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Thermodynamic characterisation of steel corrosion and inhibitor adsorption of pyridazine compounds in 0.5 M H_2SO_4

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Abstract

The influence of 5-(2-chlorobenzyl)-6-methylpyridazine-3(2*H*)-thione (P_1) and 5-(4-chlorobenzyl)-6-methylpyridazine-3(2*H*)-thione (P_2) on the corrosion of steel in 0.5M H_2SO_4 solution has been studied using weight loss measurements at various temperature. The inhibiting action is more pronounced with P1 than P2. The inhibition efficiency increases with P1 concentration to attain the maximum value of 100% at 5×10^{-4} M. P1 adsorbs on the surface of steel according to the Langmuir isotherm model. The thermodynamic data of activation and adsorption are determined.
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1. Introduction

Nowadays the search for new and efficient corrosion inhibitors has become a necessity to secure metallic materials against corrosion. The effectiveness of organic compounds containing sulphur as corrosion inhibitors for steels in sulphuric acid is well developed [1–7]. The adsorption of inhibitors takes place through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bounds or aromatic rings. The inhibition efficiency should increase in the order O<N<S<P [8].

Past studies have examined the relationship between the structure of the inhibitor molecule and its efficiency but much less attention has been paid to the dependence of the protection efficiency on the size of the inhibitor molecule and the electronic distribution in the inhibitor molecule.

The development of corrosion inhibitors is based on organic compounds containing nitrogen, oxygen, sulphur atoms, and multiple bonds in the molecules that facilitate adsorption on the

metal surface. The corrosion inhibition efficiency of organic compounds is related to their adsorption properties. Adsorption depends on the nature and the state of the metal surface, on the type of corrosive medium and on the chemical structure of the inhibitor [4]. Studies report that the adsorption of organic inhibitors mainly depends on some physicochemical properties of the molecule, related to its functional groups, to the possible steric effects and electronic density of donor atoms; adsorption is suppose also to depend on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, which induce greater adsorption of the inhibitor molecules onto the surface of carbon steel, leading to the formation of a corrosion protecting film [9].

Pyridazine derivatives containing sulphur atom offer good inhibitory effect of the corrosion of steels in acidic media [10–12]. The choice of pyridazine compounds is based on their much known pharmaceutical application in inhibiting aldose reductase and exhibiting antioxidant properties [13,14] and the presence of two nitrogen atoms in pyridazine ring with various substituents.

In the present work, we investigate the corrosion of steel in 0.5 M H_2SO_4 by some newly synthesised pyridazine compounds Fig. 1, and observe any relation between molecule
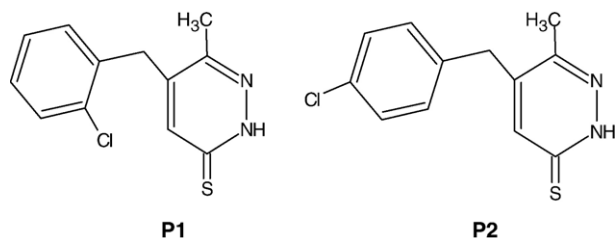

Fig. 1. Molecular structure of 5-(2-chlorobenzyl)-6-methylpyridazine-3(2*H*)-thione (P$_1$) and 5-(4-chlorobenzyl)-6-methylpyridazine-3(2*H*)-thione (P$_2$).

structure of these pyridazines and their inhibitive action. Weight loss measurements have been used to study the effect of addition of these compounds on the corrosion of steel in sulphuric acid solution.

2. Experimental

The pyridazine compounds were synthesised according to the method of Taoufik et al. [15] and Delmasure and Lasserre [16], purified and characterised by N.M.R and I.R. spectroscopies and element analysis before use. The molecular structures of new pyridazines studied are shown in Fig. 1.

Prior to all measurements, the steel samples (0.21% C; 0.38% Si; 0.09% P; 0.01 %Al; 0.05% Mn; 0.05% S and the remainder iron) were ground with different emery paper up to 1200 grade, washed thoroughly with bidistilled water degreased and dried with acetone.

The aggressive solution (0.5 M H$_2$SO$_4$) was prepared by dilution of analytical grade 98% H$_2$SO$_4$ with bidistilled water.

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 60 cm^3. The steel specimens used had a rectangular form (2×2×0.05 cm).

3. Results and discussion

The effect of addition of pyridazine compounds tested at different concentrations on the corrosion of steel in 0.5 M H$_2$SO$_4$ solution was studied by weight-loss at 298 K after 6 h of immersion period. Inhibition efficiency (E$_w$%) is calculated as follows:

$$E_w\% = \left(1 - \frac{W_{corr}}{W_{corr}^{\text{\o}}}\right)100 \tag{1}$$

W_{corr} and W_{corr}^{o} are the corrosion rates of steel with and without organic compound, respectively.

Table 1 regroups the results of weight loss of steel in 0.5 M H$_2$SO$_4$ with and without the addition of various concentrations of the pyridazine compounds. It is clear that the corrosion rate decreases with the concentration of pyridazine compounds tested. The influence of P1 is hugely marked and the corresponding efficiency increases with P1 concentration to attain its maximum 100% at 5×10^{-4} M. Then P1 is the best inhibitor and a detailed study in function of temperature is conducted to evaluate the thermodynamic data and the adsorption isotherm model.

The protective properties of such compounds are probably due to the interaction between π-electrons of the pyridazine and phenyl rings with positively charged steel surface. The sulphur and nitrogen

Table 1
Gravimetric results of the steel corrosion in 0.5 M H$_2$SO$_4$ at various concentrations of P$_1$ and P$_2$ at 298 K at 6 h

Concentration (M)		W_{corr} (mg/cm^2 h)	$E_W\%$
0.5 M H$_2$SO$_4$		1.608	–
P$_1$	5×10^{-4}	0.006	100
	2.5×10^{-4}	0.049	97
	10^{-4}	0.130	92
	7.5×10^{-4}	0.219	86
	5×10^{-5}	0.662	59
	10^{-5}	1.802	−12
	5×10^{-6}	1.838	−14
P2	5×10^{-4}	0.890	45
	2.5×10^{-4}	0.984	39
	10^{-4}	1.456	9
	7.5×10^{-4}	1.611	0
	5×10^{-5}	1.753	−9
	10^{-5}	1.754	−9.1
	5×10^{-6}	1.759	−9.4

atoms are the adsorption centers for their interaction with the metal surface [17]. The hump in E% observed in P1 and P2 may be explained by the presence of the chloride atom which is in *ortho* and *para* position in benzyl substituent. This phenomenon is discussed by Popova et al. in their recent work [3] in attempting to explain adsorption of molecules with *ortho*, *meta* and *para* substituents by Hammett equation. An anomalous behaviour of the *ortho* substituent called *ortho*-effect is observed. They concluded that the *ortho*-effects are expected to hamper the chemisorption to a greater extent than the physical adsorption.

In our study the same phenomenon is encountered and we may conclude that the presence of Cl in *ortho*-position in the molecule reinforces the adsorption compared to that in *para* position.

3.1. Effect of time

Fig. 2 shows the effect of increasing time on the weight loss of carbon steel in uninhibited and inhibited acid solutions. It is obvious that the weight loss varied linearly with immersion period. The curves obtained in presence of the additive fall significantly below that of free acid. The linear variation of weight loss with time in plain acid and inhibited acid indicates the absence of insoluble surface films during corrosion. The relatively large divergence of the plots indicates the
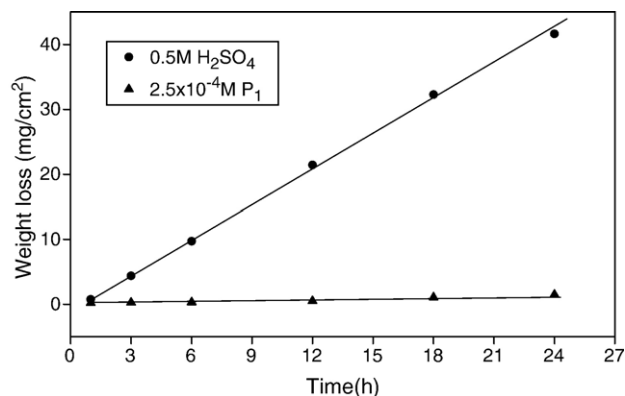

Fig. 2. Weight loss as a function of time of the steel in free acid and added of 2.5×10^{-4} M P$_1$.