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Petrochemical Compound-Based Corrosion Inhibitors

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Abstract. The results of applying intermediate products and petrochemical wastes for making corrosion inhibitors are analyzed herein. Behavior of a number of 1,3-diheterocycloalcanes-based corrosion inhibitors is reviewed. Analysis of corrosion-electrochemical test results with steel samples to be applied in oil and gas facilities construction has become the principal approach to this study. Kinetic parameters of cathodic reactions are found by analyzing Tafel sections of polarization curves taken in the blank medium while injecting various compounds thereto. Experimental criteria defining the mechanism of cathodic release of hydrogen both in uninhibited and inhibited acidic corrosive media are found. 1,3-dioxolane derivatives are not demonstrated to actually affect the cathodic reaction parameters but they are blocking inhibitors; while oxazines and carbamates are mixed inhibitors. The results of corrosion-electrochemical tests may be used to study the mechanism of the corrosion inhibition with the studied compounds.

1. Introduction

Nowadays the majority of industrial facilities of chemical, petrochemical, oil-production enterprises and refineries are complicated large-scale metal-intensive groups [1].

Importance of the problem under analysis is stipulated by the fact that protection of metals against corrosion over the last years has become global and international challenge [2]. Great losses of metals, numerous economic losses take place due to accidents in pipelines and industrial chemical and technological installations, etc. because of acceleration of corrosion processes. Therefore, actually all the developed countries of the world pay much attention to protection against corrosion in all manifestations thereof. Corrosion prevention is one of the most important problems in the Republic of Bashkortostan of the Russian Federation where much share belongs to chemical and petrochemical enterprises and due to extraction and refining of high-sulfur crude. Therewith most part of underground facilities and chemical-engineering equipment was manufactured at the time when there were no corrosion-resistant materials (or they were quite expensive). Now there are several directions of protection against corrosion [2, 3].

Engineering, manufacturing and application of corrosion-resistant materials for making pipelines, structures, manufacturing equipment, etc. are considered to be the most promising ones. Taking into account high value of new corrosion-resistant materials the researching engineers are engaged in selection of the most durable and efficient materials to be applied under certain conditions [4, 5].

Science has made great contribution to making corrosion-resistant coatings and methods and technologies for treating surfaces of materials exposed to aggressive action. The most popular in this direction are papers devoted to application of special compositions both to inner and outer surface of pipelines exposed to chemically aggressive media.

Electrochemical methods to protect engineering equipment and pipelines are widely applied. However, such methods do not result in metal loss decrease, although they greatly increase reliability of systems. In this respect the primary focus of a majority of scientists is on formation of new design for anode beds, determination of effective range thereof, optimization of number of cathodic protection stations and anode beds to decrease both energy- and metal losses.

Thorough analysis of accidents with pipelines and engineering equipment has revealed that it is the so-called "metal stress" sections that are greatly affected by the corrosion. Extra stress appears in bends, curves, buckles, welding spots, insulation defects, etc. Corrosion intensification because of mechanical loading and hereditary-type technological deformation - mechanochemical corrosion [6] – is stipulated by mechanochemical effect mainly caused by changes within the dislocation structure of metal occuring in the course of deformation. This kind of corrosion gave rise to a new direction in metal protection consisting of range of measures for making, engineering, manufacturing and operation of pipelines, structures and engineering equipment preventing metal stress.

Ufa State Petroleum Technological University together with Research Institute for fine chemicals and agents (NIIReaktiv) headed by Professor D.L.Rakhmankulov for more than 25 years have been engaged in studying methods for producing, analyzing reactivity and practical application of 1,3-diheterocycloalcanes, and 1,3-dioxanes, 1,3-tetrahydrooxazines, and others, in particular. Under results of the study many monographs and majority of reviews, over 1,000 research papers have been published both in Russia and abroad, over 1,000 author's certificates and patents have been received. One of practical applications of indicated compounds is using thereof as corrosion inhibitors [7, 8, 9].

2. Materials and methods

Some data to be obtained under corrosion-electrochemical and adsorption research are required to evaluate corrosion inhibitors activity [10-14]. As inhibitors have complex composition and, as a rule, they are not individual chemical substances further analysis has been done with application of separate compounds that are basic components in the proposed inhibiting compositions or simulate properties thereof. 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 widely applied in construction of oil-and-gas facilities.

Corrosion test and electrochemical measurements have been done at room temperature. NACE (US National Association of Corrosion Engineers) blank medium saturated with hydrogen sulfide has been used as the working solution. Generally accepted corrosion testing procedure was used [2, 7]. Polarization measurements have been taken in stationary electrode at potentiostatic mode using P-5827M potentiostat. Specially made electrochemical cell has been used for making electrochemical measurements [2, 7].

3. Research

Application of corrosion inhibitors combining high efficiency and optimum producibility of the process implementation is economically quite reasonable. There are no universal corrosion inhibitors, therefore new kinds thereof are to be actually made for each certain system. Intermediate products and different industrial wastes are often used nowadays for making inhibitors. Application of petrochemicals, including intermediate products and petrochemical wastes is promising for making new highly efficient and quite cheap corrosion inhibitors [2, 7].

4. Theoretical

Values of $\dfrac{\partial E_k}{\partial pH}$ and $\dfrac{\partial \lg i_k}{\partial pH}$ derivatives characterizing dependence of kinetic parameters of reaction on

pH medium are known [15-17] to be experimental criteria defining cathodic release of hydrogen both in uninhibited and inhibited acidic corrosive media. Main features of hydrogen release are thoroughly analyzed in summarized papers [17-19].

For instance, in slow-discharge theory $b_k = \dfrac{\partial E_k}{\partial \lg i_k} = 0.118$; $-\dfrac{\partial E_k}{\partial pH} = 0.118$; $-\dfrac{\partial \lg i_k}{\partial pH} = 1$. In slow-recombination theory at $b_k = 0.118 - \dfrac{\partial E_k}{\partial pH} = 0.059$; $-\dfrac{\partial \lg i_k}{\partial pH} = 0.5$.

In slow electrochemical desorption theory values of kinetic parameters of reactions are actually the same as in slow-discharge theory under quite high overpotentials [17].

5. Practical relevance, experimental results

Cathodic polarization curves that were used for calculation of kinetic parameters of the electrode process are given in Fig.1. Blank corrosion medium has been used as test medium.

Comparing calculated and experimental data indicated in Fig.1 it can be inferred that parameters of cathodic release of hydrogen in the test solution neither fully correspond to slow-discharge theory, nor to slow-recombination theory, although they are similar to requirements of the latter. The recombination mechanism is likely to be realized in the major part of the metal surface, while the discharge and desorption ones – in the other part thereof.
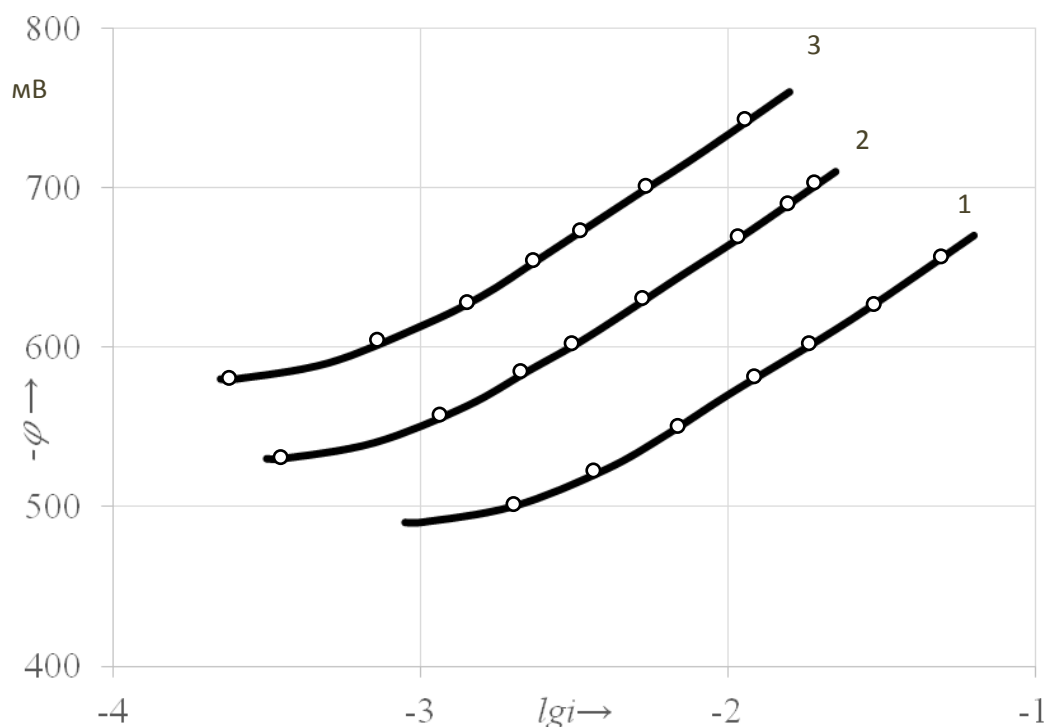

Figure 1. Cathodic polarization curves to 17G1S steel in blank corrosion medium at pH medium: *1 – 3.2; 2 – 2.2; 3 – 1.2.*

Polarization curves for the analyzed steel in inhibited ADME and MFPOZ blank solutions are given in Fig.2 and 3. The analyzed compounds are cathodic inhibitors according to the polarization curves analysis. Kinetic parameters of cathodic reaction (Table 1) are found by analyzing Tafel sections of the polarization curves taken in the blank medium while injecting various compounds thereto.
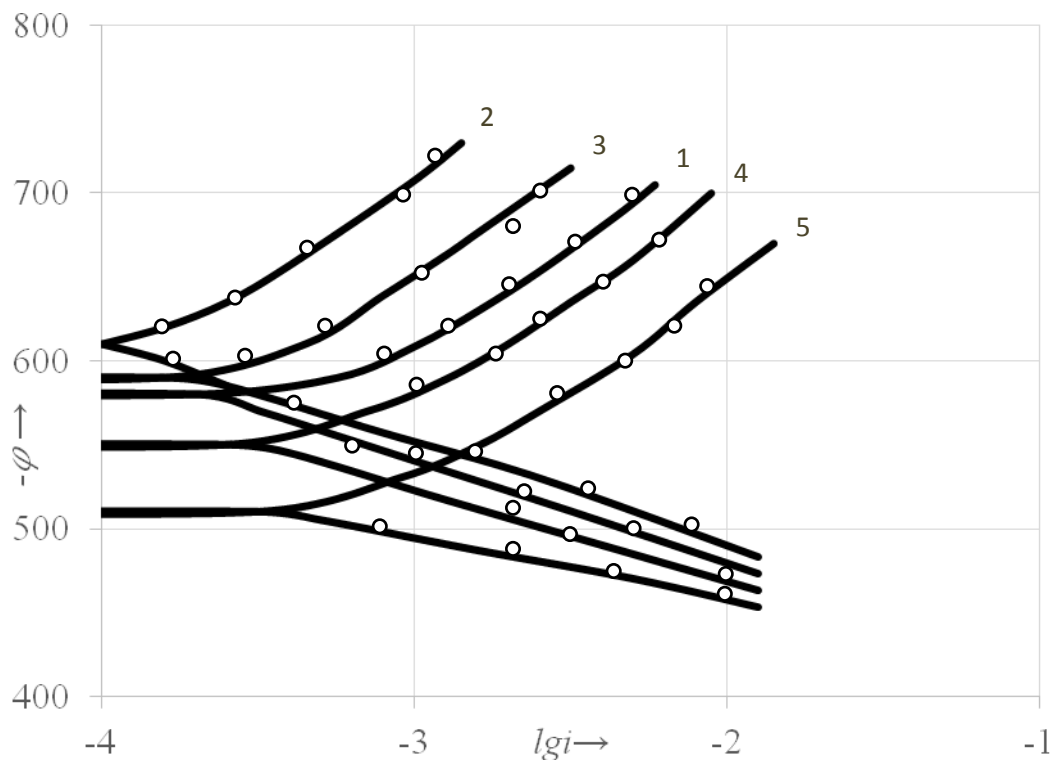
Figure 2. Polarization curves to 17G1S steel:
1 – in blank corrosion medium; 2, 3, 4, 5 – after adding ADME thereto; pH solutions: 1 and 2 – 3.2; 3 – 2.6; 4 – 1.8; 5 – 1.2.
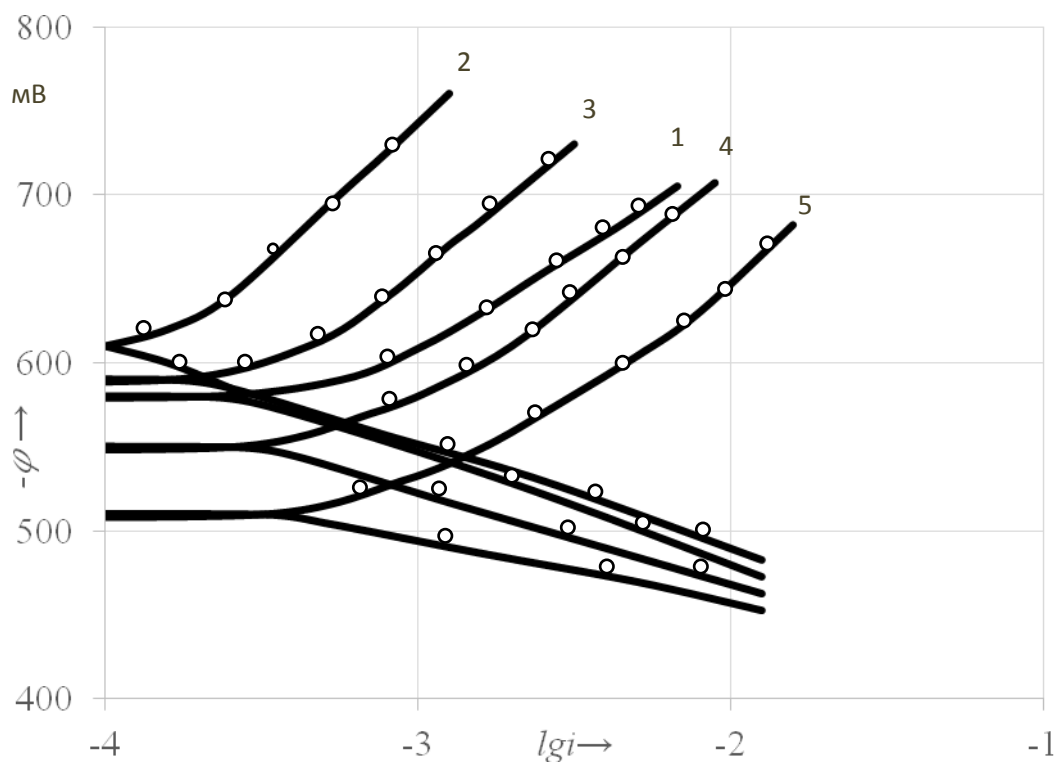

Figure 3. Polarization curves to 17G1S steel:
1 – in blank corrosion medium; 2, 3, 4, 5 – after adding MFPOZ thereto; pH solutions: 1 and 2 – 3.2; 3 – 2.6; 4 – 1.8; 5 – 1.2.

Table 1. Kinetic parameters of cathodic hydrogen for 17G1S steel.

	b_k	$-\dfrac{\partial E_k}{\partial pH}$	$-\dfrac{\partial \lg i_k}{\partial pH}$
Blank (corrosion medium)	0.120	0.080	0.64
After adding:			
ADME	0.125	0.085	0.67
DDME	0.125	0.089	0.69
AFME	0.124	0.082	0.65
MDP	0.126	0.086	0.68
MFOZ	0.135	0.112	0.76
MFPOZ	0.137	0.113	0.77
GDP	0.139	0.115	0.80
KB	0.142	0.118	0.82

ADME, DDME, AFME and MDP affect neither parameters of cathodic reaction, nor consequently hydrogen release mechanism. When adding MFOZ, MFPOZ, KB and GDP to corrosion medium values of kinetic parameters are similar to the calculated values in slow-discharge theory. In this case discharge step is likely to be limiting.

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 ψ_1-effect occurs due to changing both of double layer structure in "metal-corrosion medium" interface and adsorption ψ_1-potential in the presence of inhibitor.

Blocking inhibitors (ADME, DDME, AFME и MDP) do not change the reaction mechanism but simply reduce the area of the metal surface where the reaction is taking place [20].

When applying mixed inhibitors (MFOZ, MFPOZ, KB и GDP), corrosion current is also decreased because of inhibition of one of hydrogen release steps [21].

6. Results
Acetal compounds and heterocyclic compounds are found to be efficient corrosion inhibitors in acidic media. Corrosion electrochemical test results may be used to study corrosion inhibition mechanism by the analyzed compounds.

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