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# STUDY OF 1,3-INDANDIONE DERIVATIVES FOR THEIR USE AS STEEL CORROSION INHIBITORS IN ACIDIC MEDIA

#### Assoc. Prof. Temenuzhka Haralanova, PhD

Department of Chemistry and Chemical Technologies, University of Ruse, Razgrad subsidiary, 7200 Razgrad, Bulgaria e-mail: tharalanova@uni-ruse.bg

#### Assist. Prof. Christian Girginov, PhD

Department of Physical Chemistry, University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria e-mail: girginov@uctm.edu

## Assist. Prof. Angel Dishliev, PhD

Department of Mathematics, University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria e-mail: adishliev@gmail.com

**Abstract:** The inhibiting properties of a group of organic substances (derivatives of 1,3-indandion) during the corrosion of steel in sulphuric acid solution  $(0.1 M H_2SO_4)$  have been studied by using a weight method. The present study has been conducted in corrosive solutions with and without the addition of potassium iodide (KI). As a criterion for the efficiency of the inhibiting action of the studied substances has been calculated the degree of protection (Z). It was determined that adding potassium iodide increases the degree of protection, i.e. the anti-corrosive properties of the studied compounds is enhanced.

*Keywords*: steel, inhibitors, derivatives of 1,3-indandion, corrosion rate

## **INTRODUCTION**

Low alloy carbon steels have very good functional properties and therefore are among the most commonly used structural materials. In their operation, the articles of these materials are almost always in contact with oxygen-containing media. Upon contact with such environments, in which almost always are present different chemical compounds, the steel products are subject to corrosion. It should be noted that carbon steels have low corrosion resistance. Moreover, aqueous solutions of various inorganic acids (H<sub>2</sub>SO<sub>4</sub>, HCl, H<sub>3</sub>PO<sub>4</sub>, etc.) are used in a large number of industrial technologies. In such cases, protection against corrosion is required using various inhibitors. The effect of most organic inhibitors is related to their adsorption to the surface of the metal. As a result the corrosion rates decrease and also the dissolution of corrosion products is hindered. The efficiency of the inhibitors to a large extent is determined by their concentration, the nature of the corrosive environment, the temperature and others. As a protection against corrosion of low-carbon steels in sulfuric acid media, a variety of organic compounds have been investigated (Chiang, K. & Mintz, T., 2008). As a model corrosion medium H<sub>2</sub>SO<sub>4</sub> is used with different concentrations: 0.1 M (Haralanova, T. et al., 2014, 2015, 2016, Abd El-Nabey, B. A., Khamis, E. M., & Shaban, A. E. 1986, Mehmeti, V., Kalcher, K., Podvorica, F., & Berisha, A., 2017, Zhou, Y., Guo, L., Zhang, S., Kaya, S., Luoa, X., & Xiang, B., 2017, Hao, Y., Sani, L. A., Ge, T., & Fang, Q., 2017), 0.5 M [Bammou, L., Belkhaouda, M., Salghi, R., Benali, O., Zarrouk, A., Zarrok, H. & B. Hammouti, 2014, Vashisht, H., Bahadur, I., Kumar, S., Goyal, M. S., Kaur, G., Singh, G., Katata-Seru, L. & Ebenso, E. E., 2016, Chidiebere, M. A., Oguzie, E. E., Liu, L., Li, Y. & Wang F. , 2015), 1 M (Haralanova, T. & Girginov, Ch. ,2015, Migahed, M.A., Azzam, E.M.S., & Al-Sabagh, A.M. 2004, Anusuya, N., Saranya, J., Sounthari, P., Zarrouk, A. & Chitra, S., 2017), etc. It

has recently been reported (Elayaperumal, K., & Raja, V. S., 2015) that in the presence of iodide ions, the metal surface (iron and steel) is recharged, which facilitates the adsorption of cation active compounds.

In the present study, the corrosion of low-carbon steel in acidic medium  $(0.1 \text{ M H}_2\text{SO}_4)$  was investigated in the presence of three 1,3-indandione derivatives, which were synthesized especially for this research.

## **EXPERIMENTAL**

All experiments were carried out in a thermostat, where the pre-set temperature (25°C) was kept constant with a precision of (±1°C). The samples were prepared from low-carbon steel with the following composition: [C] = 0.16; [Mn] = 0.65; [S] < 0.05; [P] < 0.04; [Ni] < 0.3; [Gr] < 0.3; [As] < 0.08; [Si] = 0.05 (in wt %), having a working surface of  $20 \times 10^{-4} m^2$ .

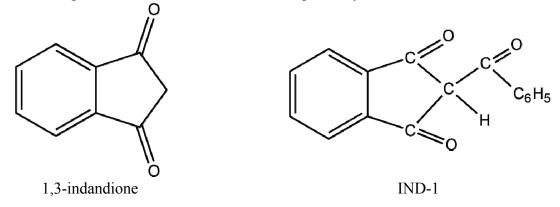
The corrosive medium used was a 0.1 M aqueous solution of  $H_2SO_4$  (Merck). As corrosion inhibitors three 1,3-indandione derivatives were studied in varying concentrations  $(0 - 4x10^{-4} mol dm^{-3})$ . These organic compounds were synthesized in the department of Chemistry and Chemical Technologies, University of Ruse "A. Kanchev", Razgrad subsidiary, by prof. N. Stoyanov, Ph.D.

Corrosion is usually studied by means of electrochemical methods (polarization curves, cyclic voltammetry, electrochemical impedance spectroscopy, etc.). In the present study however, the inhibitory action of the synthesized organic substances was evaluated by the conventional gravimetric method (Chiang, K. & Mintz, T., 2008). It is worth noting that in most cases there is a decrease, while in others an increase of the mass of the tested samples. In the current investigation only mass loss was found due to the good solubility of the corrosion products in the corrosive medium. Using this method, the weighed samples were introduced for a certain time (48 h) to the corrosive medium and were then removed, dried and re-weighed. The mass of the samples was measured before  $(m_0)$  and after (m) they were in the corrosive environment.

## **RESULTS AND DISCUSSION**

Steel samples were subjected to testing by exposure to corrosive media  $(0.1 \text{ M H}_2\text{SO}_4)$  in the presence of three types of 1,3-indandione derivatives, with different concentrations. For comparison, data were recorded in the absence of inhibitor, respectively.

Figure 1 presents the structural formulae of the used 1,3-indandione derivatives. These compounds were designated as IND-1, IND-2, IND-3, respectively.



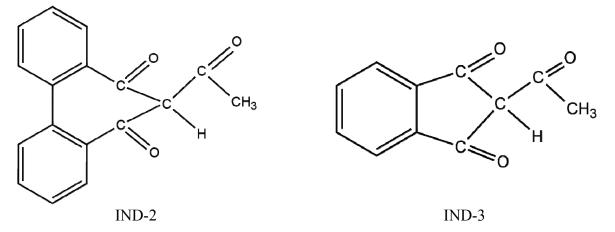


Fig. 1. Structural formulae of 1,3-indandione and its three investigated derivatives

Using the experimental data obtained by the gravimetric method the corrosion rate, the degree of inhibition protection and factor inhibition factor were all assessed.

**Corrosion rate** (k) The corrosion rate of the samples was determined as a function of the inhibitor concentration in the model corrosive environment. The corrosion rate value was calculated in accordance with the equation:

$$k = \frac{m_0 - m}{S \times t} \left[ g \, m^{-2} h^{-1} \right], \tag{1}$$

where with  $m_0[g]$  and m[g] are denoted the weight of the metal sample before and after the experiment, respectively,  $S[m^2]$  is the sample surface area and t[h] is the exposure duration (48 h) in the corrosive medium (0.1 M H<sub>2</sub>SO<sub>4</sub>).

Figure 2 shows the correlation of the corrosion rate (k), in the presence of the three investigated compounds, with inhibitor concentration.

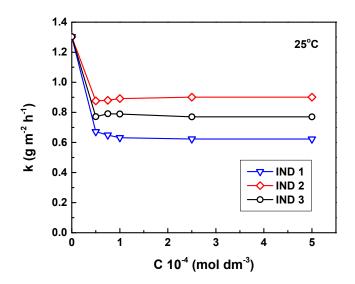


Fig. 2 Dependence of the corrosion rate as a function of the concentration of the three investigated organic compounds (25°C)

The obtained data on the corrosion rate show that these compounds demonstrate a certain inhibitory effect even at relatively low concentrations  $(<10^{-4} mol dm^{-3})$ . Above this concentration the corrosion rate practically does not change.

The experimental data analysis allowed the studied organic compounds to be ordered by their inhibitory effect: IND-1 > IND-3 > IND-2. The observed difference in the inhibitory effect of the various 1,3-indandione derivatives is probably due to the different structure of the functional groups, which in turn determines the energy of the chemisorption bond.

**Degree of protection** (Z) The degree of protection was calculated according to the equation:

$$Z = \frac{(k_0 - k)}{k_0} \times 100 \, [\%],$$
 (2)

where  $k_0$  is the corrosion rate of the metal in the corrosive environment without the addition of an inhibitor and k is the corrosion rate with addition of an organic compound.

It was of interest to evaluate the observed (Hao, Y., Sani, L. A., Ge, T., & Fang, Q., 2017, Vashisht, H., et al., 2016) effect of the  $(I^{1-})$ -ions, present in the corrosive medium on the adsorption capacity of the metallic surface, respectively on the value of the protection degree of the inhibitors. For this purpose, a certain amount of KI  $(7.5 \times 10^{-4} \text{ mol } dm^{-3})$  was introduced in the corrosive medium (0.1 M H<sub>2</sub>SO<sub>4</sub>). The results of the parallel investigations (corrosion environment with and without KI addition) are presented in Table 1.

Inhibitor	Z (%) (without addition of KI)	Z (%) (with addition of KJ)
IND-1	52.15	56.04
IND-2	30.80	60.41
IND-3	40.85	54.26

Table 1. Degree of protection (Z) values with and without addition of KI

The obtained results convincingly show that the presence of  $(I^{1-})$ -ions in the system significantly increases the value of the degree of protection for the investigated inhibitors. This effect is particularly noticeable for IND-2. For a more detailed explanation of these results, further studies on the adsorption of the organic compounds on the surface of the samples are necessary.

The inhibition action coefficient (Y) was also calculated:

$$Y = \frac{k_0}{k}.$$
 (3)

Logically, the obtained values correspond to the established efficiency of the inhibitors in the order: IND-1 > IND-3 > IND-2.

#### **CONCLUSIONS**

As a result of the conducted research, the following main conclusions can be drawn:

• The three investigated 1,3-indandione derivatives exhibit a good inhibition effect on samples in the studied corrosive environment  $(0.1 \text{ M H}_2\text{SO}_4)$ .

• The concentration of the inhibitors at which maximum protection is achieved, is relatively small:  $(<10^{-4} mol dm^{-3})$ .

• The presence of  $(I^{1-})$ -ions in the corrosion environment greatly improves the inhibitory effect of the studied organic compounds.

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## REFERENCES

Chiang, K. & Mintz, T. (2008) Techniques for Corrosion Monitoring, *A volume in Woodhead Publishing Series in Metals and Surface Engineering, Chapter 9 - Gravimetric techniques, p.* 247 – 264

Haralanova, T., Gigirnov, Ch. & Filipova, M. (2014) Investigation of the inhibition properties of 2-(4-substituted phenyl)-isoquinoline-1,3(2H)diones, *Science and Technologies* 4, p. 84-89

Haralanova, T. & Girginov, Ch. (2014) Investigation of the effect of inhibitory action of 5-[2-(methylsulfanyl)ethyl]-2-thioxoimidazolidin-4-one-methane (1:1) and 4-thioxoimidazolidin-2-one-cyclopentane (1:1) on the corrosion of steel in 2acidic environment *Proceedings University of Ruse* "Angel Kanchev" Chemical Technologies, 53, book (10.1), p. 137-141

Haralanova, T., & Girginov, Ch. (2015) Reducing the aggressiveness of sulfuric acid corrosion medium on steel by adding organic substances, *Proceedings University of Ruse "Angel Kanchev" Chemical Technologies*, 54, book (10.1), p. 79-83

Haralanova, T., Ilieva, M., & Girginov, Ch. (2016) Corrosion of low carbon steel in 0.1 M H<sub>2</sub>SO<sub>4</sub> with addition of D-5-isobutyl-mono-thiohydantoin, *Proceedings University of Ruse "Angel Kanchev" Chemical Technologies*, 55, book (10.1), p. 68-73

Abd El-Nabey, B. A., Khamis, E. M., & Shaban, A. E. (1986) Impedance studies of the inhibition of the corrosion of mild steel in 0.1M sulphuric acid with 10% methanol by thiosemicarbazide derivatives, *Surface and Coatings Technology* 28, p. 67 - 82

Mehmeti, V., Kalcher, K., Podvorica, F., & Berisha, A. (2017) Corrosion inhibition of mild steel in aqueous sulfuric acid solution using heterocyclic mercapto compounds - an experimental and theoretical study, *Radiation and Applications* 2, p. 41 - 45

Zhou, Y., Guo, L., Zhang, S., Kaya, S., Luoa, X., & Xiang, B. (2017) Corrosion control of mild steel in 0.1 M  $H_2SO_4$  solution by benzimidazole and its derivatives: an experimental and theoretical study, *RSC Advances* 7, p. 23961–23969

Hao, Y., Sani, L. A., Ge, T., & Fang, Q. (2017) The synergistic inhibition behaviour of tannic acid and iodide ions on mild steel in H<sub>2</sub>SO<sub>4</sub> solutions, *Corrosion Science* 123, p. 158 – 169

Bammou, L., Belkhaouda, M., Salghi, R., Benali, O., Zarrouk, A., Zarrok, H. & B. Hammouti (2014) Corrosion inhibition of steel in sulfuric acidic solution by the Chenopodium Ambrosioides Extracts, *Journal of the Association of Arab Universities for Basic and Applied Sciences* 16, p. 83 - 90 (Review article)

Vashisht, H., Bahadur, I., Kumar, S., Goyal, M. S., Kaur, G., Singh, G., Katata-Seru, L. & Ebenso, E. E. (2016) Synergistic interactions between tetra butyl phosphonium hydroxide and iodide ions on the mild steel surface for corrosion inhibition in acidic medium, *Journal of Molecular Liquids* 224, p. 19-29

Chidiebere, M. A., Oguzie, E. E., Liu, L., Li, Y. & Wang F. (2015) Ascorbic acid as corrosion inhibitor for Q235 mild steel in acidic environments, *Journal of Industrial and Engineering Chemistry* 26, p. 182 – 192

Haralanova, T. & Girginov, Ch. (2015) Organic compounds as inhibitors for mild steel in 1M H<sub>2</sub>SO<sub>4</sub>, *Chemistry: Bulgarian Journal of Science Education* 24, p. 397-403

Migahed, M.A., Azzam, E.M.S., & Al-Sabagh, A.M. (2004) Corrosion inhibition of mild steel in 1 M sulfuric acid solution using anionic surfactant, *Materials Chemistry and Physics* 85, p. 273 – 279

Anusuya, N., Saranya, J., Sounthari, P., Zarrouk, A. & Chitra, S. (2017) Corrosion inhibition and adsorption behaviour of some bis-pyrimidine derivatives on mild steel in acidic medium, *Journal of Molecular Liquids* 225, p. 406 - 417

Elayaperumal, K., & Raja, V. S. (2015), Corrosion Failures: Theory, Case Studies and Solutions ISBN: 978-0-470-45564-7.