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

Investigation of the synergetic effect of some organic corrosion inhibitors and hydrogen sulphide

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The aim of this paper is to evaluate, on the basis of laboratory experiments, the applicability of cationic organic inhibitors in acidic aqueous systems containing hydrogen sulphide. Experimental results obtained by intermittent galvanostatic polarization suggest that the inhibiting effect of dicyclohexylamine — used as a model compound — is due to a synergetic effect, as supposed by JOFA and HACKERMAN.

Introduction

According to the principles of electrochemical kinetics the effect of organic corrosion inhibitors as surface active agents upon the corrosion reaction is associated with the change in the structure of the electric double-layer, caused by their adsorption. This change has considerable influence on the exchange current and on the overvoltage of the electrochemical corrosion reactions.

The schematic diagram shown in Fig. 1 shows the polarization behaviour of a corroding metal in oxygen-free aqueous solutions. The construction of the diagram has been based on the assumption that two oxidation-reduction systems are involved in the corrosion reaction and that the potential of the $Me \rightleftharpoons Me^{++} + 2 e^-$ equilibrium is more negative than that corresponding to the $2 H^+ + 2 e^- \rightleftharpoons H_2$ equilibrium. Under such conditions the dissolution of the metal proceeds with simultaneous hydrogen evolution. Under steady state conditions the potential of the corroding metal is represented by ε_{corr}. At this potential the rate of the anodic dissolution of the metal ($Me \rightarrow Me^{++} + 2 e^-$) expressed in current density is equal to the rate of the hydrogen ion discharge ($2 H^+ + 2 e^- \rightarrow H_2$). Heavy lines on Fig. 1 represent the polarization curves obtainable by externally applied polarizing current; β_a and β_c are the Tafel slopes of the anodic and cathodic polarization curves.

The effect of corrosion inhibitors on the polarization characteristics of the corroding metal is shown by Fig. 2. It can be established that the decrease of the corrosion current density from i_{corr_1} to i_{corr_2} is due to the decrease in the exchange currents of the anodic and cathodic reactions (i_{0_H} and $i_{0_{Me}}$) and also to the increase in the Tafel slopes β_a and β_c. In Fig. 2 the increase of β_a is somewhat higher than that of β_c, accordingly, on addition of the inhibitor the corrosion potential shifts towards the positive potential region. As seen in Figs. 1 and 2 the value of the corrosion currents can be established by extrapolating the anodic and cathodic Tafel-
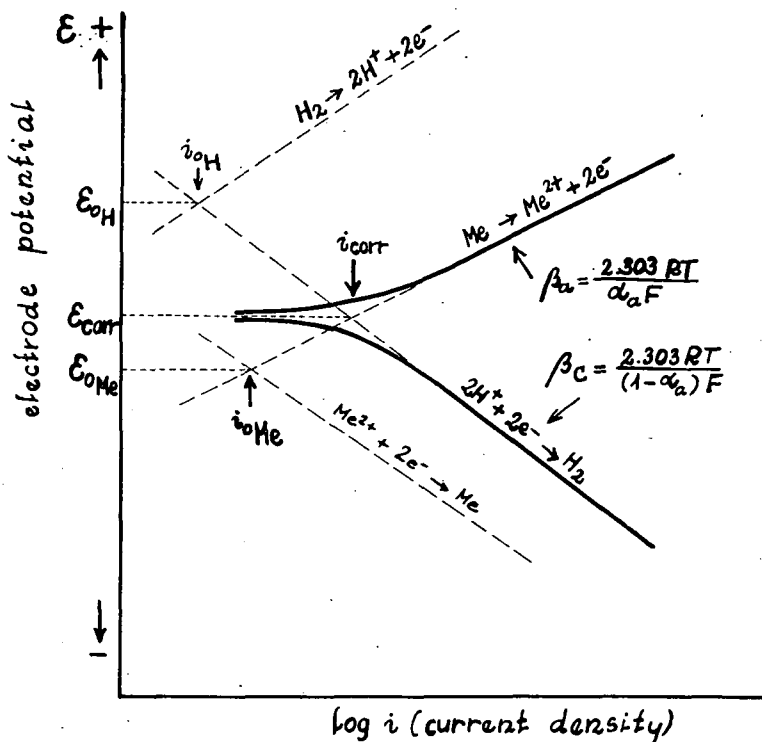
Fig. 1. Schematic polarization diagram for a corrosion
reaction involving two redox systems

lines towards the corrosion potential ε_{corr}. Similar curves can be obtained by inten-
siostatic (galvanostatic), intensiokinetic and also by potentiostatic or potentiokine-
tic methods. Thus the effect of inhibitors on the corrosion rate can be studied on
the basis of polarization diagrams obtained by the above methods, provided that the
polarization curves obey the Tafel equation within one order of magnitude of cur-
rent density.

Polarization curves obtained by step-wise or continuously increased polarizing
current, however, cannot provide information about the change of the overvoltage
of the anodic or cathodic reaction in time. For the study of this problem the inter-
mittent galvanostatic polarization method may be used with advantage. The elec-
trode potential — time diagram obtained by this method is essentially a series of
subsequent galvanostatic charging curves, providing a stripe the width of which
represents the potential difference between the corrosion potential and the polari-
zation potential developed by the polarizing current i_{pol}. This difference is charac-
teristic of the overvoltage of the anodic and cathodic reaction. The correlation
between the polarization data obtained by different methods are shown in Fig. 3.

For the sake of better comparison Fig. 3 has been constructed to represent a
special case where the decrease of the corrosion current density in the presence
of adsorption inhibitor does not involve the change of the corrosion potential ε_{corr}.
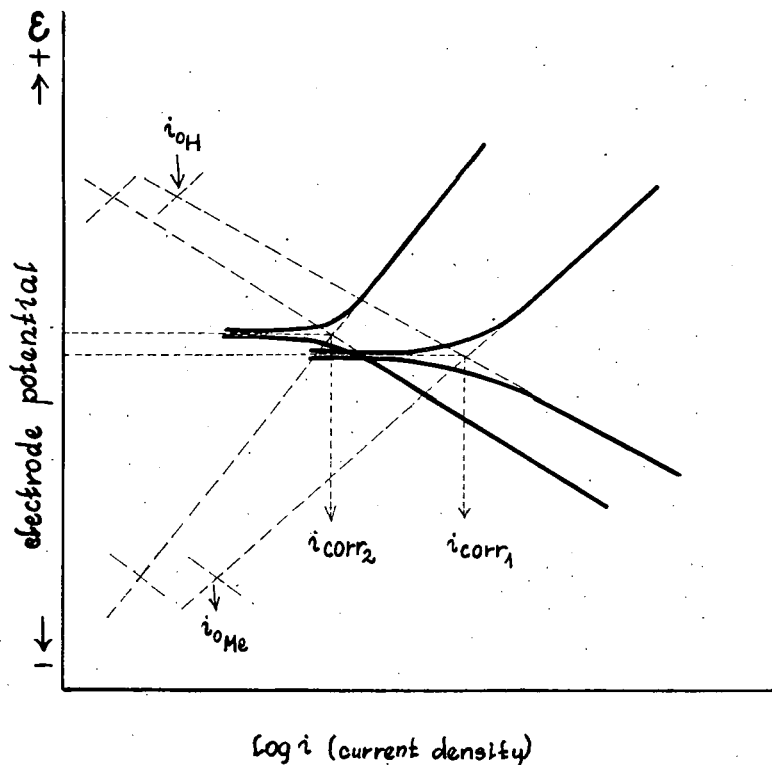
Fig. 2. Demonstration of the effect of an adsorption inhibitor
by schematic polarization diagrams

Comparing the corrosion currents in Fig. 3 in the absence (i_{corr_1}) and presence (i_{corr_2}) of the inhibitor with the potential difference between ε_{corr} and the potential developed by the polarizing current density i_{pol} it is seen that the decrease of the corrosion current density is proportional to the increase of this potential difference, provided that the same electrode reactions are taking place in both cases with different overoltages. This suggests that under relatively simple conditions, *i.e.* if the anodic and cathodic polarization curves obey the Tafel equation and concentration or resistance overvoltage or new electrode reactions do not complicate the picture, intermittent galvanostatic polarization can provide a useful method for the study of the effect of corrosion inhibitors on the overvoltage of anodic and cathodic reactions and of the change of their effectiveness in time.

Applicability of dicyclohexylamine as adsorption inhibitor

Considering the inhibitor efficiency of organic amines HACKERMAN and MAKRI-DES [1] supposed, that the interaction between the nitrogen atom of the amine group and the unoccupied *d*-orbitals of the metal surface is an acid-base interaction of the
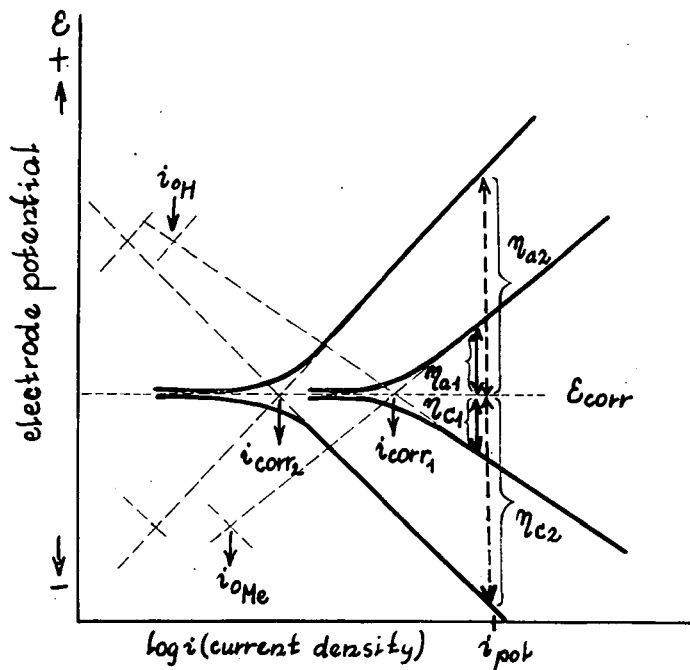
Fig. 3. Correlation between polarization data obtainable with continuous galvanostatic and intermittent galvanostatic polarization

Lewis-type. KAESCHE and HACKERMAN [2] furthermore suggested that the adsorption or rather chemisorption of the inhibitor is by means of the free amine. Recently, however, JOFA *et al.* [3, 4], FISCHER [5, 6] and HACKERMAN [7] have found that in the presence of halide anions and HS^- the adsorption of amines and of some other organic compounds takes place in the form of onium cations. Considering the characteristics of organic corrosion inhibitors it can be concluded that among other factors the basicity of the amines is important from the point of view of corrosion inhibitor efficiency. For the experiments described in this paper we have selected dicyclohexylamine as a model compound. Being a secondary amine with saturated rings, DCHA is a strong base with a relatively high electron density on the nitrogen atom. Considering the extreme forms — the free amine and the cationic form — in acidic solutions the equilibrium is shifted towards the cationic form. In the presence of H_2S the following equilibrium can be suggested:

(1)
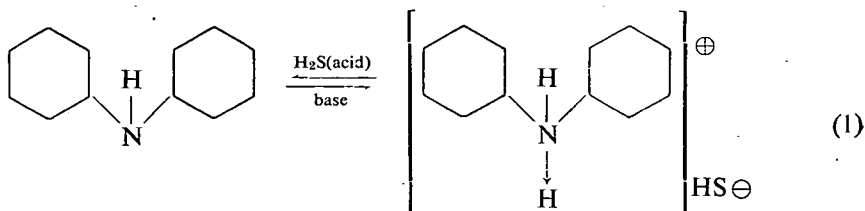
Considering the basicity of DCHA, it can be supposed that in the presence of H_2S in aqueous solutions the amine is predominantly present in 'the form of onium cations, producing a water-soluble salt with H_2S. By increasing pH and decreasing H_2S content the equilibrium shifts towards the free amine form. The solubility of DCHA is relatively low in aqueous solutions, very good in mineral oils and organic solvents like alcohols [8]. These properties should be considered for determining the applicability of DCHA in complex systems encountered e. g. in the petroleum industry.

Experimental

To investigate the effect of DCHA on the overvoltage of the anodic and cathodic reactions, measurements were carried out by steady-state and intermittent galvanostatic polarization. This method was first applied by NAGEL, LANGE and OHSE [9, 10] for the investigation of the equilibrium potentials of electrode processes taking place in metal/water binary systems. Recently the method was applied by the authors for the investigation of Me—S—H_2O ternary systems [11]. Theoretical aspects of the method have been discussed in details by LANGE and GÖHR [12]. A detailed description of the experimental cell and the block scheme of the measuring equipment is given in a previous paper of the authors [11]. Registration of the curves was carried out by a Metrohm Potentiograph Type E-336. The stock solution contained 5% Na_2SO_4. Acidic and alkaline pH values were set by addition of H_2SO_4 and NaOH (Reanal, of p. a. quality). Saturation with H_2S was carried out by bubbling H_2S gas through the solution, previously de-areated with nitrogen. The inhibitor was first dissolved in 10 ml methyl alcohol, then added to the experimental solution. Results described in this paper were obtained in stagnant solution, at 25 C°. Working electrodes were forged from mild steel and electrolytic iron. Cylindrical surface area was about 2 cm². Prior to the experiments, electrode surfaces were polished with different grades of emery paper, degreased in acetone and pickled at room temperature in a solution containing 15% HNO_3 and 5% HF. Pickling was followed by rinsing in distilled water and in the experimental solution.

Results and discussion

In 0.1 N H_2SO_4 solution containing 5% Na_2SO_4 the overvoltage of the anodic dissolution of iron and that of the cathodic hydrogen evolution is relatively low, as seen on Fig. 4. a. The corrosion potential is between $-0,25$ and -0.26 V (NHS). On addition of 0.01 M/1 DCHA there is only a slight increase in the overvoltage of the anodic dissolution of iron. The increase in the overvoltage of the cathodic reaction, however, is definitely higher. This behaviour can be explained by the predominantly cationic nature of DCHA in acidic solutions. As it was pointed out by ANTROPOV [13], the action of organic corrosion inhibitors, determined by their adsorption, is strongly dependent on the surface charge of the metal and consequently on the position of the steady-state corrosion potential (or of the potential of an electrode polarized anodically or cathodically) relative to the zero charge point. Differential capacitance measurements carried out in H_2SO_4 solutions show that for

iron $\varepsilon_{q=0}$ is between $-0,33$ and $-0,37$ V (NHS) [14, 15]. This value was recently confirmed by the crossed wires method [16]. Considering -0.37 to be the zero charge potential, the corrosion potential of the iron surface on the Φ scale is:

$$\mathrm{Fe}_{\Phi_{corr}} = \mathrm{Fe}_{\varepsilon_{corr}} - \mathrm{Fe}_{\varepsilon_{q=0}} \qquad (2.\,a.)$$

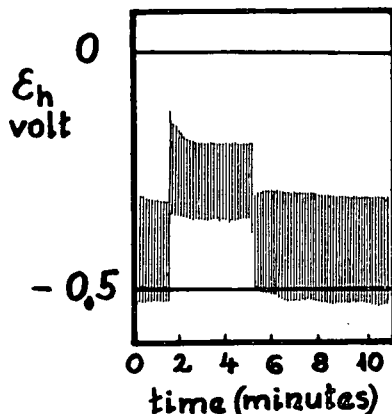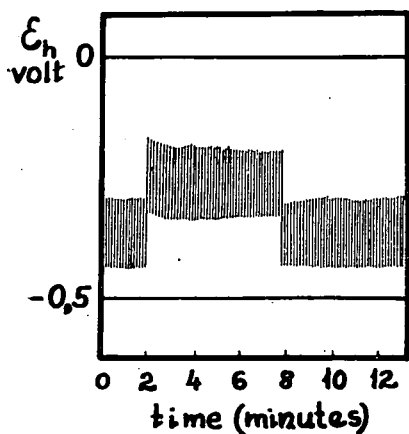$$\mathrm{Fe}_{\Phi_{corr}} = -0.25 - (-0.37) = 0.12 \text{ V (NHS)} \qquad (2.\,b.)$$

Fig. 4a. Electrode potential — time diagram obtained by intermittent galvanostatic polarization with iron electrode immersed into 0,1 N H_2SO_4 containing 5% Na_2SO_4. The upper and lower line series have been obtained by anodic and cathodic polarization, respectively. Current density: 1 mA/cm².

Fig. 4b. Potential — time diagram obtained in the same solutiou as in Fig. 4a. after addition of 0,01 M/1 DCHA. C.d.: 1 mA/cm².

It follows that under the experimental conditions discussed above the iron surface is positively charged. This charge hinders the adsorption of organic cations and promotes that of anions. For this reason at the corrosion potential DCHA$^+$ cations cannot adsorb on the iron surface. This is in good agreement with the experimental results of JOFA et al. [3, 4], who established that organic compounds of the cationic type are only weakly adsorbed on the iron surface from solutions of H_2SO_4. On anodic polarization the adsorption of cations is even less probable. The very slight increase in the overvoltage of the anodic dissolution of iron may be due to chemisorption of the free amine by the unshared electrons of its nitrogen atom. Since the concentration of the free amine is very low in acidic solutions, its effect on the overvoltage of the anodic dissolution may not be considerable. On the other hand, if the electrode is polarized towards the negative potential region from the corrosion potential, the adsorption of cations on a negatively charged metal surface will be possible. Thus on a cathodically polarized iron surface DCHA$^+$ ions can adsorb and inhibit the hydrogen ion discharge process. This is a possible explanation for the polarization behaviour shown in Fig. 4a and b.

The effect of H_2S on the anodic dissolution of iron and on the cathodic reduction of hydrogen ions is shown in Fig. 5a. It is seen that the overvoltage of the anodic

and cathodic reaction is considerably decreased, as compared to Fig. 4a. It has been shown by JOFA and TOMASHOVA [17] that the stimulating action of H_2S on the corrosion of iron increases with the increase of H_2S concentration in the solution.
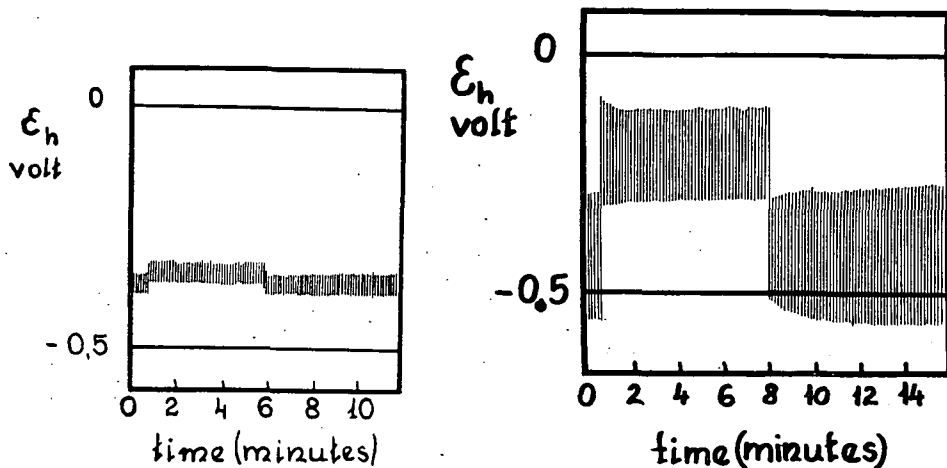

Fig. 5a. Potential — time diagram obtained in acidic solution saturated with H_2S. C.d.: 1 mA/cm²
Fig. 5b. Potential — time diagram obtained in acidic solution saturated with H_2S after the addition of 0.01 M/1 DCHA. C.d.: 1 mA/cm².

Similar results were obtained by HORVÁTH [18] in aqueous culture media inoculated with sulphate-reducing bacteria. The shift of the corrosion potential towards the negative region can be attributed to a decrease in the overvoltage of the anodic reaction giving rise to higher corrosion rate. In an earlier paper the accelerating action of H_2S on electrochemical reactions was attributed by JOFA [19] to the development of a negative adsorption potential ψ_1 as a result of HS^- adsorption on a positively charged metal surface. Recently JOFA [3] advanced the hypothesis that the action of H_2S is due to the formation of a surface catalyst acting in a similar manner as proposed by FRUMKIN [20] for OH^- ions. For iron the formation of this hypothetical catalyst has been described by JOFA et al. [3] by the following equations:

$$Fe + H_2S + H_2O \rightleftharpoons (FeHS^-)_s + H_3O^+ \qquad (3)$$
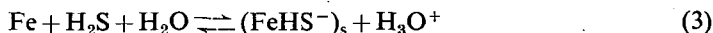
The concentration of the catalyst may be given by

$$(FeHS^-)_s = K \frac{[H_2S]}{[H_3O^+]} \qquad (4)$$

It follows that the anodic charge transfer reaction should be the oxidation of the surface catalyst:

$$(FeHS^-)_s \longrightarrow FeHS^+ + 2e^-. \qquad (5)$$

followed by the hydrolysis of the $FeHS^+$ ion or by the formation of FeS, depending on the pH of the solution. On the basis of equation (4) it can be expected that by lowering pH the concentration of the catalyst decreases parallel to the decrease of the stimulating effect of H_2S.

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Fig. 5*b* demonstrates the synergetic effect of H_2S and DCHA in acidic solutions. It is seen that the overvoltage of both the anodic and cathodic reaction is highly increased. According to HACKERMAN [7] the synergism of the effect of anions and organic cations in corrosion inhibition 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 dissolved H_2S an ionic or dipole compound is formed on the iron surface — which may be considered as a surface catalyst — oriented with its negative end towards the solution. Then the negatively charged surface may promote tha adsorption of $DCHA^+$ cations, which in turn stabilize the $(FeHS^-)_s$ surface compound formed according to equation (3). In the case of cathodic polarization the explanation of the increased overvoltage may be similar to that given previously for the H_2S-free system.

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ЭЛЕКТРОХИМИЧЕСКОЕ ИЗУЧЕНИЕ ИНГИБИЦИИ КОРРОЗИИ ЖЕЛЕЗА И СТАЛИ В ТЕРНИРНЫХ СИСТЕМАХ МЕТАЛЛА—СЕРЫ—ВОДЫ. II.

Изучение совместного действия органических коррозионных ингибиторов и сероводорода

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

Цель настоящей работы на основе лабораторных экспериментальных данных оценивать возможностей применения органических соединений как коррозионных ингибиторов катионного типа в кислых растворах, содержащих сероводород. Экспериментальные данные, полученные при помощи прерывной гальваностатичной поляризации указывают, что эффективность дициклогексиламина, употребленного в качестве модельного соединения приписывается совместному действию H_2S и ингибитора, предположенному авторами Иофа и Гаккерман.