Application of Petrochemical Heterocyclic Compounds as Corrosion Inhibitors

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Abstract. Theoretical concepts of inhibition mechanism in metal corrosion and forecasting of protective properties of substances are connected with experimental research of surface-active materials adsorption on metal surface. Application of petrochemicals, including intermediate products and petrochemical wastes for making new highly efficient and quite cheap corrosion inhibitors is promising. Research results of adsorption of some 1,3-diheterocycloalcanes-based compounds by method for measuring double-electric layer capacity appearing in “metal-electrolyte” interface in blank corrosion medium are reviewed herein. Therewith both blocking and energy effects of inhibitors are found to be the most efficient at first approach. Blocking effect is reducing area of metal surface affected by corrosion. Energy or \( \varphi_1 \)-effect occurs due to changing of double-electric layer structure in “metal-corrosion medium” interface. Adsorption results may be used to study corrosion inhibition mechanism by the analyzed compounds.

1. Introduction

Protection of metals against corrosion by inhibitors is based on properties of certain chemical compounds or compositions being added to corrosion medium in small quantities either to reduce rate of attack or absolutely inhibit the corrosion process [1]. Corrosion inhibitors are used in numerous facilities both in water supply systems and actually any energy installations, and protection of microelectronics and the newest military hardware. Given that metal corrosion damage exceeds 5% of the national product in the industrialized countries, making and application of inhibitors being one of major methods to prevent the corrosion should be considered as the urgent problem of modern science [2]. Inhibitors are changing the surface to be protected by absorption or formation of poorly-soluble compounds together with metal cations. Such compounds reduce the area of active surface of metal and/or increase corrosion activation energy which is of electrochemical nature in water environment as a rule [3, 4].

2. Materials and methods

Adsorption of organic inhibitor on the surface of the metal to be protected is [2, 5, 6] the essential condition of the first stage of protection thereof. Such polar groups as OH, SO\(_2\), SO\(_2\)NH\(_2\), SO\(_2\)NHR, SO\(_2\)NR\(_2\), NH\(_2\) and heteroatoms N, S and O play an important role in the process of absorption [7]. Both experimental and theoretical methods are applied to analyze absorption [8-11]. As inhibitors have complex composition and, as a rule, they are not individual chemical substances further experiments have been done using separate compounds that are basic components in the proposed inhibiting compositions. Let us analyze the results obtained with the following compounds of 1,3-
diheterocycloalcanes conditionally labeled as ADME; DDME; AFME; MDP; GDP; MFOZ; MFPOZ; KB.

The research has been done with samples made from St 3 construction steel, 20 quality carbon steel and 17G1S construction low-alloy steel. NACE (US National Association of Corrosion Engineers) blank medium saturated with hydrogen sulfide has been used as the working solution [12, 13]. Generally accepted corrosion testing procedure was used [14]. Adsorption of organic inhibiting compositions has been studied by method for measuring double-electric layer capacity appearing in “metal-electrolyte” interface (measurements were made using AC bridge P-5021) [15, 16].

3. Research
Analysis of inhibition mechanism of various compounds and making of new inhibitors thereunder enables us to expand inhibiting compositions range and to find the most efficient and technologically advanced ones among them. Theoretical concepts of inhibition mechanism in metal corrosion and forecasting of protective properties of substances are connected with experimental research of surface-active materials adsorption on metal surface [17, 18]. Application of petrochemicals, including intermediate products and petrochemical wastes is promising for making new highly efficient and quite cheap corrosion inhibitors [14, 15].

4. Theoretical
Adsorption isotherms of 4-hydroxymethyl-1,3-dioxolane alkyl esters may be described either by Frumkin equation

$$ B \cdot C = \frac{\theta}{1-\theta} \exp(-2a \cdot \theta) $$

or, by Temkin logarithmic equation:

$$ \theta = A + \frac{2.3}{f} \lg C, $$

where,

- $C$ – bulk concentration of inhibitors in corrosion medium, mol/l;
- $A, B$ – constants;
- $f$ – metal surface energy irregularity factor;
- $a$ – attraction constant;
- $\theta$ – coverage ratio of metal surface by inhibitor molecules.

Frumkin isotherm corresponds to inhibitor adsorption on uniform metal surface considering interaction of adsorbed particles in the adsorbed layer, while Temkin isotherm corresponds to adsorption on non-uniform metal surface with equal distribution of adsorbed centers along adsorption energies [6, 19].

To distinguish between these isotherms in describing adsorption of 4-hydroxymethyl-1,3-dioxolane alkyl esters, Podlovchenko and Damaskin criterion [20] has been used according to which values

$$ a = \frac{\partial \ln C}{\partial \theta} $$

and

$$ f = -2a \quad (\text{at } \theta = 0.5) $$

are to be calculated. Temkin isotherm is realized at $f_a \approx f_a$, while Frumkin isotherm - at $f_a > f_a \geq 4$, and the isotherms are indiscernible at $f_a \leq 4$. Proceeding from DDME calculation (Fig.1),

- $f_a = 6.9$;
- $a = -2.85$;
- $f_a = -2a = 5.9$; i.e. $f_a \approx f_a$. Therefore, adsorption of this compound may be described by modified Temkin equation, where attraction interaction on non-uniform surface is considered.

Within the studied concentrations ADME, AFME and MDP adsorption isotherms (see Fig.1) are linear in $\theta - \lg C$ coordinates thereby enabling to describe absorption thereof by Temkin equation

$$ B \cdot C = \exp (f \cdot \theta). $$
Frumkin isotherm is either realized at some approximation, e.g. for ADME at \( a = -3.2 \). Under calculation by Podlovchenko-Damaskin criterion we got \( f_a = 7.1; f_a = -2a = 6.4 \), i.e. \( f_a \approx f_a \). In case of AFME and MDP \( f_a \) and \( f_a \) are almost equal. Therefore, Temkin isotherm is realized under adsorption of these compounds on steel.

Analysis of adsorption data for MFOZ, MFPOZ, KB and GDP (Fig.2) has demonstrated that their absorption is realizing in accordance with Frumkin equation at \( a = 0.4 \) (for MFOZ); \( a = 0.6 \) (for KB) and at \( a = 0.55 \) (for GDP).

![Figure 1. Adsorption isotherms on steel: 1 – MDP; 2 – ADME; 3 – AFME; 4 – DDME.](image1)

![Figure 2. Adsorption isotherms: 1 – KB; 2 – GDP; 3 – MFOZ.](image2)

Consequently, ADME, DDME, AFME and MDP adsorption is described by Temkin equation thereby demonstrating chemisorption “inhibitor-metal” bond. Adsorption therewith is monomolecular and actually irreversible.
MFOZ, MFPOZ, KB and GDP adsorption is described by Frumkin isotherm (at $a>0$). Positive value of attraction constant means attractive interaction of inhibitor molecules in adsorption layer. Monomolecular occupation of the surface occurs therewith either.

Blocking and energy effects of inhibitors are found to be the most efficient at first approach when evaluating various factors affecting corrosion inhibition. Blocking effect is reducing vacant area of metal surface affected by corrosion. Energy or $\psi_1$-effect occurs due to changing both of double layer structure in “metal-corrosion medium” interface and adsorption $\psi_1$-potential in the presence of inhibitor.

According to [6] the corrosion inhibition process may be presented by comparing the values. Linear dependences $z$ on $\theta$, $\lg\gamma$ on $\theta$ and $\lg[\gamma(1 - \theta)]$ on $\theta$, accordingly are observed under blocking, energy or mixed (i.e. blocking and energy together) inhibition effects.

The indicated dependences to the studied compounds are given in Fig.3. When analyzing the obtained data $z$ and $\theta$ values are seen to be connected linearly when corrosion is inhibited by ADME, DDME, AFME and MDP compounds demonstrating blocking effect; while $\lg[\gamma(1 - \theta)]$ linearly depends on $\theta$, i.e. demonstrating both blocking and energy effects when applying MFOZ, MFPOZ, KB и GDP compounds.
Blocking inhibitors (ADME, DDME, AFME and MDP) decrease the corroding current by reducing the metal surface area where the cathodic reaction of hydrogen evolution takes place. Anode area therewith being constant, total corrosion rate is reducing [21].

Total corrosion inhibition under application of mixed inhibitors (MFOZ, MFPOZ, KB and GDP) may be achieved by blocking the surface as well as by some other effects increasing inhibition of composition which absorption is of specific or chemisorption interaction character [22].

5. Results

Petrochemical heterocyclic compounds are found to be efficient corrosion inhibitors with acetals and analogues thereof taken as an example. Main directions in finding new inhibiting compositions as well as increasing efficiency thereof may be defined by identifying the quantitative interaction between adsorption and inhibition.

6. References

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