EFFECT OF THE NATURE OF CORROSIVE MEDIA ON THE RATE AND MECHANISM OF PROTECTION OF STEELS WITH AZINES

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We study the effect of polarity of substituents in quinolines on their inhibiting activity under the conditions of hydrogen-sulfide corrosion and generalize the data on the influence of the nature of corrosive (sulfuric-acid or hydrogen-sulfide-containing) media on the efficiency and mechanism of corrosion protection with amines.

As a promising approach to the solution of the problem of protection of metals against corrosion, one can mention the possibility of purposeful synthesis of corrosion inhibitors with required properties. Thus, the structure and protective efficiency of organic compounds are determined by the influence of the chemical nature of corrosive media on the rate of corrosion and the mechanism of inhibiting action of heterocyclic amines.

We studied the sensitivity of the polarity of substituents in derived azines (pyridines and quinolines) to changes in corrosive media as well as some specific features of the mechanisms of inhibition in different media. As model media, we used sulfuric acid (pH = 1) [1, 2] and hydrogen sulfide (pH = 5) [3]. As inhibitors, we studied quinoline and its derivatives: 2-methylquinoline, 4-methylquinoline, 6-methylquinoline, 8-methylquinoline, 8-oxyquinoline, 3-aminoquinoline, 3-chloroquinoline, 6-chloroquinoline, and 3-bromoquinoline. They were identified either by vacuum distillation or by repeated crystallization with subsequent determination of physical properties and their comparison with the literature data [4]. The rate of corrosion in specimens of 20 steel in the hydrogen-sulfide-containing medium was measured by using the method suggested in [5] for a concentration of the inhibitor C of $5 \cdot 10^{-3}$ mole/dm$^3$ and an area of the specimen surface $S$ of 7.2 m$^2$ at a testing temperature $t$ of 30°C for 20 h.

The process of inhibition [6] can be regarded as a reaction of nucleophilic substitution of hydrogen-sulfide corrosion by the derivatives of heterocyclic amines [7-9]. On the surface of the metal, we observe the formation of an intermediate adsorption complex. In this complex, the atom of iron may, probably, play a role of the electrophilic center in the reaction of nucleophilic substitution due to the presence of vacant d-orbitals. In the process of inhibition by substituted azines, the role of the nucleophilic center is played by the atom of nitrogen. The nucleophilic attack of the inhibitor which leads to the formation of a new covalent bond by an unshared electron pair of the atom of nitrogen and a free d-orbital of the atom of iron is described by the following relation:

$$\left[ Fe(H_2S)_{n+1} \right]_{ads} + \text{R} \rightarrow \left[ (H_2S)FeN \right]_{ads} + nH_2S.$$
This direction of the nucleophilic attack in the pyridine ring can be explained by the stability of the $\sigma$-complex formed in the course of the reaction.

In analyzing the protective action of azines, one must also take into account the specific features of the influence of corrosive media, in particular, the synergistic effect of hydrogen sulfide. This effect is explained by the fact that hydrosulfide ions adsorbed on the metal surface form dipoles whose negative ends are directed toward the solution which facilitates the adsorption of organic cations and the formation of surface complexes [8-9]. This approach makes it possible to take into account the chemical nature of the components of solutions and to develop efficient methods for the inhibition of hydrogen-sulfide corrosion of metals.

It is known that, in the case of inhibition of corrosion processes in steel placed in hydrogen-sulfide-containing media, the protective effect of substituted quinolines is stronger than that of the substituted pyridines with the same substituents. In this case, nucleophilic agents attack positions 2 and 4. This can be explained by the fact that, as a result of the electron-acceptor influence of the heteroatom, the electron density in the molecule of quinoline is not uniformly distributed and, moreover, in the pyridine ring, it is lower than in the benzene ring [10]. Therefore, under the action of nucleophilic agents, we observe substitution according to the pyridine cycle. As the electron-donor or electron-acceptor influence of substituents in the quinoline ring becomes more pronounced, its protective ability increases. The influence of substituents in substituted quinolines on their protective ability is described by the linear Brönsted equation both for the electron-donor (1) and electron-acceptor (2) substituents and the entire dependence is V-shaped (see Fig. 1):

$$\log \gamma = (-9.36 \pm 2.70) + (2.10 \pm 0.43) p K_{aw}$$

$$r = 0.952, \quad S_0 = 0.10, \quad n = 4,$$