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ORIGINAL PAPER

Piperazine derivatives as inhibitors of the corrosion of mild steel in 3.9 M HCl

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Abstract The inhibitory action of two piperazine derivatives, 1-benzyl piperazine (P1) and *bis*(1-benzylpiperazine) thiuram disulfide (P2) on the corrosion of mild steel in 3.9 M HCl at different concentrations has been investigated in the temperature domain 298–333 K. Both weight loss measurements and potentiodynamic polarization methods showed that P2 was the best inhibitor and that its inhibition efficiency increased with concentration to a value >92% at 10^{-3} M. Potentiodynamic polarization studies clearly revealed that P2 acts as cathodic-type inhibitor. The activation energy for the corrosion rates was evaluated in the temperature range 298–333 K. Adsorption of P2 on the mild steel surface in 3.9 M HCl followed a Langmuir isotherm model. A physical adsorption phenomenon is proposed.

Keywords Corrosion · Inhibition · Piperazine · Carbon steel

1 Introduction

To remove undesirable scale, metal objects may be treated in acid pickling baths. The desired function of the acid is scale removal without attack on the metal itself and for this reason corrosion inhibitors are added to the acid solution. A common pickling medium is aqueous HCl at concentrations from 5 to 15 mass% (1.4–4.4 M) and at temperatures up to 60 °C [1]. We have chosen to investigate 3.9 M HCl (13.4% HCl) as an aggressive solution with the same acidity function (−1.9) as 5.5 M H_3PO_4 and 3.2 M H_2SO_4 [2–5]. The selection of appropriate inhibitors mainly depends on the type of acid and its concentration, temperature, and on the nature of the metal [6–8]. In general, organic compounds containing polar groups including nitrogen, sulfur, and oxygen, and heterocyclic compounds with polar functional groups and/or conjugated double bonds [9–11] have been reported to inhibit steel corrosion. Inhibition by these organic compounds is usually attributed to their interaction with the metal surface via adsorption, either physisorption or chemisorption involving coordinate bond formation [1, 12].

Organic compounds containing the dithiocarbamate group have been used as pesticides and rubber additives. They have received a deal of attention as radical polymerisation catalysts, because stable dithiocarbamate radicals can be generated thermally or by UV activation. A very extensive coordination chemistry is known for dithiocarbamates and many of the complexes have unique properties, iron dithiocarbamates, for example, being the basis of one of the very few methods available to study the formation of nitric oxide (NO) radicals in biological materials [13]. Dithiocarbamates can be oxidised readily to thiuram disulfides, which in turn can be reduced by metals to give dithiocarbamate complexes, a reaction which is presumably possible on an iron surface as involved in the present work. Previous work has shown that piperazine derivatives can be effective inhibitors of mild steel corrosion [14–16]. The present work is aimed to investigate the inhibition effect of 1-benzyl piperazine (P1) and *bis*(1-benzylpiperazine) thiuram disulfide (P2) on the corrosion of mild steel in

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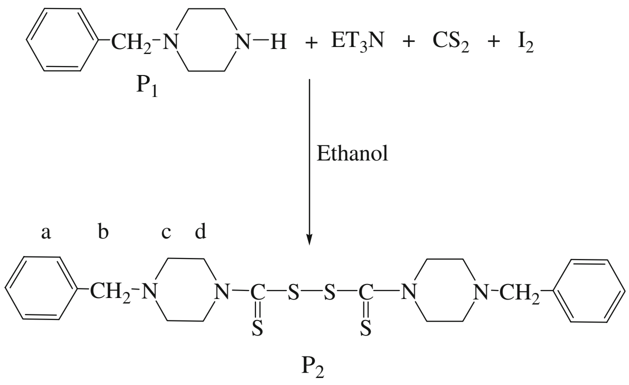
3.9 M HCl using both weight loss and potentiodynamic polarization methods.

2 Experimental

The compound P2 was synthesised from commercially available P1 according to the following procedure as described elsewhere [17]. CS_2 (1.8 g; 2.28×10^{-2} mol) was added to a vigorously stirred, cold (<5 °C) solution of 1-benzylpiperazine (2.1 g; 2.30×10^{-2} mol) and triethylamine (2.3 g; 2.30×10^{-2} mol) in ethanol (20 mL) and the stirring and cooling continued for 1 h. To oxidise the dithiocarbamate thus formed to the corresponding thiuram disulfide, I_2 (2.8 g) was then added in portions, complete discharge of the colour being awaited after each addition. Finally, methanolic I_2 was added dropwise until a yellow colour persisted. The salt, dithiocarbamate, is oxidized to the corresponding thiuram disulfide. The excess of iodine was neutralized with a solution of $Na_2S_2O_3$ (10% by weight). The mixture was then cooled and thiuram disulfide precipitate was filtered and allowed to dry. The solid compound obtained (P2) was yellow in colour, and soluble in organic solvents such as CH_2Cl_2 and $CHCl_3$. Yield: 3.70 g (80%); m.p = 136 °C. ^{1}H-NMR in $CDCl_3$ (δ ppm). 7.3 (10Ha); 4.27 (4Hb); 3.54 (4Hc), 2.59 (4Hd); the Hc and Hd are coupled. IR: max/cm^{-1} 1280–1190 (NCSS). The chemical structures of the inhibitors are shown in Scheme 1.

The mild steel samples (0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron) were polished with emery paper up to 1200 grade and then washed with double-distilled water and degreased with AR grade ethanol.

Weight loss experiments were carried out in a thermostatted double-walled glass cell. The solution volume was 100 mL. The mild steel specimens used had a rectangular form (2.5 cm × 2 cm × 0.05 cm). The immersion time for the weight loss was 4 h at all temperatures in the range 298–333 K. After the corrosion test, the specimens of mild steel were carefully washed in double-distilled water, dried and then weighed. Duplicate experiments were performed in each case and the mean value of the weight loss is reported.



Scheme 1 Molecular structure of the 1-benzyl piperazine (P1) and *bis*(1-benzyl piperazine) thiuram disulfide (P2)

Electrochemical measurements were carried out in a conventional three-electrode, cylindrical Pyrex glass cell with a capacity of 1000 mL. The working electrode (WE) in the form of disc cut from mild steel had a geometric area of 1 cm^2 and was embedded in polytetrafluoroethylene (PTFE). A saturated calomel electrode (SCE) and a platinum disc electrode were used, respectively, as reference and auxiliary electrodes. The temperature was thermostatically controlled at 308 ± 1 K. The WE was abraded with silicon carbide paper (grade P1200), degreased with AR grade ethanol and acetone, and rinsed with double-distilled water before use. All potentials are reported versus SCE.

Potentiodynamic polarisation experiments were conducted using an EG&G Potentiostat–Galvanostat (model 263A), coupled to a computer equipped with the software 352 Soft Corr™ III. The potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from −800 to −100 mV at a scanning rate of 1 mV s^{-1}. Before measurement, the working electrode was immersed in the test solution at the natural potential (open circuit potential) for 30 min, in which time a steady state was reached. The WE was polarized at −800 mV for 10 min in order to remove oxide film from the electrode. The linear Tafel segments of the anodic and cathodic curves were extrapolated to the corrosion potential to obtain the corrosion current densities (i_{corr}). De-oxygenation of the test solution with pure nitrogen was carried out prior to starting the polarization measurements. Each test was run in duplicate to verify the reproducibility and the average values are reported.

3 Results and discussion

3.1 Weight loss tests

Figure 1 shows the values of the inhibition efficiencies (E_W) and corrosion rates obtained from the weight loss method at different concentrations of P1 and P2 in 3.9 M HCl after 4 h. E_W (%) was calculated from the following equation:

$$E_w\% = \frac{W_{corr} - W_{corr}^{inh}}{W_{corr}} \times 100 \tag{1}$$

where W_{corr} and W_{corr}^{inh} are the corrosion rates of mild steel in the absence and presence of the inhibitor, respectively.

The corrosion rate was found to decrease with increasing concentrations of P1 and P2, i.e. these compounds inhibit the corrosion of mild steel and consequently E_w (%)

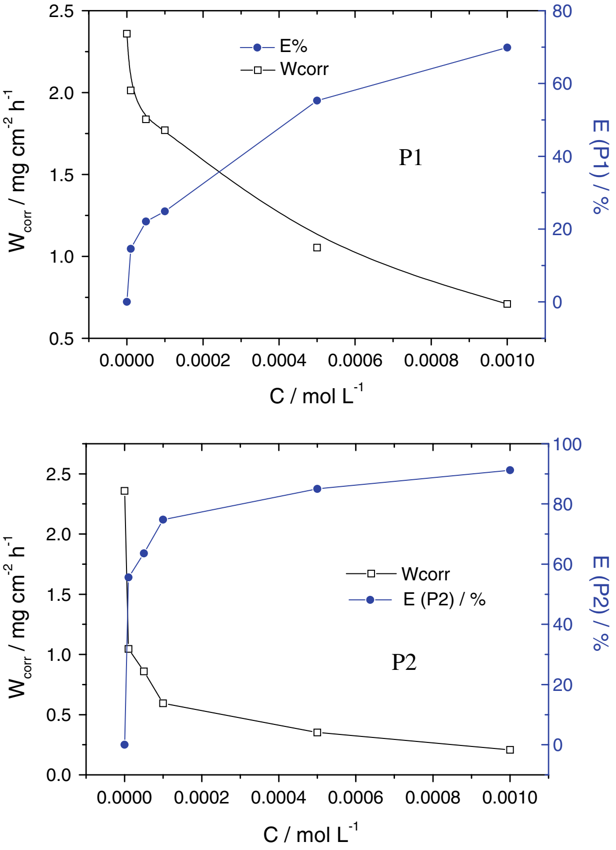


Fig. 1 Variation of corrosion rate and efficiency of P1 and P2 against of the inhibitor concentration

increases with increasing inhibitor concentration. The maximum values of E_W were 69.9 and 91.2% for P1 and P2 at 10^{-3} M, respectively. The good inhibitory effect of P2 in comparison to P1 may explained by the doubled molecular area and molecular weight. Thus one can suggest that the presence of N–(C=S)–S and (C–S–S–C) increases the inhibiting effectiveness of P2. A detailed study of P2 was then conducted.

3.2 Polarization measurements

Polarisation characteristics of mild steel in 3.9 M HCl with different concentrations of P2 at 308 K are shown in Fig. 2.

Corresponding electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) and the calculated E_i (%) are collected in Table 1. In this case the inhibition efficiency is defined as follows:

$$E_i\% = \frac{i_{corr} - i_{corr}^{inh}}{i_{corr}} \times 100 \qquad (2)$$

where i_{corr} and i_{corr}^{inh} are the corrosion current density values without and with the inhibitor, respectively, determined by extrapolation of the cathodic Tafel lines to the corrosion potential.

It is clear that the addition of P2 decreases the cathodic current density and then the reduction of hydrogen ion is limited. At 10^{-3} M, the value of i_{corr} is small and thus E_i (%) attains its maximum inhibition efficiency (90%). Also, the addition of P2 shifts E_{corr} to more negative values. The Tafel plot cathodic slopes decrease to lower values, indicating that the mechanism of hydrogen evolution is affected in the presence of P2.

In the anodic domain (Fig. 2), it seems that P2 has no effect on the current density. This result indicates that P2 acts preferentially as a cathodic inhibitor.

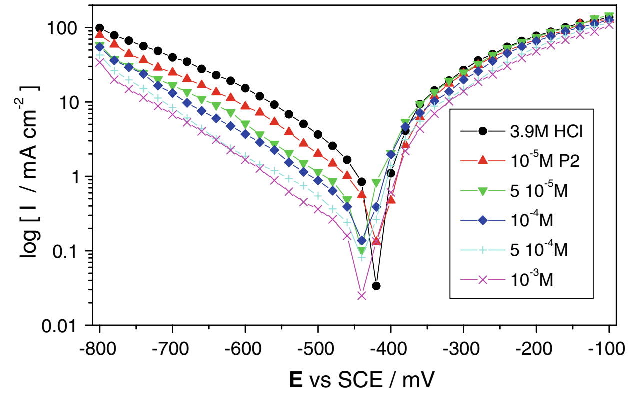


Fig. 2 Polarization curves of mild steel in 3.9 M HCl at various concentrations of P2

Table 1 Polarization parameters for mild steel in 3.9 M HCl in the presence and absence of P2

Inhibitor	C/M	E_{corr} versus SCE (mV)	β_C (mV dec^{-1})	I_{corr} (µA cm^{-2})	E (%)
Blank	3.9	−407	228	1354.1	–
P2	10^{-5}	−426	246	621.1	54.1
	5×10^{-5}	−436	256	473.5	65.0
	10^{-4}	−435	207	323.5	76.1
	5×10^{-4}	−438	185	177.3	87.1
	10^{-3}	−442	153	135.7	90.0

3.3 Effect of temperature

The effect of temperature (298–333 K) on the corrosion behaviour of mild steel in the presence and absence of P2 at 10^{-3} M in 3.9 M HCl was studied using the weight loss method for a 4 h reaction period (Table 2). Both in the absence and presence of P2 the corrosion rate of mild steel increases with temperature. The inhibition efficiency of P2 decreases with temperature to reach a value of only 24% at 333 K. The activation energies for the corrosion process were calculated from the Arrhenius equation:

$$W = A\exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where E_a represents the apparent activation energy, R the gas constant, T the absolute temperature, A the pre-exponential factor and W the corrosion rate, obtained from the weight loss method.

Arrhenius plots for the corrosion rate of mild steel are given in Fig. 3. Values of E_a for mild steel in 3.9 M HCl in the absence and presence of various concentrations of P2 were determined from the slopes of ln W versus 1/T plots. $R = 0.996$.

Table 2 Effect of temperature on the corrosion of mild steel in HCl and HCl + 10^{-3} M P2 after 4 h

T (K)	W (mg cm^{-2} h^{-1})	W′ (mg cm^{-2} h^{-1} P2)	E (%)
298	2.359	0.208	91.2
303	3.531	0.4	88.7
308	6.001	0.925	84.6
313	7.747	1.997	74.2
318	11.378	4.151	63.5
323	14.694	8.301	43.5
333	26.398	20.122	23.7

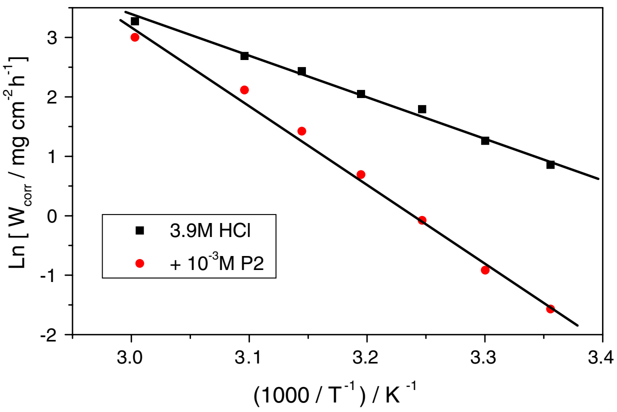


Fig. 3 Arrhenius plots of steel for 10^{-3} M of P2 in 3.9 M HCl

The value of E_a in the absence of an inhibitor (56.7 kJ mol^{-1}) in 3.9 M HCl agrees well with literature data on E_a for iron and mild steel in hydrochloric acid, which are in the range 58–88 kJ mol^{-1}. In the presence of P2, E_a is 112.0 kJ mol^{-1}.

It is clear from this study that the values of E_a in the presence of P2 are higher than those for the uninhibited acid solution. Previous studies have shown that, while chemisorption of an inhibitor leads to a decrease in activation energy, physisorption is associated with an increase [18–20]. We therefore conclude that P2 exerts its effects through physisorption on the surface. It retards corrosion at lower temperature but its inhibition effect diminishes at elevated temperatures.

3.4 Adsorption isotherm

The θ values for different inhibitor concentrations (P2) were tested by fitting to various isotherms. According to this isotherm, the surface coverage θ is related to the equilibrium adsorption constant k_{ads} and concentration of inhibitor C by the rearranged Langmuir equation [21]:

$$\frac{C}{\theta} = \frac{1}{k_{ads}} + C \tag{4}$$

The standard adsorption free energy $\left(\Delta G^{\circ}_{ads}\right)$ was obtained by the relation:

$$k_{ads} = \frac{1}{55.5}\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \tag{5}$$

where 55.5 is the concentration of water in solution expressed in mol L^{-1}.

The best fit was obtained with the Langmuir isotherm (Fig. 4), the slope is close to unity (1.08) with $R = 0.9995$. The deduced value of ΔG°_{ads} obtained (-36.5 kJ mol^{-1}) is negative and means that the adsorption of P2 is a spontaneous process, and furthermore the negative values of

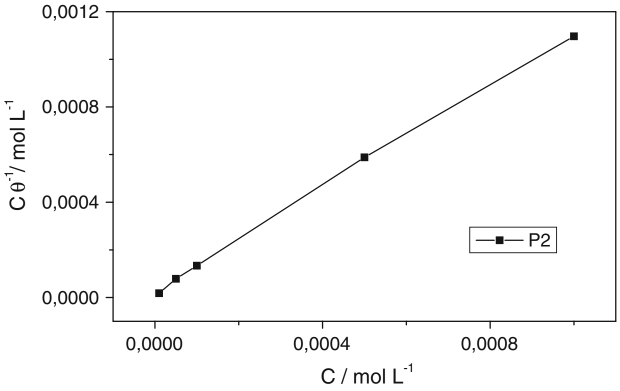


Fig. 4 Langmuir adsorption isotherm of P2 on steel surface in 3.9 M HCl

ΔG°_{ads} also show the strong interaction of the inhibitor molecule with the surface [22, 23].

It is well known that values of ΔG°_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). Those more negative than -40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate bond (chemisorption) [24, 25]. The calculated ΔG°_{ads} value in our case indicates, therefore, consistent with deductions based on the corrosion rates, that the adsorption mechanism of the P2 on mild steel in 3.9 M HCl solution was one of physisorption.

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References

1. Schmitt G (1984) Br Corros J 19:165
2. Elouafi M, Abed Y, Hammouti B, Kertit S (2001) Ann Chim Sci Mat 26:79
3. Hammouti B, Oudda H, El Maslout A, Benayada A (2001) Abhath Al-yarmouk: Basic Sci Eng 10:273
4. Babalé DD, Wandji R, Bessière J (1990) J Chem Eng Data 35:345
5. Hammouti B, Bekkouch K, Kertit S (1998) Bull Electrochem 14:49
6. Quraishi MA, Rawat J, Ajmal M (2000) J Appl Electrochem 30:745
7. Hammouti B, Aouniti A, Taleb M, Brighli M, Kertit S (1995) Corrosion 51:411
8. Tebbji K, Aouniti A, Benkaddour M, Oudda H, Bouabdallah I, Hammouti B, Ramdani A (2005) Prog Org Coat 54:170
9. Huynh N, Bottle SE, Notoya T, Trueman A, Hinton B, Schweinsberg DP (2002) Corros Sci 44:1257
10. Khitrov VA, Zadorozhnyi VP, Smolyaninov IS, Zhukova GP, Dugin NA, Ya Konyaev B (1964) Khim Prom 4:307
11. Levin IA, Solomon EM (1963) Khim Prom 1:69
12. Suroor Athar SM, Ali H, Quraishi MA (2001) Anti-Corros Methods Mater 48:251
13. Vanin AF, Huisman A, van Faassen EE (2002) Methods Enzymol 359:27
14. Babić-Samardžija K, Khaled KF, Hackerman N (2005) Anti-Corros Methods Mater 52:11
15. Babić-Samardžija K, Khaled KF, Hackerman N (2005) Appl Surf Sci 240:327
16. Bereket G, Ögretir C, Özahin Ç (2003) J Mol Struct Theochem 663:39
17. Thom GD, Ludwig RA (1962) The dithiocarbamates and related compounds. Elsevier, Amsterdam
18. Tebbji K, Faska N, Tounsi A, Oudda H, Benkaddour M, Hammouti B (2007) Mater Chem Phys 106:260
19. Herrag L, Chetouani A, Elkadiri S, Hammouti B, Aouniti A (2008) Port Electrochim Acta 26:211
20. Popova A (2007) Corros Sci 49:2144
21. Langmuir I (1947) J Am Chem Soc 39:1848
22. Elachouri M, Hajji MS, Salem M, Kertit S, Aride J, Coudert R, Essassi E (1996) Corrosion 52:103
23. Ali SA, Al-Muallem HA, Saeed MT, Rahman SU (2008) Corros Sci 50:664
24. Khaled KF (2008) Electrochim Acta 53:3484
25. Kaddouri M, Cheriaa N, Souane R, Bouklah M, Aouniti A, Abidi R, Hammouti B, Vicens J (2008) J Appl Electrochem 38:1253