

CARBOXYLIC ACIDS: PITTING CORROSION INHIBITORS FOR CARBON STEEL IN ALKALINE MEDIUM AND IN THE PRESENCE OF CHLORIDES

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The effect of phthalic acid, salicylic acid, benzoic acid, o-aminobenzoic acid, and oxalic acid on pitting corrosion of carbon steel in a 0.01 M NaOH solution in the presence of NaCl is evaluated using potentiodynamic anodic and cathodic polarization measurements. The results show that the carboxylic acids shift the pitting corrosion potential toward more positive values, indicating that they have an inhibiting effect. Of the studied acids, phthalic acid has the greatest inhibiting effect and oxalic acid has the lowest inhibiting effect. All the carboxylic acids are mixed corrosion inhibitors, with predominantly anodic inhibition. We discuss the pitting corrosion inhibition mechanism, taking into account the structure of the acid molecules, their behavior in alkaline medium, and the electron density on the COO⁻ group.

Key words: corrosion, electron microscopy, carboxylic acids, inhibitor.

In most cases, anodic dissolution of iron and steel in alkaline medium exhibits passivation behavior [1–11] due to γ -Fe₂O₃ film formation [8, 12–14]. The presence of Cl⁻ anions in solution leads to local breakdown of the film and initiation of pitting corrosion [15, 16]. It is specifically at these localized points that anodic dissolution occurs, while the major portion of the metal surface continues to be passivated.

A number of papers [17–26] are devoted to study of the inhibiting effect of organic and inorganic compounds for pitting corrosion of steel in alkaline medium. However, to date the available information is contradictory on the effectiveness of corrosion inhibition in steel by organic compounds in alkaline medium. Furthermore, very little information is available on the mechanism of corrosion inhibition by organic compounds [17]. The first stage in inhibition involves adsorption of the organic compound (generally containing nitrogen, sulfur, or oxygen atoms) on the metal surface [27, 28] via heteroatomic groups, multiple

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bonds, or aromatic rings [29–31]. The effectiveness of a specific inhibitor is different under different conditions, and so we should consider different inhibition mechanisms [32–34].

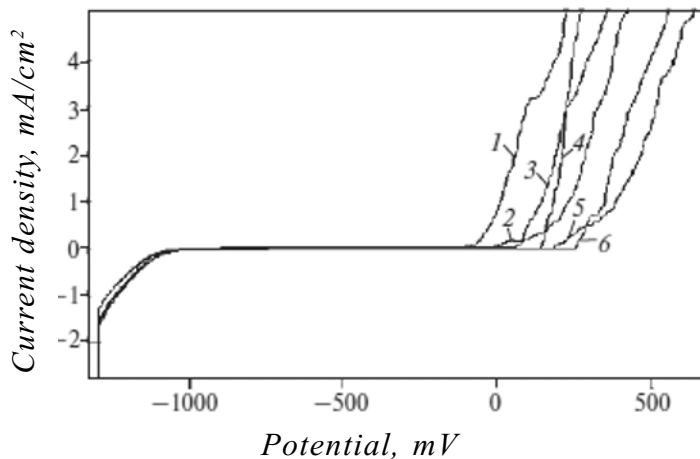


Fig. 1. Potentiodynamic anodic polarization curves for steel in the absence of phthalic acid (1) and in the presence of phthalic acid in a concentration of: 2) 10^{-4} M; 3) $2.5 \cdot 10^{-4}$ M; 4) $5 \cdot 10^{-4}$ M; 5) $7.5 \cdot 10^{-4}$ M; 6) 10^{-3} M.

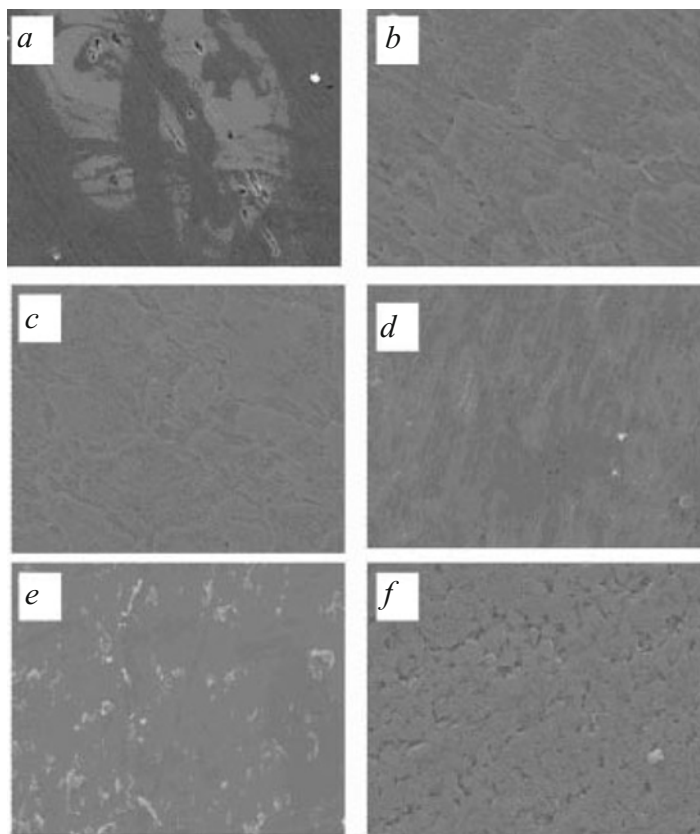


Fig. 2. Micrographs for carbon steel after holding in a 0.01 M NaOH + 0.01 M NaCl solution in the absence of an inhibitor (a) and in the presence of 10^{-3} M: b) phthalic acid; c) salicylic acid; d) benzoic acid; e) *o*-aminobenzoic acid; f) oxalic acid.

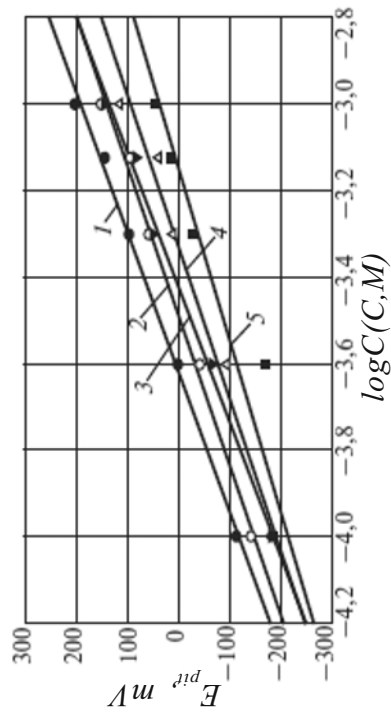


Fig. 3. Pitting potential vs. carboxylic acid concentration: 1) phthalic acid; 2) salicylic acid; 3) benzoic acid; 4) *o*-aminobenzoic acid; 5) oxalic acid.

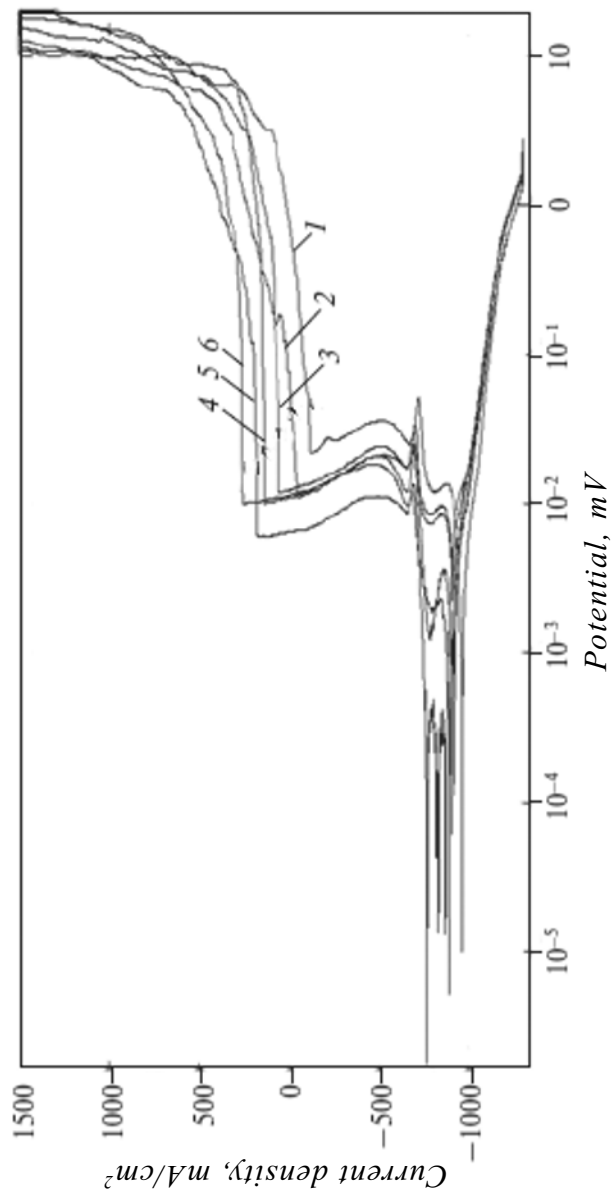


Fig. 4. Potentiodynamic cathodic and anodic polarization curves for steel in the absence of phthalic acid (1) and in the presence of phthalic acid in a concentration of: 2) 10⁻⁴ M; 3) 2.5 · 10⁻⁴ M; 4) 5 · 10⁻⁴ M; 5) 7.5 · 10⁻⁴ M; 6) 10⁻³ M.

The objective of this work is to establish the roles of some organic compounds containing a carboxyl group in improving the resistance of the passivating film on carbon steel to pitting corrosion by chloride ions in alkaline medium.

We used a carbon steel rod with the following composition (wt.%):

Table 1

b_c , mV	E_{corr} , mV	I_{corr} , mA/cm ²	Acid concentration in solution, M
<i>No inhibitor</i>			
109.6	-967.5	0.00539	-
<i>Phthalic acid</i>			
106.1	-926.7	0.00301	1.010 ⁻⁴
102.8	-921.2	0.00271	2.5-10 ⁻⁴
111.4	-898.2	0.00242	5.0-10 ⁻⁴
114.6	-886.9	0.00191	7.5-10 ⁻⁴
112.2	-846.2	0.00187	1.010 ⁻³
<i>Salicylic acid</i>			
108.5	-953.2	0.00375	1.010 ⁻⁴
106.8	-949.7	0.00298	2.5-10 ⁻⁴
108.2	-944.2	0.00279	5.0-10 ⁻⁴
109.3	-932.8	0.00248	7.5-10 ⁻⁴
107.5	-921.5	0.00190	1.010 ⁻³
<i>Benzoic acid</i>			
108.4	-938.6	0.00418	1.010 ⁻⁴
106.2	-725.2	0.00362	2.5-10 ⁻⁴
109.5	-922.7	0.00312	5.0-10 ⁻⁴
106.4	-911.5	0.00255	7.5-10 ⁻⁴
112.5	-707.3	0.00235	1.010 ⁻³
<i>o-Aminobenzoic acid</i>			
110.2	-960.2	0.00428	1.010 ⁻⁴
109.5	-955.4	0.00414	2.5-10 ⁻⁴
111.2	-915.2	0.00346	5.0-10 ⁻⁴
108.5	-909.7	0.00323	7.5-10 ⁻⁴
112.9	-784.5	0.00240	1.010 ⁻³
<i>Oxalic acid</i>			
108.4	-959.6	0.00432	1.010 ⁻⁴
112.7	-952.5	0.00428	2.5-10 ⁻⁴
106.7	-945.2	0.00365	5.0-10 ⁻⁴
110.9	-940.7	0.00335	7.5-10 ⁻⁴
107.6	-762.7	0.00261	1.010 ⁻³

0.333 C; 0.406 Si; 0.63 Mn; 0.017 P; 0.014 S; 0.064 Cr; 0.057 Ni; 0.002 Mo; 0.002 Al; 0.059 Cu; 0.017 Co; 0.001 Ti; 0.004 Nb; 0.001 V; 0.003 Pb; 0.001 Mg; 0.0025 B; 0.025 Sn; 0.019 Zn; 0.003 Ca; the remainder was iron. The rod was embedded in Araldite; the exposed area of the surface was 0.25 cm². To create an electrical contact, a thick copper wire was soldered to the end of the rod but not immersed in the solution. Before each experiment, the rod (i.e., the working electrode) was polished with emery paper down to formation of a mirror surface. After polishing, the electrode was washed with acetone and distilled water, and then dried.

A 0.01 M NaOH solution was used as a blank. Phthalic acid, salicylic acid, benzoic acid, *o*-aminobenzoic acid, and oxalic acid in a concentration ranging from 10⁻⁴ M to 10⁻³ M were added to the solution. Before each experiment, the previously polished working electrode was mounted in the cell containing the blank and subjected to cathodic treatment by holding the potential at -1.25 V relative to a saturated calomel electrode (SCE) for 15 minutes, in order to remove any oxide film from the surface.

All the polarization measurements were made in a three-compartment glass cell at a temperature of 25°C±1°C. A computer-controlled ACM Instruments Gill AC 875 (UK) was used for the potentiodynamic anodic polarization studies. The polarization curves were recorded in the range from -1.25 V to +1.25 V at scan rate 1 mV/s. A Joel JSM 50 scanning electron microscope was used to study the steel surface after exposure to the solutions.

Potentiodynamic anodic polarization measurements. Figure 1 shows the effect of the phthalic acid concentration on the potentiodynamic anodic polarization curves in a 0.01 M NaOH solution containing 0.01 M chloride anions. We see that in the absence of phthalic acid, the anodic polarization curve is characterized by a very low passivating current, followed by a sudden rise in the current at a characteristic potential. Scanning electron microscopy revealed the presence of pitting corrosion on the sample surface (Fig. 2a). The characteristic potential at which the current suddenly rises is defined as the pitting potential E_{pit} ; at this potential, the passivating film breaks down and pitting corrosion begins [35, 36].

Increasing the concentration of the studied organic acids shifts the pitting potential toward more positive values and leads to its increase; on micrographs of the steel surface, no pitting corrosion is observed and the presence of a surface layer is noted (Fig. 2b-f). Consequently, organic acids facilitate passivation and prevent pitting corrosion in the presence of chloride anions.

The dependence of the pitting potential on the logarithm logC of the molar concentration of the acids is shown in Fig. 3. As we see, the acids can be placed in the following order of their ability to shift the pitting potential toward more positive values (for the same concentration in solution):

phthalic acid > salicylic acid > benzoic acid > *o*-aminobenzoic acid > oxalic acid.

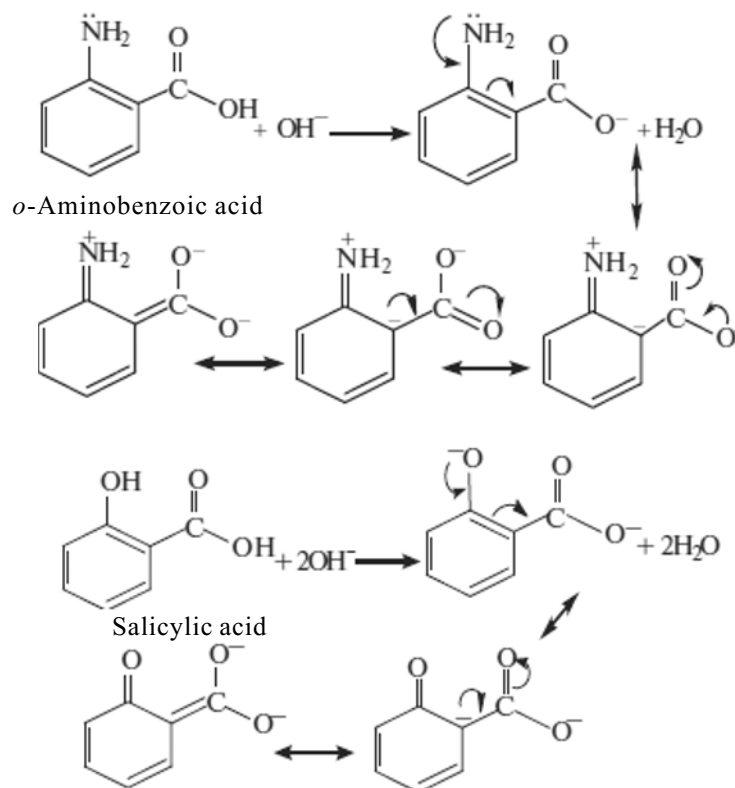
This order reflects the effectiveness of these acids as corrosion inhibitors. We can conclude that the size of the molecule and the type of substituent play a large role in the inhibition process [37, 38].

Tafel polarization. Figure 4 (Tafel plots) shows the results of measurement of the potentiodynamic cathodic and anodic polarization of steel electrodes in the absence of and in the presence of phthalic acid in different concentrations. The parameters of the corrosion process are summarized in Table 1. Increasing the concentration of any of the acids leads to a shift in the corrosion potential E_{corr} toward less negative values. Furthermore, we observe an appreciable shift in the anodic branches and a less appreciable shift in the cathodic branches toward lower current densities I_{corr} . The results of this series of experiments show that all the studied carboxylic acids reduce corrosion of carbon steel in alkaline medium containing Cl⁻ ions, and exhibit properties of mixed inhibitors with a predominantly anodic inhibition mechanism.

From Table 1, we see that the presence of the acids does not significantly change the slope of the cathodic branch, b_c . This suggests that the acids do not change the mechanism of the oxygen depolarization reaction. The inhibition mechanism involves simple blocking of reaction sites on the steel surface [38]. Increasing the concentration of all the acids results in a decrease in the corrosion current density I_{corr} . We can note that for identical concentrations, we can place the acids in a series in order of the extent of decrease in I_{corr} relative to the blank (no inhibitor), similar to that given above (according to their ability to shift the pitting potential toward more positive values).

The inhibition mechanism includes adsorption of the carboxylic acid molecules on the steel surface or the oxide film. Adsorption may occur due to formation of bonds between electrons of the d orbital of the iron atoms and the unshared electron pairs of the nitrogen and oxygen atoms in the inhibitor molecules. In general, adsorption is affected by the nature and surface charge of the metal, the type of aggressive medium, the chemical structure of the inhibitor and the number of functional groups in its molecule.

The studied carboxylic acids are not oxidizing agents. These acids contain the functional groups $-\text{COOH}$, $-\text{NH}_2$, and $-\text{OH}$. In alkaline medium, deprotonation of the $-\text{COOH}$ occurs, but the $-\text{NH}_2$ group and the $-\text{O}^-$ anion can exist as $=\text{N}^+\text{H}_2$ and $=\text{O}$:



Adsorption of *o*-aminobenzoic acid on the steel surface via the $=\text{N}^+\text{H}_2$ group is ruled out, since it is assumed that the oxide surface film on the steel contains Fe(III) cations and is positively charged, and so cannot interact with the positive charge on the acid molecule. As shown above, in the salicylic acid molecule the $-\text{O}^-$ anion cannot participate in adsorption on the steel surface because it is converted to the $=\text{O}$ group. Thus adsorption of the carboxylic acids on the steel surface occurs via the $-\text{COO}^-$ groups.

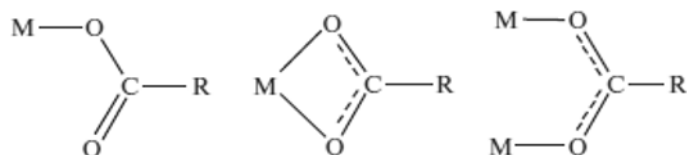
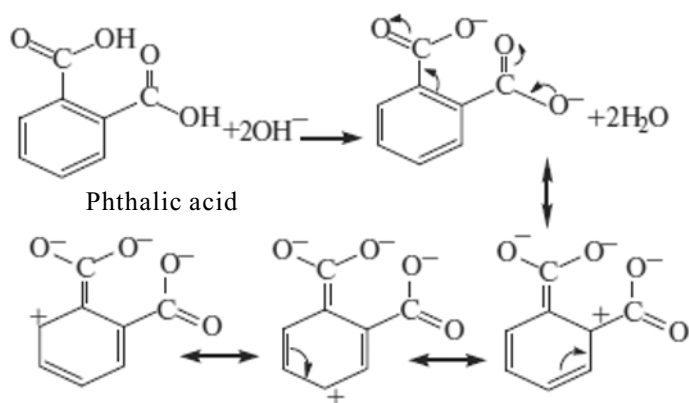


Fig. 5. Three types of complexes between the -COO^- group and a metal [39]

We know that the -COO^- group can participate in formation of three types of complexes with a metal surface [39] (Fig. 5). It is also reported [17, 40, 41] that surfaces containing metal ions (such as Fe(III)) included in an oxide film form complexes with ligand atoms such as oxygen. Consequently, the inhibiting effect of carboxylic acid anions involves their chemisorption on the iron oxide surface with formation of a strong protective film, reducing the reactivity of a significant number of iron atoms and facilitating passivation of the remaining atoms when exposed to oxygen and water. Therefore the presence of an oxide film facilitates adsorption of the acids and formation of a complex with Fe(III) ions. For complex formation, obviously the presence of a sufficient number of Fe(III) ions on the surface is important. The possibility of interaction between the acids and the oxide film and also the presence of Fe(III) ions in the oxide film are shown in [27, 40, 41]. Adsorption of the acids is facilitated by electrostatic interactions between the negatively charged oxygen atoms and the positively charged oxide film [27, 31, 38].

The effectiveness of the inhibitor depends on the electron density at the adsorption center (the -COO^- group). Higher electron density means a more effective inhibitor [27]. Accordingly, determination of the electron density on the -COO^- group of the studied acids is of interest. The electron density on the carboxyl group of salicylic acid is higher than on the same group in benzoic acid, which is due to the presence of the electron donor group -OH in the salicylic acid molecule. The two carboxyl groups of phthalic acid have higher electron density than the -COO^- group of salicylic acid, which is connected with the existence of two resonance structures. One -COO^- group is in resonance with the benzene ring and with itself, while the second group is in resonance only with itself:



The fact that phthalic acid is the most effective inhibitor among the studied acids may be due to the presence of two adsorption centers in the molecule. It has been reported [27, 38] that the inhibiting effect of organic compounds increases with the number of functional adsorption centers in their molecule.

The electron density on the carboxyl group of *o*-aminobenzoic acid is higher than on the carboxyl group of benzoic acid, due to the presence of the first electron-donor group -NH_2 in the molecule. However, its inhibiting effect is less than for benzoic acid, which is explained by intramolecular electrostatic interaction

between the $-\text{COO}^-$ and $-\text{NH}_2$ groups and a decrease in the interaction between the molecules of this acid and the surface of the oxide film.

Oxalic acid is the least effective corrosion inhibitor among the studied compounds, which is connected with the fact that this is an aliphatic acid with electron density on the carboxyl groups significantly lower than in aromatic acids. Furthermore, the small size of the oxalic acid molecule means less surface coverage by the inhibitor.

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