

ELECTROCHEMICAL STUDIES ON THE INHIBITION OF THE CORROSION OF IRON AND STEEL IN METAL-HYDROGEN SULPHIDE-WATER TERNARY SYSTEMS. III

Possibilities of Passivation in the Presence of Dicyclohexilamine Corrosion Inhibitor

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On the basis of experimental results it can be concluded that dicyclohexilamine and its salts are effective corrosion inhibitors of iron in aqueous solutions containing H_2S due to the synergetic effect of H_2S and $DCHA^+$ cations. Results obtained by steady-state and intermittent galvanostatic polarization and also by potentiostatic polarization suggest that the application of $DCHA$ provides a possible means of supporting cathodic and anodic protection of iron and steel in aqueous hydrogen sulphide environments.

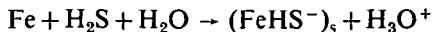
Introduction

In a previous paper it has been demonstrated that in acidic solutions containing hydrogen sulphide the overvoltage of both the anodic dissolution of iron and that of the hydrogen evolution is very low, in accordance with the high corrosion rate of iron [1]. On addition of dicyclohexilamine, however, the overvoltage of both the anodic and cathodic reaction is highly increased, resulting in a marked decrease in corrosion rate. It has been established that the inhibiting effect of $DCHA$ is promoted by the presence of H_2S and its dissociation products. According to HACKERMAN [2] the synergism of the effect of anions and organic cations can be attributed to the stabilization of the adsorbed or chemisorbed anion layer by organic cations. Considering that H_2S promotes the inhibiting effect of $DCHA$ it is reasonable to assume that in the presence of H_2S an ionic or dipole compound is formed on the iron surface — which has been described by JOFA *et al.* [3] as a surface catalyst — oriented with its negative end towards the solution. Then the negatively charged surface may promote the adsorption of $DCHA^+$ cations, which in turn, stabilize the $(FeHS^-)_s$ surface compound. In this paper the polarization behaviour of iron and the mechanism of inhibition in nearly neutral solutions is discussed.

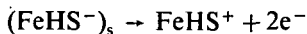
Results and discussion

Electrode potential/current density curves obtained by steady-state galvanostatic polarization under different experimental conditions are shown in Fig. 1. On the basis of curves 2, 2' and 3, 3' it can be established that, in a similar manner as observed at low pH values, the addition of $DCHA$ to the experimental solution saturated with H_2S causes a marked decrease in the value of corrosion current density due to the increase in the overvoltage of the anodic and cathodic reaction. The cathodic polarization curve and the initial section of the anodic curve can be explained by the same mechanism as given for acidic solutions [1]. The low corrosion current density in the presence of H_2S and $DCHA$ (i_{corr_3}) may be attributed to the

adsorption of DCHA^+ cations on the $(\text{FeHS}^-)_s$ surface catalyst formed according to the following reaction [3]:



The adsorption of DCHA^+ cations promotes the stabilization of this layer and prevents its oxidation:



followed by the formation of FeS .

Passivation phenomena, however, observed at higher current densities and at electrode potentials more noble than $-0,1$ V (NHS) suggest that under these conditions the mechanism of inhibition is different from that described above. As shown on curve 3 (Fig. 1.) above $80-100 \mu\text{A}/\text{cm}^2$ current density and above $-0,1$ V (NHS)

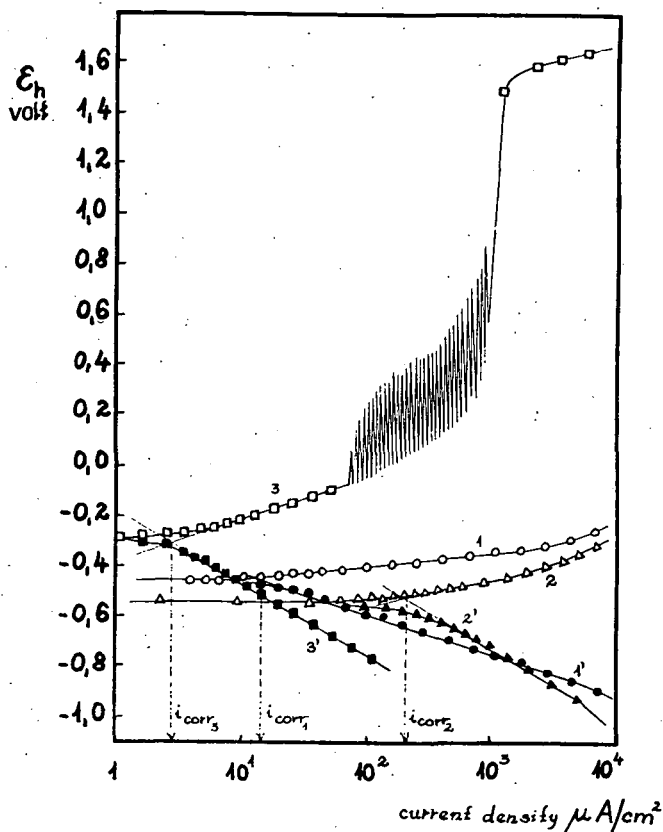


Fig. 1. Electrode potential-current density curves obtained by steady-state galvanostatic polarization with iron electrode immersed into 10^{-6} N H_2SO_4 containing 5% Na_2SO_3 , H_2S and DCHA .

- 1, 1' $\circ \bullet$ — 10^{-6} N H_2SO_4 + 5% Na_2SO_3
 2, 2' $\triangle \blacktriangle$ — 10^{-6} N H_2SO_4 + 5% Na_2SO_3 + H_2S
 3, 3' $\square \blacksquare$ — 10^{-6} N H_2SO_4 + 5% Na_2SO_3 + H_2S + DCHA (0,01 M/l)

the electrode potential starts to fluctuate and then rises rapidly to values far nobler than 1,0 V (NHS), corresponding to the transpassive region of iron. On the basis of the potential/pH equilibrium diagram of the Fe-S-H₂O ternary system [4, 5] especially considering the stability domain of FeS and FeS₂ it is reasonable to assume that at electrode potentials more noble than -0,1 V (NHS) the (FeHS⁻)_s species or any other iron-sulphur dipole cannot be stable. Although we have no thermodynamic data for the hypothetical (FeHS⁻)_s surface catalyst we may assume that the domain of its thermodynamic stability does not extend to much more noble potential values than those corresponding to the oxidation of FeS and FeS₂ [4, 5]. Comparing the potential/pH equilibrium diagram of the Fe-S-H₂O ternary system shown in Fig. 2 with the anodic curve 3 in Fig. 1 it is seen that fluctuations on the galvanostatic polarization curve start above electrode potentials corresponding nearly to the FeS₂/Fe₂O₃ equilibrium. On the basis of this correlation it can be assumed that above this potential region sulphides of iron are oxidized — at least in the vicinity of the metal surface — and thus the mechanism suggested previously for the synergetic effect ceases to be valid. Passivation observed above this potential region cannot be explained simply by the formation of a passive oxide or a chemisorbed oxygen film. Anodic polarization measurements carried out with iron electrode in aqueous solutions saturated with H₂S suggest that any oxide formed by the oxidation of iron sulphides cannot provide passivation by itself. Thus for the explanation of the passive behaviour represented by curve 3 in Fig. 1 the participation of DCHA in the passive film should be assumed. Since the adsorption of DCHA⁺ cations on a positively charged metal surface cannot take place, we have to assume that in this case the free amine forms a chemisorption bond with the surface atoms of the metal by the unshared electrons of its nitrogen atom, at least at defect points of the passive film. This seems to be a possible explanation, since in nearly neutral solutions amines can be present as onium cations and as free amine as well:

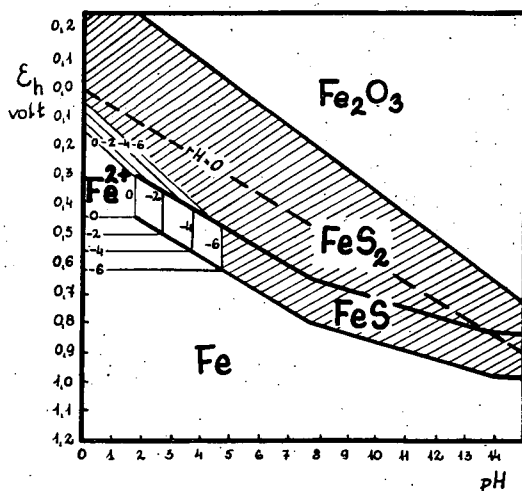
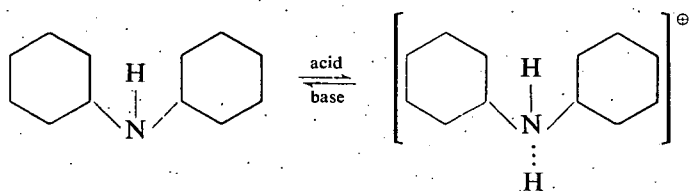


Fig. 2. Potential/pH equilibrium diagram of the Fe-S-H₂O ternary system

be present as onium cations and as free amine as well:



The passivation of iron in the presence of H_2S and DCHA can also be observed by intermittent galvanostatic polarization. If an iron electrode is polarized anodically applying at least 1 mA/cm^2 or higher current density, its electrode potential shifts immediately after switching on the polarizing current to high noble potentials as seen in Fig. 3. It means that above a critical current density iron can be passivated even in aqueous hydrogen sulphide media if the formation of a passive film is supported by an appropriate corrosion inhibitor.

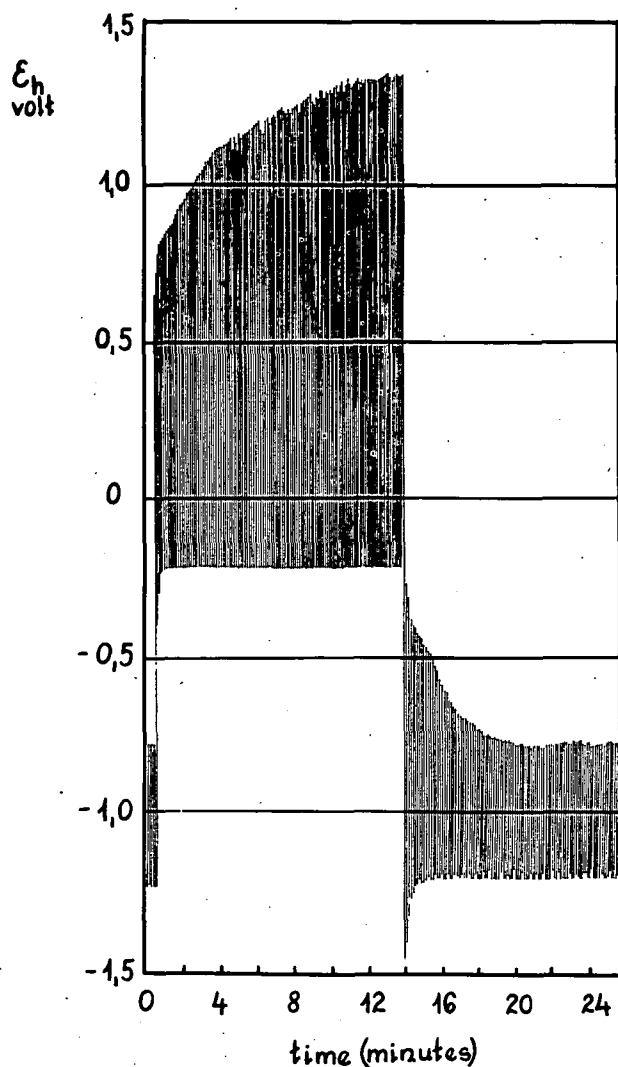
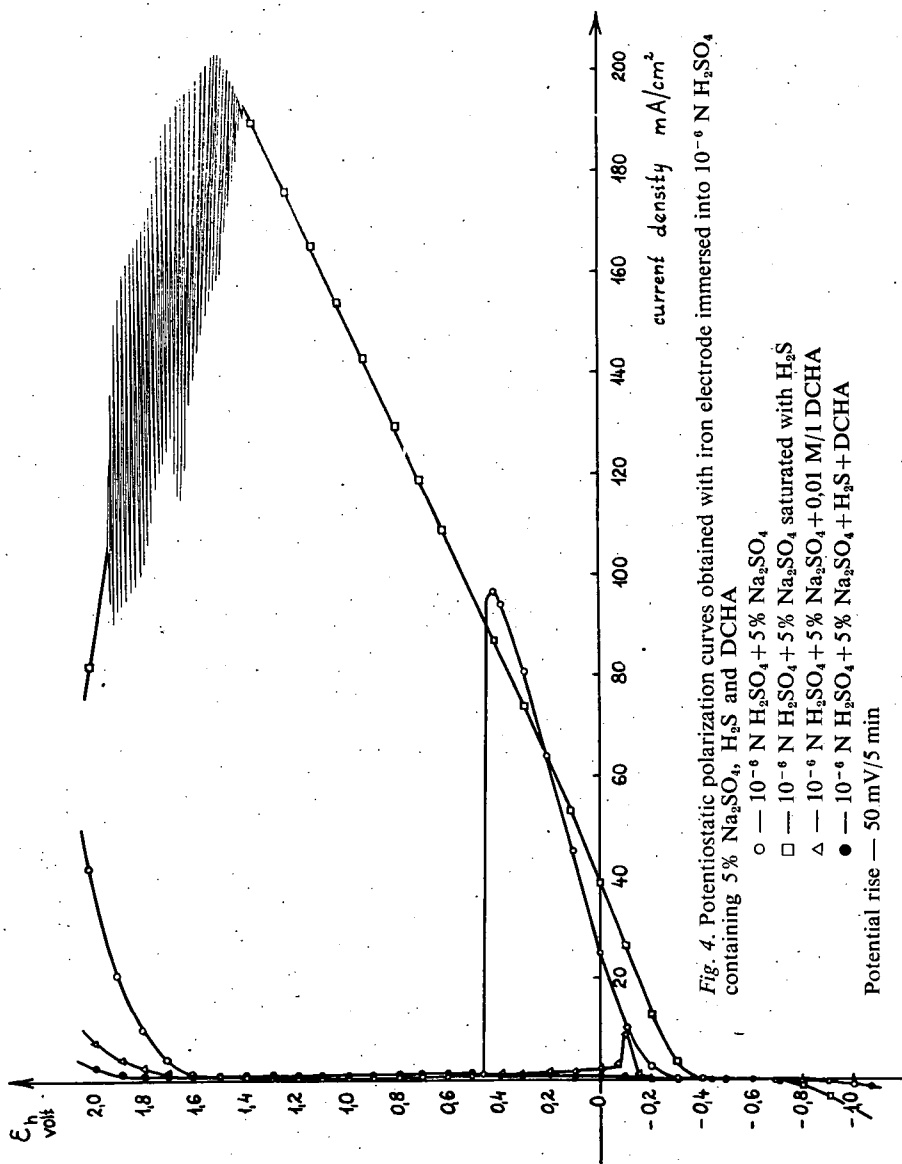


Fig. 3. Electrode potential-time diagram obtained by intermittent galvanostatic polarization with iron electrode immersed into $10^{-6}N$ H_2SO_4 saturated with H_2S and containing 5% Na_2SO_4 and 0,01 M/l DCHA. The upper and lower line series have been obtained by anodic and cathodic polarization respectively

Fig. 3 suggests that anodic protection of iron and steel is not impossible in the presence of hydrogen sulphide if the breakdown of the passive film is prevented. The passive film, however, should be maintained by constant polarizing current, since if polarization by externally applied current is interrupted, the electrode potential shifts immediately to the value of the corrosion potential without any potential arrest corresponding to the Flade potential.

The value of the anodic current density in the passive region in the presence and absence of H_2S and DCHA is shown in Fig. 4. On the basis of the potentiostatic polarization curves of Fig. 4 it can be established that in the presence of DCHA inhibitor the anodic section representing the active dissolution of iron is considerably depressed especially in the presence of H_2S . On the other hand, the cathodic section of the curves proves that DCHA increases



the overvoltage of hydrogen evolution and thus provides a possible means of supporting cathodic protection, too. For the sake of better comparison of the current densities representing the passive sections, curves of Fig. 4 are plotted semilogarithmically in Fig. 5. It is seen that although the active section is almost entirely depressed by the addition of DCHA to the solution containing H_2S , the current density representing the passive state is higher than that observed in H_2S -free solution. Even this relatively higher current density is, however, low enough to prevent considerable metal dissolution. The authors suggest that in the passive

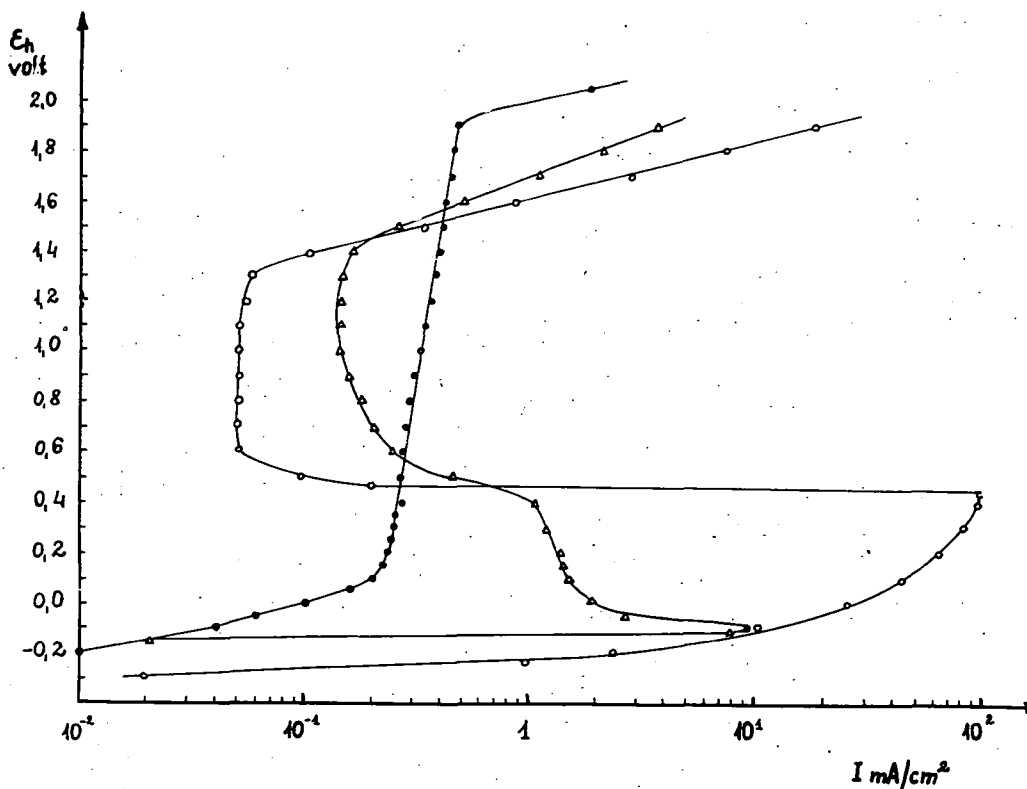


Fig. 5. Electrode potential vs $\log i$ curves obtained by potentiostatic polarization. Experimental conditions are same as given under Fig. 4

section DCHA participates in building up the passive film by the chemisorption of the free amine form. Further experimental evidence and detailed discussion of the problem will be given in subsequent papers. Double-layer capacity measurements are also in progress with DCHA and other organic amines in the presence and absence of H_2S .

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ЭЛЕКТРОХИМИЧЕСКОЕ ИЗУЧЕНИЕ ИНГИБИЦИИ КОРРОЗИИ ЖЕЛЕЗА
И СТАЛИ В ТЕРНИРНЫХ СИСТЕМАХ МЕТАЛЛА-СЕРЫ-ВОДЫ. III

Возможности пассивации в присутствии дициклогексиламина, как ингибитора коррозии

А. Раушер, Л. Хакл, И. Хорват, и Ф. Марта

На основе экспериментальных данных можно установить, что дициклогексиламин и его соли в результате совместного действия сероводорода и катиона, дициклогексиламина оказались эффективными ингибиторами коррозии железа в водных растворах, содержащих сероводород. Экспериментальные данные, полученные при помощи стационарной прерывной гальваностатичной и также потенциостатической поляризации показывают, что дициклогексиламин в растворах, содержащих сероводород, является способным к поддержке катодной и анодной защиты железа и стали.