J Appl Electrochem (2009) 39:1497–1501
DOI 10.1007/s10800-009-9829-y

ORIGINAL PAPER

Corrosion inhibition of mild steel in acidic media by Basic yellow 13 dye

H. Ashassi-Sorkhabi · B. Masoumi ·
P. Ejbari · E. Asghari

Received: 4 November 2008 / Accepted: 2 February 2009 / Published online: 26 February 2009

Abstract The inhibition performance of Basic yellow 13 dye on mild-steel corrosion in hydrochloric acid solution was studied at 25 °C using weight loss and electrochemical techniques. The effect of inhibitor concentration on inhibition efficiency has been studied. Inhibition efficiency increased with increase of Basic yellow 13 concentration. The results showed that this inhibitor had good corrosion inhibition even at low concentrations (95% for 0.005 M Basic yellow 13) and its adsorption on mild-steel surface obeys Langmuir isotherm. ΔG_{ads} was calculated and its negative value indicated spontaneous adsorption of the Basic yellow 13 molecules on the mild-steel surface and strong interaction between inhibitor molecules and metal surface. The value of ΔG_{ads} was less than 40 kJmol^{-1}, indicating electrostatic interaction between the charged inhibitor molecules and the charged metal surface, i.e., physical adsorption.

Keywords Corrosion inhibition · Basic yellow 13 dye · Adsorption · Langmuir isotherm

1 Introduction

Corrosion of steel is the most common form of corrosion, especially in acid solution. It has practical importance, for example, in the acid pickling of iron and steel, chemical cleaning of scales in metallurgy, in the oil recovery and petrochemical industry, etc.

Organic compounds have been accepted as effective inhibitors for metals corrosion in various solutions [1–3]. It has been found that dyes can also be used as organic corrosion inhibitors. The use of different dyes for corrosion inhibition applications has been reported by several authors [4–6]. These inhibitors, which are usually organic substances containing nitrogen, sulfur, and/or oxygen in the conjugated system, have been reported as efficient corrosion inhibitors, which act through adsorption on metal surface, forming complex with metal ions and thereby retarding metal dissolution; polar groups act as the reaction center for the adsorption process [1–11]. Protection efficiency depends on adsorption ability of inhibitor molecules, where the resulting adsorption film acts as a barrier that separates the metal from the corroding medium [8, 9]. During corrosion, the products will constitute a new distinct phase between the metal and the aqueous solution; the inhibitor thereby interacts with this interphase [10]. The efficiency of corrosion inhibitors depends on the mechanical, structural, and chemical properties of the layer formed. Thus, the nature of inhibitor interaction with metal and its inhibition efficiency may be dependent on the chemical, mechanical, and structural characteristics of this layer [1].

In recent years, attention has been focused on the investigation of organic dyes as potential inhibitors in metal-corroding systems. The results obtained so far reveal that the processes involved in corrosion inhibition are not identical for all classes of studied compounds, and are not even constant or consistent for one inhibitor in a given system. Indeed, the overall process is a function of metal type, aggressive solution, inhibitor structure, and concentration as well as temperature. Inhibition efficiency is also closely related to inhibitor adsorption abilities [7, 11–14].

H. Ashassi-Sorkhabi (✉) · E. Asghari
Electrochemical Research Laboratory, Physical Chemistry Department, Faculty of Chemistry, University of Tabriz, Tabriz, Iran
e-mail: ashassi@tabrizu.ac.ir; habib.ashassi@gmail.com

B. Masoumi · P. Ejbari
Payam-Noor University of Tabriz, Tabriz, Iran

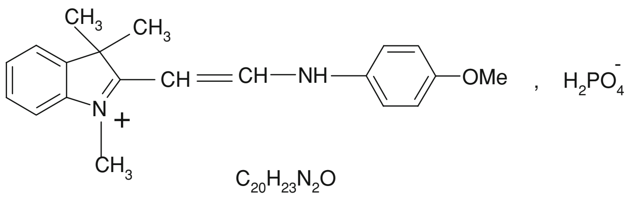

Fig. 1 Molecular structure of Basic yellow 13 ($C_{20}H_{23}N_2O$)

The aim of this work is to study the adsorption characteristics and inhibition performance of Basic yellow 13 dye on mild-steel corrosion in 0.1 M HCl. The molecular structure of the compound is given in Fig. 1. The azo and amine groups and the electron cloud on the aromatic ring suggest that Basic yellow 13 should be a good corrosion inhibitor.

2 Experimental

2.1 Materials

The working electrode was mild steel with chemical composition (wt.%): Si (1.25%), Mn (0.221%), Cr (0.018%), S (0.016%), P (0.007%), C (0.005%), and Fe (balance). Aggressive solutions with concentration of 0.1 M were made from analytical-grade 37% HCl (Merck Co.) and double-distilled water. Basic dye, purchased from Chinachem Company, was used at concentrations of 5×10^{-6}, 5×10^{-5}, 2.5×10^{-4}, 5×10^{-4}, and 5×10^{-3} M, in 0.1 M HCl.

The steel specimens were polished with SiC paper up to 1500 grade, degreased with acetone, rinsed with double-distilled water, and finally dried before immersion in the acid solution.

2.2 Weight loss measurements

Weight loss measurements were carried out as described elsewhere [16]. The solution volume was 50 mL. The steel specimens had rectangular form (length 1.5 cm, width 1 cm, thickness 0.08 cm). The samples were immersed for 24 h in both blank and inhibited solutions. At the end of tests, the specimens were carefully washed in acetone, dried, and then reweighed.

2.3 Electrochemical studies

Electrochemical experiments, including polarization and electrochemical impedance spectroscopy (EIS) measurements, were carried out using an Autolab PGSTAT30 potentiostat-galvanostat. A conventional three-electrode configuration was used for electrochemical studies. The working electrode was prepared from mild-steel sheet, mounted in polyester in such a way that the area exposed to solution was 1 cm^2. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and counter electrodes, respectively. All potentials are reported versus SCE. In the polarization measurements, the potential sweep rate was 2 mVs^{-1}. EIS tests were performed after 30 min immersion at 25 ± 1 °C in open-circuit potential over a frequency range between 10 kHz and 10 mHz; a sine wave with 10 mV amplitude was applied. EIS data were analyzed using Zview2 software and the double-layer capacitance, C_{dl}, and charge transfer resistance, R_{ct}, were obtained from Nyquist plots as described elsewhere [11, 12].

3 Results and discussion

3.1 Polarization measurements

In order to study the effect of Basic yellow 13 dye on the polarization behavior of mild steel and to analyze the inhibition action of dye on steel corrosion in 0.1 M HCl, polarization curves for different concentrations of inhibitor were plotted. Figure 2 presents polarization curves for mild-steel electrode in 0.1 M HCl, in the absence and presence of inhibitor at different concentrations. The electrochemical parameters obtained from polarization measurements are listed in Table 1. It is clear that both cathodic and anodic reactions on mild-steel electrode have been inhibited in the presence of studied compound. However, the cathodic reaction has been affected more than the anodic one in the presence of inhibitor. These results suggest that addition of inhibitor retards the

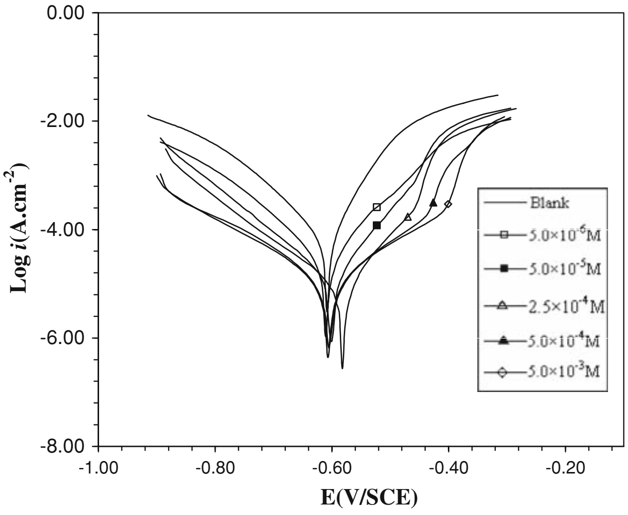

Fig. 2 Polarization curves for mild steel in 0.1 M HCl in the absence and presence of Basic yellow 13 at various concentrations at 25 °C

Table 1 Electrochemical parameters for mild-steel corrosion in 0.1 M HCl in the absence and presence of different concentrations of Basic yellow 13, at 25 °C

Inhibitor concentration (M)	R_p (Ω cm^2)	E_{corr} (mV)	b_a (mV/dec)	b_c (mV/dec)	i_{corr} (A cm^{-2})	I.E.% (η_p)
Blank	132	−631	92	71	1.199×10^{-4}	–
5.0×10^{-6}	786	−610	82	93	2.21×10^{-5}	81
5.0×10^{-5}	1378	−598	75	100	1.05×10^{-5}	91
2.5×10^{-4}	2282	−581	79	119	0.75×10^{-5}	99
5.0×10^{-4}	2638	−606	107	114	0.70×10^{-5}	99
5.0×10^{-3}	3370	−601	107	113	0.54×10^{-5}	99

hydrogen evolution reaction, which is the cathodic reaction in an acidic solution [13]. Electrochemical corrosion parameters including corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c, b_a), and corrosion current density (i_{corr}), obtained by extrapolation of Tafel lines, are given in Table 1. The inhibition efficiency, η_p, was calculated from the following equation [14] and are given in Table 1:

$$\eta_p\% = \left(\frac{i^0_{corr} - i_{corr}}{i^0_{corr}}\right) \times 100, \qquad (1)$$

where i^0_{corr} and i_{corr} are the corrosion current densities in the absence and presence of inhibitor, respectively.

These results show that Basic yellow 13 act as an effective inhibitor. Corrosion inhibition rises as the inhibitor concentration increases. Maximum inhibition efficiency (99.5%) was obtained at a concentration of 5×10^{-3} M.

3.2 Electrochemical impedance spectroscopy (EIS) measurements

The corrosion behavior of mild steel in 0.1 M HCl solution in the absence and presence of Basic yellow 13 dye was also investigated using electrochemical impedance spectroscopy. Nyquist plots of mild steel in uninhibited and inhibited acid solutions containing various concentrations of inhibitor are given in Fig. 3. As can be seen, the impedance response of mild steel in uninhibited 0.1 M HCl solution significantly changed after addition of inhibitor.

The EIS results can be interpreted in terms of the equivalent circuit of the electrical double layer shown in Fig. 4, which has been used previously to model the iron/acid interface [15]. The double-layer capacitance and charge transfer resistance were obtained from Nyquist plots. The inhibition efficiencies from EIS results were calculated using the following equation [12]:

$$\eta_z(\%) = \left(\frac{R_{ct} - R^0_{ct}}{R_{ct}}\right) \times 100, \qquad (2)$$

where R^0_{ct} and R_{ct} are the charge transfer resistances in the absence and presence of inhibitor, respectively. The

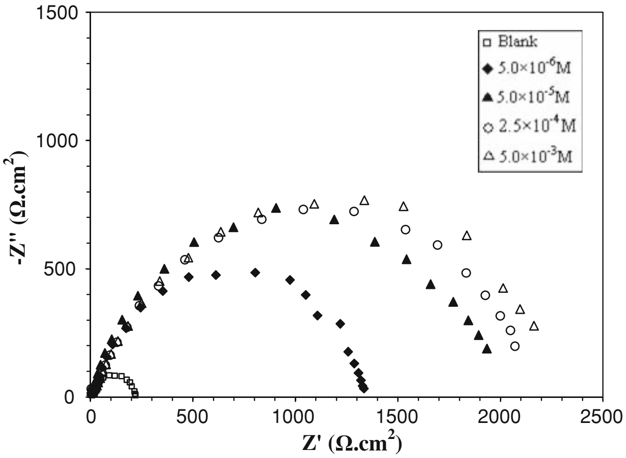

Fig. 3 Nyquist plots for mild steel in 0.1 M HCl in the absence and presence of Basic yellow 13 at various concentrations at 25 °C

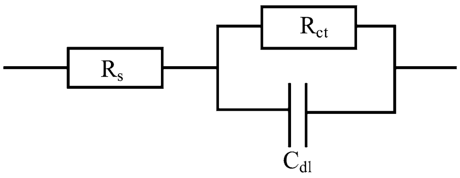

Fig. 4 The electrochemical equivalent circuit for corrosion inhibition of mild steel in 0.1 M HCl using Basic yellow 13

electrochemical parameters derived from the Nyquist plots and the inhibition efficiencies, η_z, are given in Table 2.

It is clear that R_{ct} increases and C_{dl} decreases as the inhibitor concentration increases. The decrease in C_{dl} could be attributed to the adsorption of the inhibitor, forming protective adsorption layer [17].

3.3 Weight loss measurements

The weight loss of steel specimen in uninhibited acid solution and solutions containing different concentrations of the inhibitor was determined during 24-h immersion. The inhibition efficiencies and surface coverage ($\theta = \frac{\eta}{100}$)

Table 2 Electrochemical impedance parameters for mild steel in 0.1 M HCl in the absence and presence of Basic yellow 13 at various concentrations at 25 °C

Inhibitor concentration (M)	R_{ct} (Ω cm^2)	C_{dl} (F cm^{-2})	n	I.E.% (η_z)
Blank	102	6.65×10^{-5}	0.86	–
5.0×10^{-6}	1327	2.66×10^{-6}	0.79	92
5.0×10^{-5}	1839	5.30×10^{-6}	0.86	94
2.5×10^{-4}	2171	1.31×10^{-6}	0.75	95
5.0×10^{-4}	2245	1.38×10^{-6}	0.76	95
5.0×10^{-3}	2560	3.86×10^{-7}	0.68	96

Table 3 Corrosion parameters for mild steel in 0.1 M HCl in the presence and absence of Basic yellow 13 at different concentrations, obtained from weight loss measurements

Inhibitor concentration (M)	Weight loss during 24 h (mg)	Surface coverage (θ)	I.E.% (η_w)
Blank	2.83	–	–
5.0×10^{-6}	0.81	0.71	71
5.0×10^{-5}	0.51	0.82	82
2.5×10^{-4}	0.45	0.84	84
5.0×10^{-4}	0.39	0.86	86
5.0×10^{-3}	0.25	0.91	91

obtained from weight loss method at different concentrations of inhibitor are summarized in Table 3. The η_w% values were calculated using the following equation:

$$\eta_w\% = \left(\frac{w_0 - w}{w_0}\right) \times 100, \tag{3}$$

where w_0 and w are weight losses in the absence and presence of inhibitor, respectively.

These results show that, as the inhibitor concentration increases, the weight loss decreases and therefore, the inhibition efficiency increases. It can be concluded that this inhibitor acts through adsorption on metal surface and formation of a barrier layer between metal and corrosive media. In order to confirm the adsorption of inhibitor on metal surface, the adsorption isotherms were studied. The adsorption isotherms can provide basic information on the interaction of inhibitor and metal surface. In order to obtain adsorption isotherm, the surface coverage values (θ), for different concentrations of Basic yellow 13 in 0.1 M HCl solution have been obtained from weight loss measurements and tested graphically for fitting of a suitable adsorption isotherm. The plot of $C_{(inh)}/\theta$ versus $C_{(inh)}$ (Fig. 5) yields a straight line with correlation coefficient of 1.00 and slope of 1.0962, yielding that the adsorption of Basic yellow 13 from hydrochloric acid solution on mild-steel surface obeys the Langmuir adsorption isotherm presented in Eq. 4.

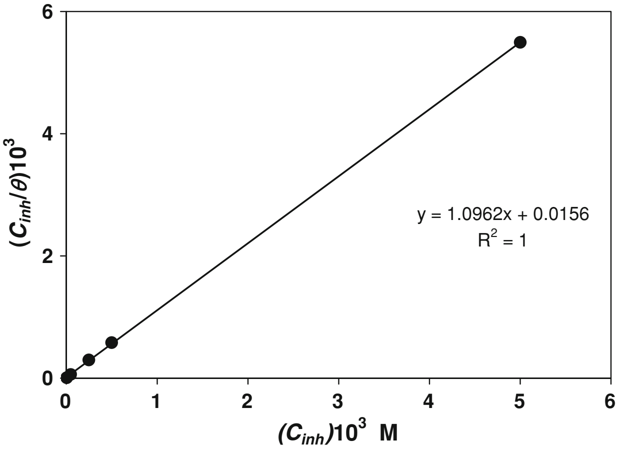

Fig. 5 Langmuir isotherm curve for adsorption of Basic yellow 13 on the steel surface

$$\frac{C_{(inh)}}{\theta} = \frac{1}{K_{ads}} + C_{(inh)}, \tag{4}$$

where $C_{(inh)}$ is inhibitor concentration, θ is the degree of coverage of metal surface, and K_{ads} is the equilibrium constant for adsorption–desorption process. The value of the equilibrium constant, K_{ads}, was calculated from the reciprocal of the intercept of the isotherm line as 6.41×10^4. The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on mild-steel surface. The free energy of inhibitor adsorption on mild-steel surface can be evaluated using the following equation:

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}). \tag{5}$$

From Eq. (5), ΔG_{ads} was calculated as -37.37 kJmol^{-1}. The negative value of ΔG_{ads} indicates spontaneous adsorption of Basic yellow 13 molecules on the mild-steel surface and strong interaction between inhibitor molecules and metal surface. The value of ΔG_{ads} is less than 40 kJmol^{-1}, indicating electrostatic interaction between the charged inhibitor molecules and the charged metal surface, i.e., physical adsorption [18].

Table 4 summarizes the inhibition efficiencies obtained from the different methods and their average values for each concentration of inhibitor with standard deviation in corrosive solution for comparison. It can be seen that there is good agreement between the results obtained from different methods.

4 Conclusion

The inhibition performance of Basic yellow 13 dye was studied using electrochemical and weight loss measurements in acid solution. It was shown that the used dye can

Table 4 Inhibition efficiencies obtained from different methods and their average values

Inhibitor concentration (M)	Polarization η_p (%)	EIS η_z (%)	Weight loss η_w (%)	Average inhibition efficiency η_m (%)
5.0×10^{-6}	81	92	71	81.3 ± 8.5
5.0×10^{-5}	91	94	82	89.0 ± 5.1
2.5×10^{-4}	99	95	84	92.6 ± 6.3
5.0×10^{-4}	99	95	86	93.3 ± 5.4
5.0×10^{-3}	99.5	96	92	95.8 ± 3.1

be a good inhibitor for mild-steel corrosion in acid media; inhibition efficiencies are more than 70% at all studied concentrations and increase as the concentration of inhibitor increases. From polarization measurements, it was found that this compound affects both cathodic and anodic reactions through adsorption on these sites at metal surface; therefore, it is a mixed-type inhibitor. The adsorption of this compound was further investigated for the adsorption type. It was shown that the dye adsorbs on steel surface spontaneously because of the negative value of ΔG_{ads} and obeys Langmuir isotherm. From the value of ΔG_{ads}, which was found to be less than 40 $kJmol^{-1}$, it was deduced that inhibitor molecules have been adsorbed onto steel surface through electrostatic interaction between the charged inhibitor molecules and the charged metal surface, i.e., physical adsorption.

References

1. Oguzie EE, Unaegbu C, Ogukwe CN, Okolue BN, Onuchukwu AI (2004) Mater Chem Phys 84:363
2. Chakrabarty C, Singh MM, Yadav PNS, Agarwal CV (1983) Trans SAEST 18:14
3. Maitra A, Singh G, Chakraborty BB (1983) Trans SAEST 18:335
4. Tang L, Mu G, Liu G (2003) Corros Sci 45:2251
5. Ashassi-Sorkhabi H, Seifzadeh D (2008) J Appl Electrochem 38:1545
6. Ashassi-Sorkhabi H, Seifzadeh D, Hosseini MG (2008) EN, EIS and polarization studies to evaluate the inhibition effect of 3H-Phenothiazin-3-one, 7-Dimethylamin on mild steel corrosion in 1 M HCl solution. Corros Sci 50:3363. doi:10.1016/j.corsci.2008.09.022
7. Bayol E, Gürten T, Gürten AA, Erbil M (2008) Mater Chem Phys 112:624
8. Keleş H, Keleş M, Dehri İ, Serindağ O (2008) Mater Chem Phys 112:173
9. Vishwanatham S, Haldar N (2008) Corros Sci 50:2999
10. Kalman E, Palinkas G (1993) Corros Sci 35:1471
11. Bentiss F, Lagrenee M, Traisnel M, Hornez JC (1999) Corros Sci 41:789
12. Ashassi-Sorkhabi H, Shaabani B, Seifzadeh D (2005) Electrochim Acta 50:3446
13. Lagrenee M, Mernari B, Bouanis M, Traisnel M, Bentiss F (2002) Corros Sci 44:573
14. Şahin M, Bilgic S, Yilmaz H (2002) Appl Surf Sci 195:1
15. El Azhar M, Mernari B, Traisnel M, Bentiss F, Lagrenee M (2001) Corros Sci 43:2229
16. Ashassi-Sorkhabi H, Mjidi MR, Seyyedi K (2004) Appl Surf Sci 225:176
17. Hassan HH, Abdelghani E, Amin MA (2007) Electrochim Acta 52:6359
18. Solmaz R, Kardas G, Yazici B, Erbil M (2008) Colloids Surf A Physicochem Eng Asp 312:7