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Study of inhibiting properties of multicomponent systems in aggressive media in the presence of surfactants

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Abstract. The article discusses the anticorrosive properties of inorganic orthophosphate compositions in relation to St-3 steel in an oil-water environment in the presence of surfactants, depending on the pH of the medium, the nature and concentration of phosphate, the nature of the modifier ion. The research was conducted using State Standard-based methods: gravimetry, potentiometry, photocolourimetry, infrared spectroscopy and scanning electron microscopy. On the basis of experimental data, quantitative indicators of corrosion process were determined: the rate of corrosion process, the degree of protection, the depth index, the coefficient of inhibition and the assessment of the stability of the formed film on the ball scale of corrosion resistance against steel. The analysis of experimental data allows to establish the influence of the above factors on the corrosion processes in the systems under study. The experimental data are supplemented by thermodynamic calculations of the corrosion process parameters, the results of which correlate well with the kinetic data of the process under study. In the course of the research work, the analysis of corrosion deposits was also carried out. The regularities established during the work contribute to the creation of effective orthophosphate inhibitors with the highest degrees of protection.

1. Introduction

Oil industry equipment operates under extremely harsh conditions. The durability and reliability of the equipment largely depend on the technical and economic characteristics of the construction materials used. They have very high requirements: they must have a certain set of strength and plastic properties. In many cases, high requirements are placed on the corrosion resistance of the material [1, 2].

During the extraction and transportation of oil, due to the presence of water, hydrogen sulfide and carbon dioxide in it, and the resulting corrosion, great damage is caused to oilfield equipment and pipelines. Currently, various non-metallic and metallic coatings, corrosion inhibitors and electrochemical protection are used to protect equipment from corrosion [3].

The choice of a method of struggle is determined by its effectiveness and economic feasibility. In many cases, it is not possible to completely protect metals and metal structures from corrosion. In such cases, the protection of metals from corrosion is carried out by inhibitory protection. The development of environmentally friendly, low-toxic inhibitors that meet sanitary standards is becoming more urgent. It is known that inorganic phosphorus-containing compounds are of the greatest interest. Such compounds are very diverse in their structure, easily transportable, economically available and easy to process and store. These compounds are widely used in the oil industry.

The modern classification of inhibitors includes oxidants, complexing and polymeric inhibitors. This classification indicates the diversity of the action of inhibitors and the possibilities of using the



achievements of various fields of chemistry for the protection of metals. Therefore, the development of measures aimed at increasing the corrosion resistance of metals and products from them is a very urgent task [4].

2. Materials and methods

The purpose of this work is to study effective corrosion inhibitors of complex action in water-oil environment.

The following were studied as inhibitors: sodium orthophosphate Na_3PO_4 , sodium hydrophosphate Na_2HPO_4 , sodium dihydrophosphate NaH_2PO_4 . Divalent ions of copper, zinc and nickel were chosen as modifier ions. Sodium dodecyl sulfate was used as a surfactant. Evaluation of the effectiveness of the inhibitory action of individual substances and mixed compositions was carried out at the ratio of reagents in the mixture: 1:1, 1:2, 1:3, and 3:1 by the method of isomolar series.

The corrosion test procedure was generally accepted [5]. Rectangular steel plates $30 \times 20 \times 3$ mm in size were used. The duration of the experiments is 24-480 hours. The corrosion rate was estimated by the weight loss of the samples after 24, 48, 72, 96, 120, 240 hours.

Quantitative indicators of corrosion processes were calculated according to the formulas, the measurement uncertainty was estimated according to the algorithm, using the Student's coefficient with a confidence probability of 0.95 [6].

In the course of the work, potentiometric determinations of the pH of corrosive media were carried out using a combined glass electrode and ionomer, the conductometric method, and photocolometric determination of the iron (III) content with potassium thiocyanate [7, 8]. And also analyses of corrosion deposits were carried out on infra-red spectroscopy and scanning electron microscopy.

3. Results

36 multicomponent systems were constructed to study the inhibitory ability of phosphate compounds in the water-oil environment.

In model systems, the progress of reactions is evidenced by a change in the concentration of modifier ions, iron (III) ions, and phosphate ions. This dependence is also shown in figure 1 for the system with the nickel ion, where the efficiency of the inhibiting action is the highest.

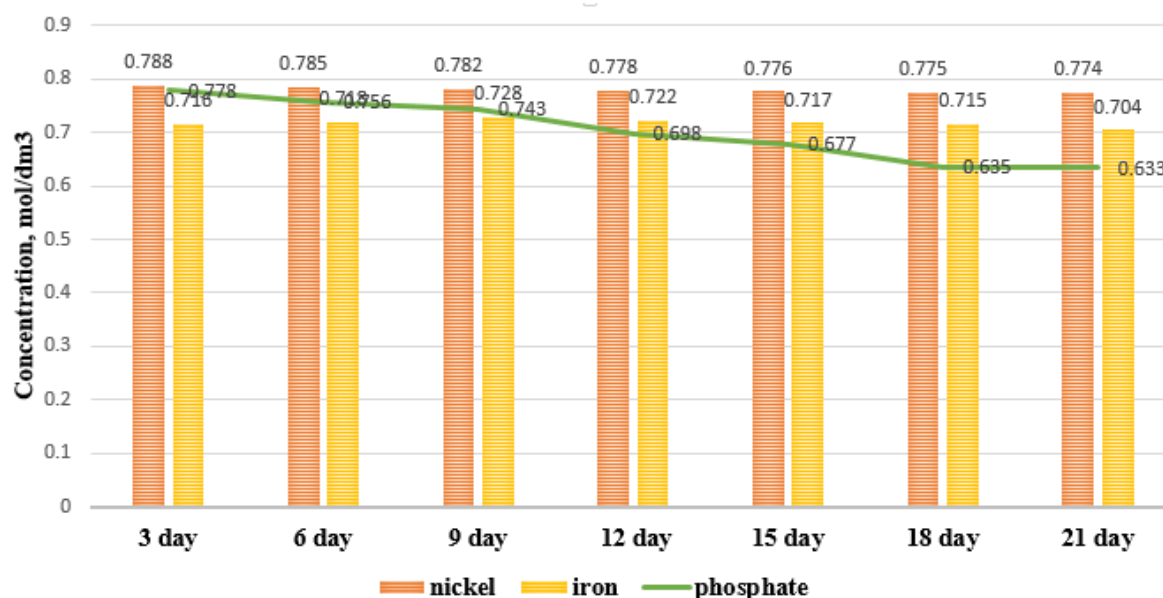


Figure 1. Dependence of the change in the concentration of the nickel, iron, and phosphate modifier ion on time for sodium dihydrogen phosphate.

As it can be seen from figure 1, at the initial stage, there is a gradual transition of iron from the plate to the solution in the form of ions. In the water-oil environment, the iron content gradually increases, but along with this, a decrease in the concentration of the modifier ion and phosphate ions is observed. After 12 days, a decrease in the iron content and a slowdown in the corrosion process are observed. These changes, apparently, are associated with the fact that the components of the system interact and form a certain stable compound that plays a protective role [9]. The formed compound on the plate was subsequently analyzed spectrometrically and by using a scanning electron microscope.

Along with this, the quantitative characteristics of the corrosion process in multicomponent phosphate systems were considered, which are shown in figure 2.

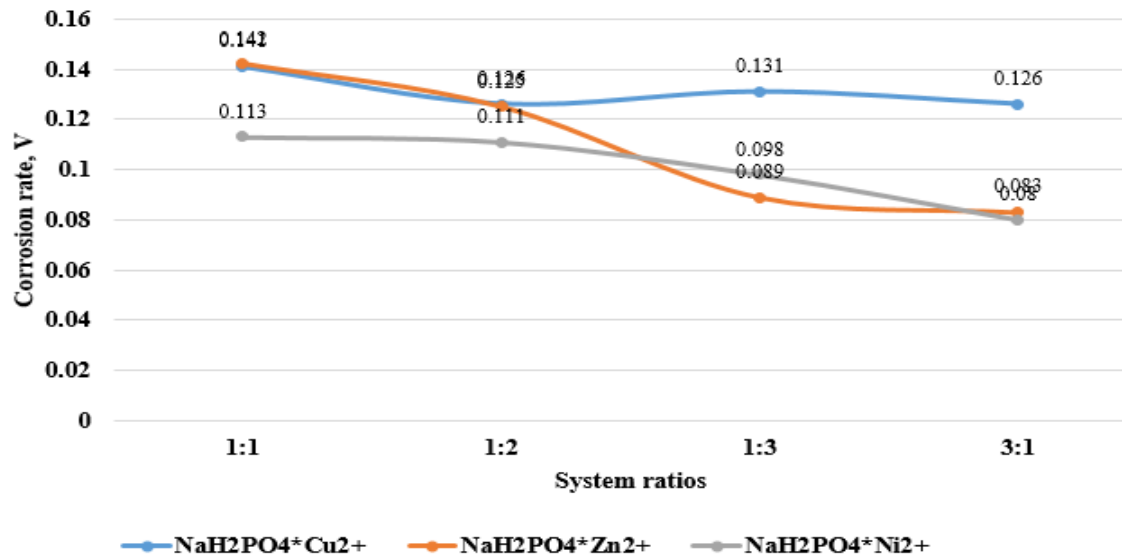


Figure 2. Dependence of the corrosion rate on the nature of phosphate at different ratios.

As it can be seen from the given dependence, in the system in the presence of a nickel modifier ion, the lowest value of the corrosion rate is characteristic of the NaH₂PO₄*Ni²⁺ composition at a ratio of 3:1. In this system, the degree of protection is 44.04%. In this system, the inhibitory effect is associated with the formation of a poorly soluble film on the surface of the metal to be protected.

Table 1. Basic thermodynamic parameters of multicomponent orthophosphate systems

Systems	$-\Delta G_{298.15}^0$, kJ/mol	ΔH , 10^{-5} kJ/mol	ΔS , 10^{-3} kJ/mol	lgK
Na ₃ PO ₄ *Ni ²⁺	48.06	4.8	161.26	8.44
Na ₂ HPO ₄ *Ni ²⁺	47.54	4.7	159.32	8.35
NaH ₂ PO ₄ *Ni ²⁺	68.61	6.8	229.91	12.05

Table 1 presents the thermodynamic characteristics of orthophosphate systems with ion modifiers. Based on the data obtained, it can be seen that the highest value of the Gibbs energy is characteristic of the NaH₂PO₄*Ni²⁺ composition at a ratio of 3:1. The higher the values of the Gibbs energy, the higher the inhibitory effect of the system.

To study the composition of corrosion deposits, analysis was carried out using an IR-spectrometer and a scanning electron microscope.

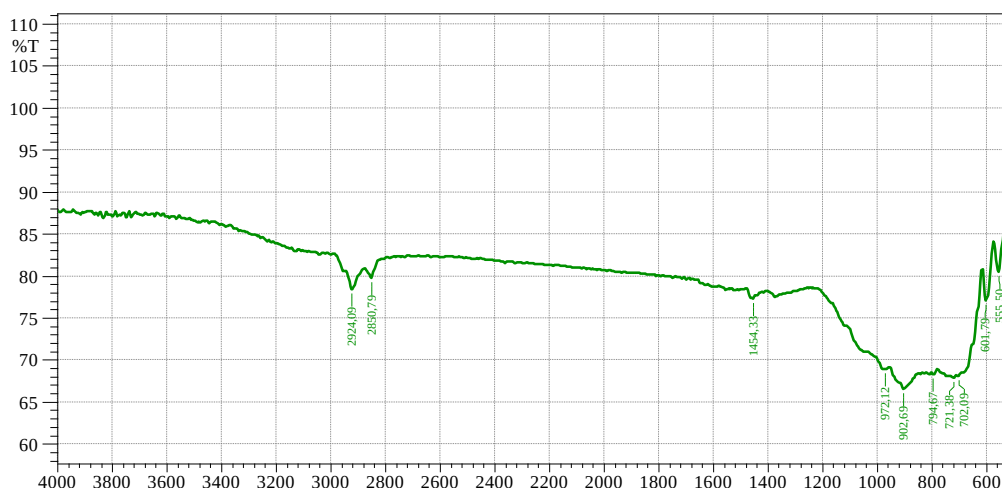


Figure 3. Analysis of corrosion deposition of sodium dihydrophosphate NaH_2PO_4 .

Figure 3 shows the spectrogram of the corrosion deposition of the sodium dihydrophosphate system with nickel at a ratio of 3:1. From literary sources it is known that sodium dihydrophosphate is characterized by bands at $1324, 1278, 1270 \text{ cm}^{-1}$ corresponding to asymmetric $\nu(\text{P}=\text{O})$, and the band at 1270 cm^{-1} are symmetric to $\nu(\text{P}=\text{O})$ vibrations. The $955\text{--}940 \text{ cm}^{-1}$ bands are asymmetric $\nu(\text{P}\text{--}\text{O}\text{--}\text{P})$, and the 1130 cm^{-1} band is symmetric to $\nu(\text{P}\text{--}\text{O}\text{--}\text{P})$ vibrations. In the IR spectrum of the corrosion deposit, the peaks are not similar to the data from the literature, which suggests that another compound was formed as a result, which forms a protective film [10].

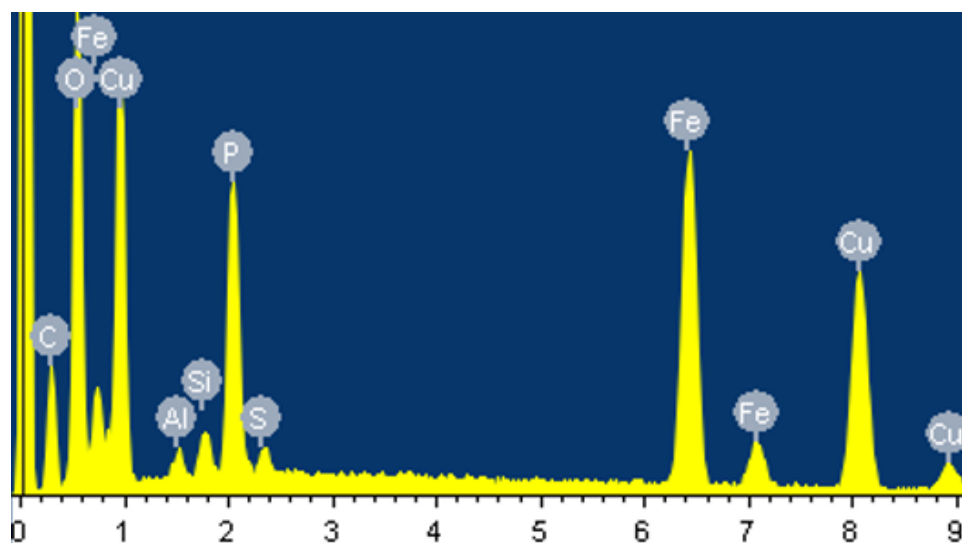


Figure 4. Spectral scale of elements for corrosion deposits of the composition $\text{NaH}_2\text{PO}_4 \cdot \text{Ni}^{2+}$ in a ratio of 3:1.

In the course of the study in a multicomponent system with sodium dihydrogen phosphate, the analysis of corrosion deposits on a scanning electron microscope was used. This analysis was carried out on a modern device - a JOOL JSM-6490 LV scanning low-vacuum electron microscope. The analysis showed that the corrosive deposits of this system contain oxygen - 22.96%, iron - 21.96%, phosphorus - 6.30%. Small amounts contain copper, silicon, carbon and aluminum.

4. Conclusion

Based on the obtained experimental data, the following conclusions can be drawn:

1. A series has been identified that demonstrate an increase in the tendency of systems to form stable phosphate compounds $\text{Zn}^{2+} < \text{Cu}^{2+} < \text{Ni}^{2+}$. The best modifying effect of the ions under consideration is

shown by the nickel ion. The nature of the modifier ions affects the change in the pH value of the medium in the studied phosphate systems towards the acidic side. In this regard, the formation of mixed and protonated complex compounds is possible, the stability of which is confirmed by thermodynamic parameters and kinetic parameters. The surfactant sodium dodecyl sulfate forms an adsorption layer due to negatively charged RCOO^- anions on the positively charged one on the metal surface [11].

2. Quantitative indicators of efficiency and thermodynamic parameters of multicomponent phosphate inhibitors have been determined: corrosion rate, depth index, degree of protection, corrosion resistance, Gibbs energy, stability constant. For the systems, the corrosion resistance was assessed in accordance with the State Standard 5272-90 based on the value of the depth corrosion index. The most effective system $\text{NaH}_2\text{PO}_4 \cdot \text{Ni}^{2+}$ has 4 points on the scale of resistance, which leads to low corrosion losses of steel [12, 13].

3. An effective modified inhibitor was established: $\text{NaH}_2\text{PO}_4 \cdot \text{Ni}^{2+}$. The degree of protection in this system is 44.04%. The compositions of corrosive deposits indicating the formation of stable protective films have been investigated by physicochemical methods.

Every year, manufacturers of far-abroad countries and the CIS announce new names for more effective metal corrosion inhibitors, however, for the industrial production of a certain product, an important factor is the cost of the product and its compliance with the requirements for chemical reagents. The solution of this problem is also relevant for Kazakh science, and in this regard, these studies have been conducted.

The patterns established during the work expand and supplement the existing understanding of the protective effect of compositions based on inorganic phosphate compounds. The data obtained make a certain contribution to the scientific direction of effective inhibitory protection of metals.

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