

INHIBITION OF CORROSION OF CARBON STEEL BY AN AMINE BASE POLYCONDENSATION PRODUCT IN ACID SOLUTIONS

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The inhibitor effect of an amine base polycondensation product on the corrosion behaviour of carbon steel, type KL-1, has been studied in acid solutions by weight loss and galvanostatic polarization methods.

The corrosion rates and the percentage protection data reveal that the polycondensation product at a concentration of 1 g dm^{-3} is suitable as a corrosion inhibitor at 30°C in 5 and 10% HCl solutions or in 20% H_2SO_4 , and at 80°C in 5% HCl solutions. In several cases the uninhibited corrosion rate and the percentage protection of the inhibitor can not be determined by the electrochemical polarization method. In spite of this, the method itself is sufficient for qualifying the inhibitor.

The inhibiting action may be interpreted by a synergetic effect, considering the structure of the inhibitor and the parameters obtained from the polarization curves.

Introduction

Metals are exposed to the action of acids for a variety of purposes in different fields of industry. Examples of such important uses are acid pickling, cleaning of boilers, heat exchange equipment and oil refinery equipment, and acidizing of oil wells. Corrosion attack on metals by acids can in many cases be controlled by means of inhibitors. The most effective and widespread inhibitors in acid systems are the organic compounds with at least one polar function, containing atoms of nitrogen, sulphur, oxygen, and in some cases selenium and phosphorus [1].

The purpose of the present work was to study the inhibition effect of an amine base polycondensation product (KL-13F) [2] in hydrochloric and sulphuric acids.

In order to correlate the action of the inhibitor on the corrosion rate with the electrochemical properties of the metal under consideration, electrochemical polarization experiments were carried out in addition to the usual methods based on weight loss of the metal specimens.

Experimental

Carbon steel type KL-1, 3 mm thick, was used in all tests. Specimens used in the electrochemical measurements measured 50×10 mm, with 15 mm handles at one end for electrical connection. Weight losses were measured on 50×20 mm specimens with a 5 mm diameter hole drilled on the vertical centreline near one end. The specimens were degreased with dichloromethane, abraded with No. 10 abrasive paper, polished with F-20 waterproof emery paper, and finally washed with acetone and dried. The plates were stored in a desiccator until use.

The inhibitor efficiency was determined

- I. in 5% HCl solution, at 353 K (80 °C), with 0.5, 1, 2 and 5 g dm⁻³ inhibitor concentrations; and
- II. at 1 g dm⁻³ inhibitor concentration
 - a) in 5, 10 and 30% HCl solutions, at 303 K (30 °C) and at 353 K (80 °C)
 - b) in 20% H₂SO₄ solution at 303 K (30 °C).

The effect of the inhibitor is expressed by the percentage inhibition:

$$P = \frac{r - r_i}{r} 100$$

where

r = uninhibited corrosion rate

r_i = inhibited corrosion rate.

Cathodic and anodic polarization curves were measured by the galvanostatic method. The intersections resulting from extrapolation of Tafel lines backwards in the low current direction provided the corrosion rates in $\mu\text{A cm}^{-2}$. These were converted to g/m² day units with the use of the following equation

$$r = \frac{864 \cdot A(\text{Fe})j}{zF}$$

where

$A(\text{Fe}) = 55.847$ g mol⁻¹

$z = 2$

$F = 96489$ C mol⁻¹

j = current density ($\mu\text{A cm}^{-2}$).

In order to measure weight loss, the specimens were immersed into a glass vessel by means of a specimen holder made of glass. The volume of corrosive agent in the test vessel provided a volume to total specimen area ratio of at least 10 cm³/cm². In 30 °C acid solutions the test duration was 24 hours, at 80 °C in 5% hydrochloric acid it was 20 hours, while in the other 80 °C solutions it was 4 hours. At the end of the exposure period, the surface of the specimens was carefully washed in methanol and in acetone. After drying, they were stored in a desiccator until weighing.

The corrosion rates were calculated from the equation:

$$r = \frac{\Delta m}{F \cdot t}$$

where

Δm = weight loss (g)

F = surface area (m^2)

t = test exposure time (day)

Experimental results

Weight loss measurements

Data obtained in experiments carried out at 80 °C in 5% HCl solutions containing inhibitors in different concentrations are listed in Table I.

From these data it can be concluded that in the absence of inhibitor the KL-1 mild steel corrodes at a high rate in 5% HCl solution at 80 °C, whereas the inhibitor gives more than 98% protection even in 0.5 g dm⁻³ concentration. As the concentration of inhibitor is raised, the percentage protection evidently increases, and in 2 g dm⁻³ concentration it provides excellent protection.

The data in Table II show the inhibitor efficiency in solutions of different HCl concentrations at 30 and at 80 °C, as well as in 20% H₂SO₄ at 30 °C.

It can be seen that the steel corrosion rate is enhanced considerably by an increase in either temperature or hydrochloric acid concentration in the absence and in the presence of inhibitor. When the temperature was raised from 30 °C

to 80 °C and the acid concentration from 5% to 10% in the presence of inhibitor, the corrosion rate increased to a smaller extent than in the absence of inhibitor, which resulted in a higher percentage inhibition. Thus, under these conditions the polycondensation product proved to be an efficient inhibitor.

In 30% hydrochloric acid the inhibitor does not retard metal dissolution at either 30 °C or 80 °C.

It should be noted that the numerical data obtained at 80 °C cannot be considered completely correct, since great changes took place in the composition of the solution and in the size of the metal surface during the corrosion process. The same holds for the corrosion rate obtained in 10% hydrochloric acid free of inhibitor at 80 °C. If the marked decrease in the surface area were taken into consideration in the calculation of the corrosion rates, higher corrosion rates would appear. Hence, the percentage inhibition in 10% HCl solution at 80 °C would be higher than 95.67%. The change in the composition of the solution with time would probably result in an opposite effect to that of change in the surface on the corrosion rate. In spite of the relatively high percentage protection, the considerable metal loss (nearly 290 g/m² day) means that the polycondensation product cannot be regarded as suitable for the inhibition of corrosion under such circumstances.

Table I
Results obtained from weight loss measurements
in 5% HCl at 80 °C

Concentration of inhibitor g/dm ³	Corrosion rate g/m ² day	Percentage protection %
—	3973.3	—
0.5	53.58	98.65
1.0	40.48	98.98
2.0	17.15	99.57
5.0	10.03	99.74

Table II
Data of weight loss measurements

Medium	Concentration of inhibitor g/dm ³	Temperature			
		30 °C		80 °C	
		Corrosion rate g/m ² day	Percentage protection %	Corrosion rate g/m ² day	Percentage protection %
5% HCl	—	80.49	94.61	3973.3	98.98
	1	4.34		40.48	
10% HCl	—	213.47	97.10	6693.8	95.67
	1	6.19		289.99	
30% HCl	—	3482.51	62.88	55 800.6	43.04
	1	1292.66		31 784.2	
20% H ₂ SO ₄	—	547.92	99.31	—	—
	1	3.79		—	

At a concentration of 1 g/dm³, the inhibitor decreased the corrosion of steel to the highest degree in 20% H₂SO₄ at 30 °C.

During weight loss measurements, it was observed that the metal dissolution was more intensive along the shorter edges of the specimens and by the side of the holes than on the plane and on the edges in the rolling direction. This phenomenon can be attributed to the structural characteristics of the steel.

Galvanostatic polarization measurements

In some of the examined acid solutions, especially at 80 °C in the absence of inhibitor, the steel dissolved with such intensive H₂ formation that polarization curves with detectable Tafel lines could not be obtained. Cathodic and anodic polarization curves obtained from different acid solutions in the absence and in the presence of inhibitor are shown in Figures 1—4. The corrosion current densities determined from the polarization curves are given in Table III, together with corrosion rate data calculated in g/m² day.

The corrosion rates determined for similar conditions with the electrochemical method and from weight loss measurements differ only slightly. The polarization curves yielded somewhat smaller values, except for 20% H₂SO₄ at 30 °C. The probable explanation of this is that the more intensively dissolved area of the edges was 5 times smaller for the electrodes applied in the electrochemical measurements than for the plates used in the weight loss measurements.

The percentage protection of the inhibitor can be calculated from the corrosion current densities only for 5% HCl and 20% H₂SO₄ at 30 °C, since the data for the other solutions free of inhibitor cannot be determined in this way. In spite of this,

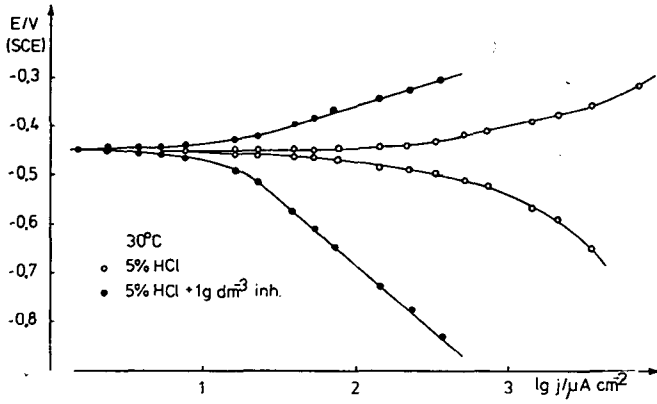


Fig. 1

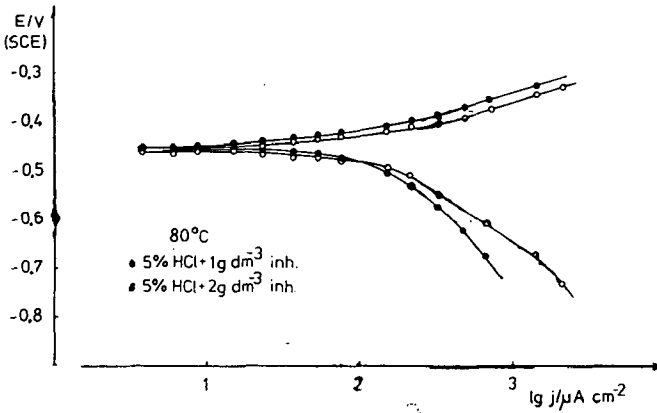


Fig. 2

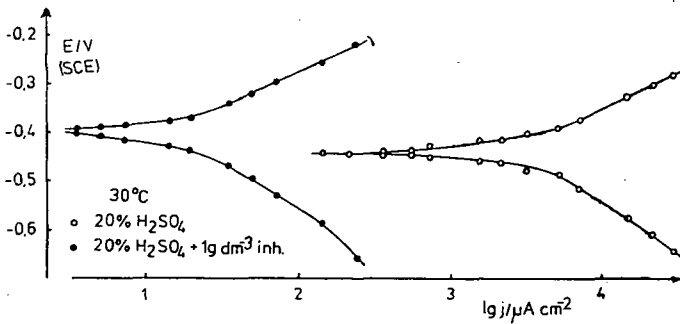


Fig. 3

Figs. 1—3. Galvanostatic polarization curves for type KL-1 carbon steel

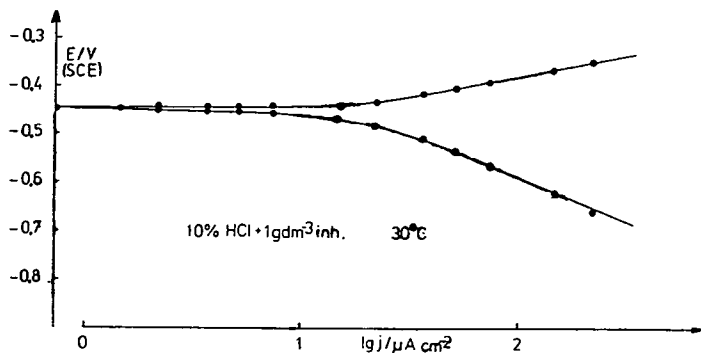


Fig. 4
Galvanostatic polarization curves for type KL-1 carbon steel

the electrochemical method itself is sufficient to qualify the inhibitor because the relatively small (max. 40 g/m² day) corrosion rates in every case give evidence regarding the proper protection of the inhibitor. Consequently, both experimental methods led to the same conclusion concerning the applicability of the inhibitor in acid cleaning.

Table III

Data obtained from galvanostatic polarization curves

Medium	Temperature °C	Corrosion current density $\mu\text{A}/\text{cm}^2$	Corrosion rate g/m^2 day	Percentage inhibition %
5% HCl	30	230	57.5	94.43
5% HCl + 1 g/dm ³ inhibitor	30	12.8	3.2	—
5% HCl + 1 g/dm ³ inhibitor	80	125	31.2	—
5% HCl + 2 g/dm ³ inhibitor	80	63.5	15.88	—
10% HCl + 1 g/dm ³ inhibitor	30	20.5	5.1	—
20% H ₂ SO ₄	30	3300	825	—
20% H ₂ SO ₄ + 1 g/dm ³ inhibitor	30	13.5	3.25	99.6

Mechanism of inhibition

The polycondensation product consists mainly (80—85%) of the secondary amine formed between benzylamine and ethyl iodide. The remaining 15—20% of the product is a mixture of primary, tertiary and quaternary compounds. The molecules are cross-linked in space with hexamethylene-tetramine. The polycondensation product may be considered as amine-type “organic-cations” in acidic systems.

Since the dissolution of steel in acids takes place according to an electrochemical mechanism, the inhibitor effect can be attributed basically to a change in the kinetics of the electrochemical reactions. Thus, conclusions on the mechanism of action of the inhibitor may be drawn only on the basis of electrochemical measurements. It is seen from the results of polarization measurements that the inhibitor does not influence the corrosion potential of the steel, except for that measured in 20% H_2SO_4 . Moreover, the polarization curves in Figures 1, 2 and 3 reveal that, in the presence of inhibitor and also as the concentration of inhibitor was raised, the overvoltage of both the anodic and the cathodic reactions increased. The Tafel slopes of the cathodic polarization curves generally increased to a higher degree than those of the anodic curves, and at 80 °C in 5% HCl in the presence of 2 g dm^{-3} inhibitor, cathodic Tafel line did not even develop due to the concentration polarization. The 45 mV positive shift of the corrosion potential in H_2SO_4 solution indicates that in this case the inhibitor has a greater effect on the anodic process than on the cathodic one. Accordingly, the conclusions may be drawn that the inhibitor affects both partial processes of the corrosion, but that its relative influence depends on the composition of the medium.

Taking into account the structure of the inhibitor and the characteristics obtained for the polarization curves, the action of the inhibitor can be attributed to a synergistic effect. JOFA [3], HACKERMAN, SNAVELY, PAYNE [4], MURAKAWA [5], HORVÁTH, RAUSCHER, HACKL, MÁRTA [6] and other authors [7, 8] assumed that different organic cation-type inhibitors in acid solutions containing certain anions (halogen anions, HS^- , CNS^- , organic anions, etc.) form chemisorbed layers on the surface of iron and carbon steel. These layers decrease the capacity of the double-layer to a great extent and inhibit both the reduction of hydrogen ions and the ionization of the metal.

In the absence of anions, organic cations usually have no, or only a low inhibiting effect. Anions (which may otherwise result in the acceleration of metal dissolution) promote the adsorption of organic materials; they are chemisorbed on the metal to form surface dipoles, the negative poles of which face the solution. The synergistic effect is found to be especially strong in the presence of I^- ions, and the polycondensation product contains this ion. Apart from the fact that the inhibitor film formed on the metal surface changes the structure of the double-layer and hence the kinetics of the electrode processes, it also has to be taken into account in connection with the mechanism of the inhibitor action that the adsorbed organic layer isolates the metal from the corrosive agent, that is it has a barrier effect as well. In this respect too the polycondensation product can be considered to be advantageous.

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ИНГИБИРОВАНИЕ КОРРОЗИИ УГЛЕРОДИСТОЙ СТАЛИ В РАСТВОРАХ КИСЛОТ ПРОДУКТАМИ ПОЛИКОНДЕНСАЦИИ АМИНОВ

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Изучено ингибирующее действие продуктов поликонденсации аминов при коррозии углеродистой стали Кл-I в растворах кислот методами гальваностатической поляризации и потери веса. Полученные экспериментальные данные показывают эффективность исследуемых ингибиторов в разбавленных растворах H_2SO_4 и HCl до температур достигающих $80^\circ C$. Ингибирующее действие может быть рассмотрено с принятием во внимание синергетического эффекта, зависящего от структуры ингибитора, и параметров полученных из поляризационных кривых.