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Mercaptopyrimidines as inhibitors of carbon dioxide corrosion of iron

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Abstract

The inhibition activity of 2-mercaptopyrimidine (**I**), 2-mercapto-4-methylpyrimidine hydrochloride (**II**), 2-mercapto-4,6-dimethylpyrimidine (**III**) and its hydrochloride (**IV**) upon carbon dioxide corrosion of iron has been studied in a wide range of concentrations at 40–90 °C using electrochemical and mass-spectrometry methods. High activity has been found for all compounds ($P = 80$–99%) at very low concentrations (0.02–5 mg/l). Adsorption of inhibitor by metal not only blocks its surface but changes the reaction mechanism as well. Charge transfer is the limiting stage of both cathode and anode reactions. The title compounds can be considered as inhibitors of what is a mixed type with prevailing effect on the anode reaction.

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1. Introduction

Till date a range of heterocyclic compounds (thiaaza-, oxaaza-, diaza- and triaza-five-membered cyclic compounds) have been studied as corrosion inhibitors of different metals [1,2]. Pyrimidines (methadiazines), however, have hardly been studied in spite of their ease of availability. Some pyrimidine derivatives, in particular mercaptopyrimidines are promising with respect to their corrosion inhibition properties [3–12]. For example, high inhibition efficiency is shown for 2-mercaptopyrimidines against corrosion of copper and its alloys in NaCl solution [9,10]. Patented is the usage of 2,4-diamino-6-mercaptopyrimidine sulfate [3], 2-mercapto-*N*-alkylhexahydro-pyrimidines [4], 4-amino-6-methoxypyrimidine [5], *N*,*N*′-dialkylhexahydropyrimidines [6], *N*-(5-butylfurfurylidene-2-)-(5′-oxypyrimidinyl-2′-)sulfanylamide [7] as corrosion inhibitors of metals. As to CO_2 corrosion of iron, various classes of heterocyclic compounds were tested for example: oxyethylated amines [13], polyamines [14], imidazolines [15–18]. All these compounds had inhibiting activity at concentrations equal 5–100 mg/l.

In spite of numerous studies [19–32], the mechanism of the iron CO_2 corrosion is still not clear, the reason being in high variability of the Fe–CO_2–brine system. Small variations in temperature, pH, CO_2 content change ion ratio of charged particles in solution [19–23,30,32]. The variability of these conditions at different fields, ecology requirements dictate the necessity of new inhibitors active at low concentrations.

The present paper presents the results on the activity of the following four mercaptopyrimidines against the carbon dioxide corrosion of iron:

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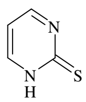
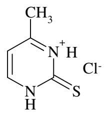
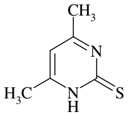


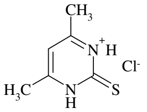
Compound **I**:
2-mercaptopyrimidine



Compound **II**:
2-mercapto-4-methylpyrimidine hydrochloride



Compound **III**:
2-mercapto-4,6-dimethylpyrimidine



Compound **IV**:
2-mercapto-4,6-dimethylpyrimidine hydrochloride

2. Experimental

Corrosion tests were carried out in a 1 l glass cell with three similar iron electrodes Pattern 44-1018MS of 30.7 mm length and 4.7 mm diameter, being used in turn during subsequent experiments. Platinum mesh and saturated silver/silver-chloride electrodes were used as counter electrode and reference electrode, respectively. Before each experiment working electrodes were treated with abrasive paper (1200 grit SiC), etched with 10% HCl solution during 10 min, washed with distilled water, then acetone and dried by warm air, immediately afterwards placed into the cell.

Two synthetic brines were used for experiments based on the ASTM D1141-90 standard (Table 1). The solution was magnetically stirred at a speed of 500 rpm. Carbon dioxide was bubbled through the solution at a rate of 80 ml/min. Upon the saturation with carbon dioxide the pH of the brine was found to be 5.3. Experiments were carried out at 40–90 °C, temperature being controlled within ±1 °C. The time of the introduction of electrodes was counted from the point when the equilibrium distribution of ions and hydrated particles, formed upon dissolution of CO_2, was reached, the equilibrium being controlled via the stability of the pH values.

Field machine ICM instruments was used for tests, pH values were measured by a pH-meter HI 9025 Hanna Instruments. Compounds **I** (98%) and **II** (99%) were purchased from Lancaster Synthesis. Compounds **III** and **IV** were synthesized following a previously published procedure [33]. The purity of the product (98%) was checked by mass-spectrometry.

Table 1
Composition of brines

Electrolyte	Concentration (g/l)	
	Brine 1	Brine 2
NaCl (98.8%)	34	24.5
KCl (98.3%)	0.4	0.66
$NaHCO_3$ (98%)	1.26	0.2
$MgCl_2$ (98.5%)		5.2
$CaCl_2$ (98.3%)		1.16
Na_2SO_4 (98.3%)		4.09

2.1. Determination of the inhibition activity

Linear polarization resistance (LPR) was measured after the introduction of electrodes in the cell at an interval of 0.5 h (±-6mV respective to corrosion potential, scan rate of the potential being equal to 0.3 mV/s).

Two types of experiments were carried out:

- an inhibitor was introduced into the brine after the introduction of electrodes, when the stable LPR values were achieved – (brine).
- an inhibitor was introduced into the before the introduction of electrodes – ($\text{brine}_{\text{ing}}$).

The polarization resistance values were transferred into corrosion rate (mmpy) using Eq. (1):

$$U_{\text{cor}} = \frac{0.016 \cdot b_a \cdot b_c}{2.3 \cdot (b_a + b_c) \cdot R_{\text{p}}} = \frac{B}{R_{\text{p}}} \tag{1}$$

where b_a and b_c – Tafel coefficients obtained graphically from potentiodynamic curves, R_{p} – polarization resistance.

Inhibition efficiency of tested compounds was calculated from electrochemical experiment data:

$$\text{IE } (\%) = \frac{100 \cdot [U_{\text{cor}}(0) - U_{\text{ing}}(t)]}{U_{\text{cor}}(0)} \tag{2}$$

and value of protection coefficient γ was calculated in accordance with:

$$\gamma = \frac{U_{\text{cor}}(0)}{U_{\text{cor}}(t)} \tag{3}$$

where U_{cor} (0) and $U_{\text{ing}}(t)$ – corrosion rates without inhibitor and time t after its introduction. Potentiodynamic curves obtained for iron electrode in the brine showed no Tafel dependence in anode region up to +200 mV respective to corrosion potential (Fig. 1). Eq. (1) overestimates corrosion rates giving the values of 13–26 mm/year at 40 °C in comparison with 2–2.2 mm/year at 40 °C and 5–7 mm/year at 80 °C, determined by the gravimetric method. This is explained by the fact that Eq. (1) is derived from the supposition of Tafel dependence of the current on potential in anode and cathode regions in the proximity of corrosion potential.

Successive recording of potentiodynamic curves with 6 h intervals showed the decrease of the corrosion rate after 16 h of experiment. The time dependence of the B value in formula (1) is probably connected with the accumulation of insoluble corrosion products on the electrode surface, as well as with the increase of the iron ions in the brine.

At low concentrations of inhibitor in solution (less than 0.5 mg/l) and the brine without inhibitor corrosion rate was occasionally determined by gravimetric method besides the electrochemical measurement. In order to do this one of the electrodes being kept during the whole experiment at the corrosion potential was used for weight loss determination. For concentrations of inhibitor in solution more than 1 mg/l such measurement were not carried

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