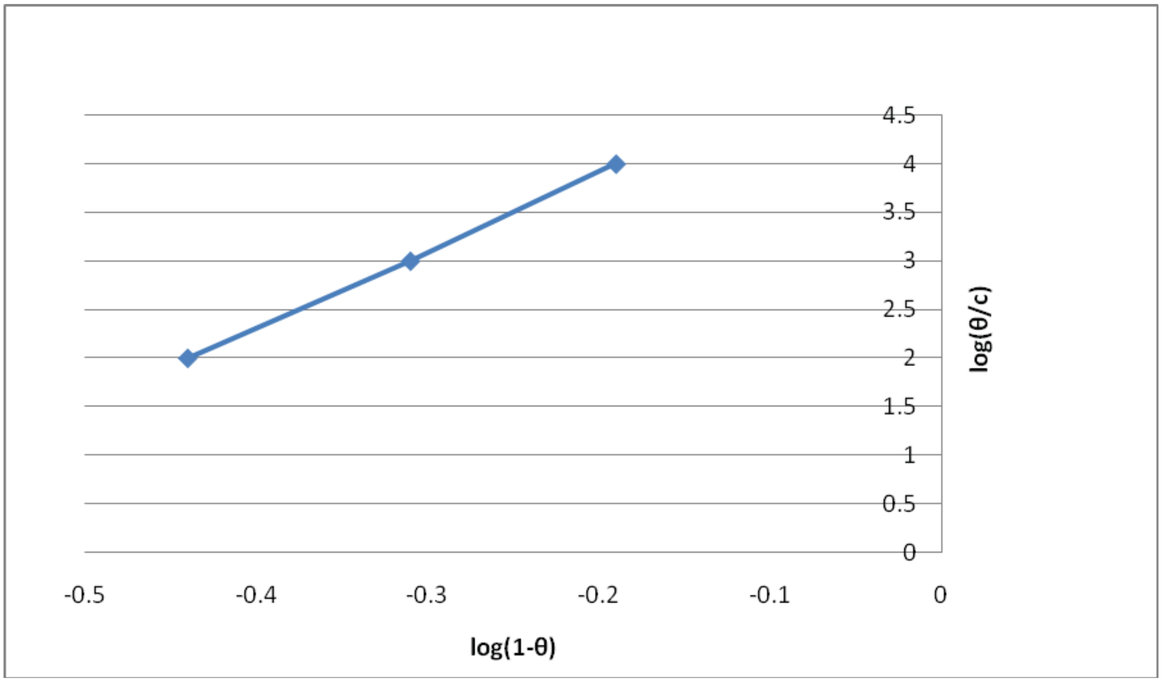

Figure 5. Flory-Huggins isotherm for adsorption of TCE on the mild steel surface.

Flory-Huggins Isotherm: The assumptions of the Flory- Huggins adsorption isotherm can be expressed according to Eq 8

$$\text{Log}(\theta/c)=\text{Log}k+x\text{Log}(1-\theta) \quad (8)$$

Where x is the size parameter and is a measure of the number of dsorbed water molecules substituted by a given inhibitor molecule. As shown in Figure 5 the plot of log (Θ/C) against log (1 - Θ) gave a linear relationship , showing that Flory-Huggins isotherm was obeyed. The value of the sizeparameter (x) is 6.84. This indicates that the dsorbedspecie of the inhibitor is bulky since it could displacemore than one water molecule from the metal steel surface (Abd-ElNabey et al., 1996). The calculated ΔG_{ads} is -22.81 kJ/mol.

Generally, the magnitude of ΔG_{ads} about -20 kJ/mol or less indicates electrostatic interactions between inhibitor and the charged metal surface is physisorption. Those about -40 kJ/mol or more are indicative of charge sharing or transferring from organic species to the metal to form acoordinate type of metal bond is chemisorptions (Keles etal., 2008). In the present study, the calculated values ΔG_{ads} at 290 K for mild steel indicated that adsorption of the inhibitor on the surface of the mild steel is physisorption adsorption which implies that the films of the inhibitor was spontaneous on the surface of the metal.

IV. CONCLUSIONS

TCE is found to inhibit the corrosion of mild steel in 1 M HCL solution at room temperature. The inhibition efficiency increases with increasing inhibitor concentration. The value of Gibbs free energy of adsorption indicates that *TCE* is physically adsorbed on the surface of the metal following the Langmuir, Frumkin and Flory-Huggins adsorption isotherm models. The interactions of the adsorbed molecules of the inhibitor are repulsive, and they are bulky on the metal surface. TCE could be used as corrosion inhibition for mild steel in 1 M HCL solution.

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