INHIBITORY EFFECTS OF SOME HETEROCYCLIC DERIVATIVES OF MERCAPTANS, CORRELATED TO THEIR ACIDITY EXPRESSED AS A PROTON LEVEL, J

By

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A quasipotentiostatic polarization method has been applied for study of the inhibitory effects of some heterocyclic dervatives of mercaptans on the corrosion behaviour of pure copper in deaerated solutions containing chloride ions. This study showed the inhibitory effectiveness to be a function of the acidity of the inhibitor, expressed as a proton level, J.

Introduction

The corrosion of copper is a common problem; it is frequently encountered in cooling systems that use hard water containing soluble chlorides. The inhibition of copper corrosion in similar media has been investigated with the use of some organic inhibitors [1—3]. Among the organic inhibitors applied for the inhibition of copper corrosion in acetic and chloroacetic acid solutions, 2-Mercaptobenzothiazole (2-MBt) proved to be an excellent inhibitor [4]. In connection with the inhibition of the corrosion of pure copper in neutral solutions containing chloride ions, our aim was to study the relative inhibitory effects of some heterocyclic derivatives of mercaptans by means of a quasipotentiostatic polarization method, and also to examine whether the relative inhibitory effects of the investigated inhibitors were related to their acidity.

Experimental

Cylindrical copper electrodes, made from high-purity copper rods supplied by Johnson Matthey Ltd., were used for the electrochemical investigations. The electrodes were abraded with 600 emery paper, degreased with acetone, washed with a jet of tap water, and finally rinsed with distilled water. The inhibitors investigated were selected from those previously applied for the inhibition of the corrosion of 316 L stainless steel [5].
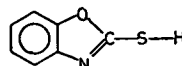
The selected inhibitors were 2-mercaptobenzimidazole (2-MBi), 2-mercaptobenzothiazole (2-MBt), and 2-mercaptobenzoxazole (2-MBo). These were chosen because of the similarity of their chemical structures, which are shown in Table I.
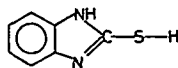
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Table I

Chemical structures of the investigated inhibitors
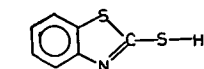
2-Mercaptobenzothiazole

2-Mercaptobenzoxazole

2-Mercaptobenzimidazole

The inhibitory effectiveness was determined at a constant concentration of 10^{-3} mol dm^{-3} in deaerated solution containing 0.10 mol dm^{-3} of Cl$^-$ ions. The chosen inhibitor was dissolved in methanol so that 50 cm^3 of the prepared solution gave the desired concentration, when diluted to 1 dm^3. The neutral chloride solution without inhibitor contained the same amount of methanol.

In the case of **2-MBt** the inhibitory effects was also determined in a slightly acidic solution (pH=4). The experiments were conducted in the same electrolytic cell as used in our previous investigations. [5]. Prior to the electrochemical measurements, deaeration was accomplished by bubbling highly-purified nitrogen gas through the solution. A nitrogen atmosphere was maintained during the measurements by passing nitrogen gas above the solution. The measurements were made at 25 ± 1 °C. The polarization experiments were performed with a PRT—100—1X Tacussel Potentiostat. The electrodes were polarized from the stationary potentials in the noble direction at a scanning rate of 25 mV/5 min (0.30 V/hr). Though the electrode potentials were measured with respect to the saturated calomel electrode, here they are given with respect to the normal hydrogen electrode.

Results and discussion

In the absence of inhibitors, both in slightly acidic (pH=4) and in neutral (pH=7) chloride solutions, copper was found to exhibit only general corrosion. No pitting corrosion was observed, up to 500 mV. This was also checked after the completion of the electrochemical measurements under a magnifying microscope. Copper exhibited active anodic dissolution at low electrode potentials, in agreement with the results found by TAYLOR ET AL [6]. The Tafel slope established in the active domain was found to be equal to 60 mV, a value close to that found by KISS ET AL [7]. Copper initially dissolves in chloride solutions as monovalent copper [8—11]. Figure 1 shows the quasipotentiostatic polarization curves of pure copper in slightly acidic chloride solutions in the absence and in the presence of **2-MBt**.

Similarly, in slightly acidic (pH=4) chloride solutions in the presence of **2-MBt**, copper was found to exhibit only general corrosion. This was checked after the completion of the electrochemical measurements, using the magnifying microscope. The electrodes were found to be unpitted. In the presence of **2-MBt**, as it can be seen from

Fig. 1, the anodic dissolution of copper was significantly depressed. The anodic Tafel slope in the presence of **2-MBt** was found to be equal to 75 mV.

The inhibitory effect of **2-MBt** proved to be better at pH = 7 than at pH = 4. As can be seen from Fig. 2, in neutral chloride solutions in the presence of **2-MBt**, the active domain of copper was completely depressed. However, at electrode potentials more noble than 475 mV, pitting corrosion occured. After the completion of the electrochemical measurements, a few small pits were detected in the electrodes under the magnifying microscope.
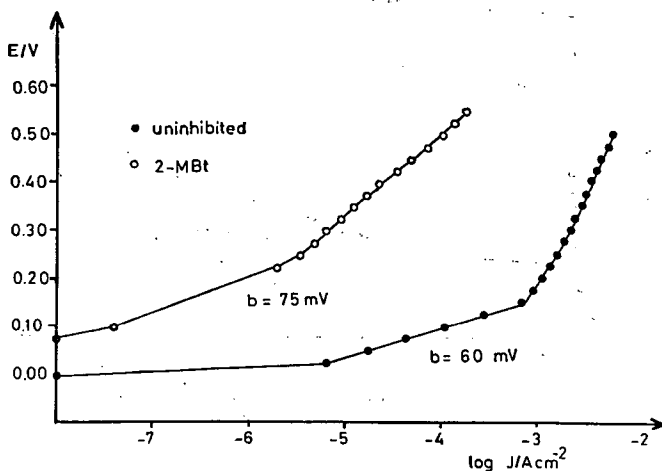

Fig. 1. Quasipotentionstatic anodic polarization curves of pure copper in the absence and in the presence of **2-MBt**, at pH = 4.
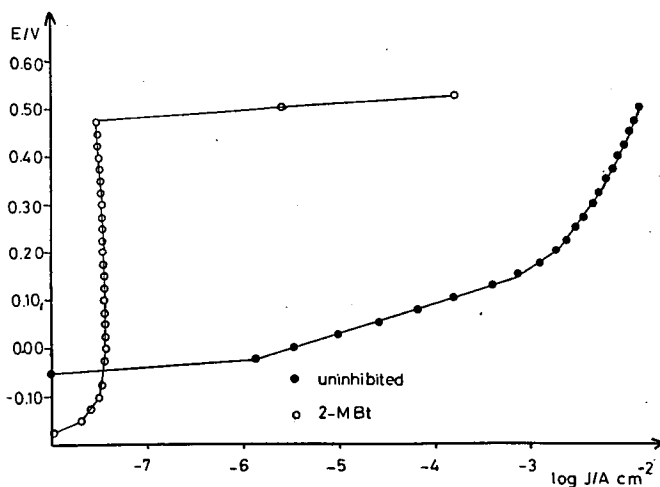

Fig. 2. Quasipotentiostatic anodic polarization curves of pure copper in the absence and in the presence of **2-MBt**, at pH = 7.

The investigated inhibitors have a common functional group (—SH) in addition to two donor atoms bonded to the carbon atom to which the —SH group is bonded. Since **2-MBt** proved to be more effective at pH = 7 than at pH = 4, the inhibitory effects of the investigated inhibitors were determined at pH = 7.
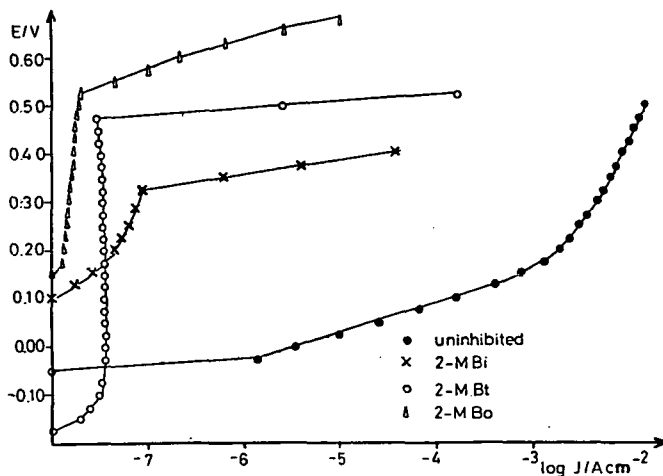

Fig. 3. Quasipotentiostatic anodic polarization curves of pure copper in the absence and in the presence of the investigated inhibitors

Fig. 3 shows the anodic polarization curves of pure copper in the absence and in the presence of the investigated inhibitors. As can be seen from Fig. 3, in the presence of the investigated inhibitors the active anodic dissolution of copper was significantly depressed, especially in the case of **2-MBo**. In the presence of the investigated inhibitors, copper was found to exhibit passivation and pitting corrosion. After the electrochemical measurements, a number of small pits were found in the electrodes.

Table II. shows the corrosion data, reflecting the relative inhibitory effects of the investigated inhibitors. As can be seen from Table II, the average current densities, j_p, established in the passivation domain in the presence of the investigated inhibitors, lay in the following sequence:

$$j_p(2\text{-MBo}) < j_p(2\text{-MBt}) < j_p(2\text{-MBi}).$$

It seems reasonable that the lower the current density in the passive state, the higher the stability of the passive films, *i.e.* the more noble the breakdown potential is expected to be. This assumption seems to fit in with our results. Thus from Table II, Fig 3. and the above comparisons, it can be seen

Table II

Corrosion data reflecting the relative inhibitory effects of the investigated inhibitors in solution containing 0.10 mol dm⁻³ Cl⁻ ions at pH = 7

Inhibitor	$E_{corr.}/V$	J_p $\mu A\ cm^{-2}$	E_b/V
—	−0.05	—	—
2-MBi	0.10	0.04	0.325
2-MBt	−0.175	0.03	0.475
3-MBo	0.15	0.012	0.525

that the relative effectiveness of the investigated inhibitors displayed the following sequence:

$$2\text{-MBi} < 2\text{-MBt} < 2\text{-MBo}.$$

Using the weight loss method, PRAPAJATI ET AL [4] found 2-MBt to be an excellent inhibitor of the corrosion of copper in acetic and chloroacetic acid solutions. They attributed the effectiveness of 2-MBt to the very high stability of the copper--2-MBt complex. Further, they also reported [12] that the ionic species of 2-MBt form an insoluble complex salt [Cu(2-MBt)$_2$] with copper cations. This acts as a protective coating on the metal surface.

Similarly, the potentiodynamic method showed that 2-MBt is effective in inhibiting the anodic dissolution of copper in 0.10 M NaCl. According to TRABANELLI ET AL [13], the inhibitory effect is due to an adherent and protective film formed by the binding between 2-MBt and copper cations through the sulphur atom of the —SH group and by means of bonds coordinated with the electron pairs of the other sulphur atom or of the nitrogen atom. However, the IR data suggested that the bonding occured only the sulphur atom [14].

Because of their common features and their similar chemical structures, 2-MBi, 2-MBt and 2-MBo were expected to exhibit similar inhibition mechanisms. This accounts for the fact that in their presence only pitting corrosion was observed to take place at more noble potentials. Thus, the inhibitory effects of each of them may be attributed to the interaction of the ionic species of the inhibitor with the copper cations in the metallic substrate, leading to the formation of an insoluble protective film. The bonding is achieved mainly between the negatively charged sulphur atom of the —SH group and the copper cations. This would explain the better effectiveness of 2-MBt at pH$=7$ than at pH$=4$, for the ionic concentration of 2-MBt is greater at pH$=7$ than at pH$=4$, and as a result the protective film is more stable at pH$=7$ than at pH$=4$. That the protective film is more stable at pH$=7$ than at pH$=4$ can also be inferred from a comparison of the anodic polarization curves of pure copper in the presence of 2-MBt at pH$=4$ and pH$=7$.

At pH$=7$ and at a constant inhibitor concentration of 10^{-3} mol dm^{-3} in our case, the concentration of any of the ionic species is expected to be higher if the acidity is greater, probably leading to the formation of a more stable passive film and consequently to a more noble break-down potential. To check this assumption, the break-down potentials recorded in the presence of the investigated inhibitors were compared with their acidity expressed as a proton level, J, given by the VERMILYEA equation [15].

VERMILYEA ET AL [15] reported that the inhibitory effectiveness is a function of the acidity of the inhibitor, expressed as a proton level, J:

$$-J = 0.059\,(1.744 - \log K_a)$$

where K_a is the acid dissociation constant of the inhibitor. Since $-\log K_a = pK_a$, the above equation may also be written in the following form:

$$-J = 0.059\,(1.744 + pK_a).$$

Table III shows the pK_a and the caculated J values. The pK_a values of the investi-

Table III

pK_a and J data on the investigated inhibitors

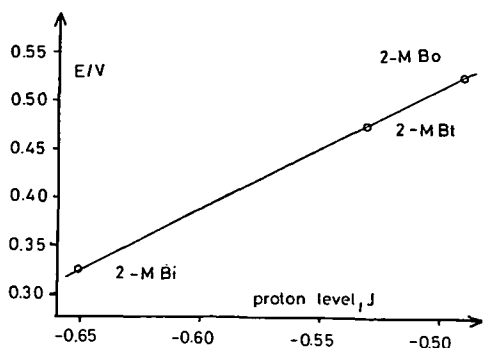| Inhibitor	pK_a	J
2-MBi	9.2	−0.65
2-MBt	7.2	−0.53
2-MBo	6.6	−0.49

Fig. 4. Dependence of the break-down potentials of copper on the acidity of the investigated inhibitors, expressed as a proton level, J

gated inhibitors have been quoted from [4].

Fig. 4 shows the dependence of the break-down potentials on the acidity of the investigated inhibitors, expressed as a proton level, **J**.

As can be seen from this Figure, the coordinates (J, E_b) of the investigated inhibitors fall on a straight line, indicating that these inhibitors have a common inhibition mechanism. The break-down potential becomes linearly more noble as the acidity of the inhibitor increases. This result illustrates the importance of the acidity of the inhibitors in the corrosion inhibition mechanism

Conclusions

The investigated heterocyclic derivatives of mercaptans appreciably inhibited the corrosion of pure copper in deaerated neutral solutions containing chloride ions. The active anodic dissolution of copper in such agressive media was significantly depressed in their presence, especially in the case of **2-MBo**. The inhibitory effect of each of them is propably due to the formation of an insoluble protective surface film. A simple relation correlating the effectiveness of these inhibitors has been obtained, based on the break-down potentials. The higher the acidity of the inhibitor, expressed as a proton level, **J**, the more effective the inhibitor proved to be. This result illustrates the importance of the acidity of the inhibitors in the corrosion inhibition mechanisms. Of the investigated inhibitors, **2-MBt** and **2-MBo** proved to be very effective for inhibition of the corrosion of copper in neutral chloride solutions.

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ИНГИБИРУЮЩИЙ ЭФФЕКТ НЕКОТОРЫХ ГЕТЕРОЦИКЛИЧЕСКИХ ПРОИЗВОДНЫХ МЕРКАПТАНОВ В СОПОСТАВЛЕНИИ С ИХ КИСЛОТНОСТЬЮ

Хигаз Надер Али

С применением квазипотенциостатического метода было изучено ингибирующее действие некоторых гетероциклических производных меркаптанов на коррозию чистой меди в растворах, содержащих постоянные концентрации хлоридов. Результаты работы показывают, что эффективность ингибиторов является функцией их кислотности.