Phospholipids from plant materials as a corrosion inhibitor in oil production

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Abstract. The article presents the assessment results of carbon steel corrosion rate in 15% hydrochloric acid (aqueous solution) in the presence of phospholipids at 60 °C. The corrosion intensity was estimated from the rate of weight loss; the intensity of electrochemical corrosion was determined from the value of the corrosion current density. Phospholipids were isolated from vegetable oil waste. Surfactants of various operating principles were used as samples for comparison and enhancing the additives efficiency. It was found that the use of phospholipids under experimental conditions made it possible to provide protective properties up to 86.5% for phospholipids individually and up to 95% in a 50:50 mixture with a cationic surfactant.

1. Introduction

Acid treatments, based most often on hydrochloric acid solutions, are used in oil production processes to stimulate the inflow and combat difficulties. Due to high acid concentrations, metal corrosion processes occur very intensively, especially at high reservoir temperatures. Existing corrosion inhibitors, that are effective against hydrogen sulphide and carbon dioxide, may not provide the claimed degree of protection in highly concentrated acid, highly mineralized water and at high reservoir temperatures. Therefore, research aimed at the development of effective, inexpensive and environmentally friendly corrosion inhibitors is of particular relevance. Annually, the financial losses of the oil and gas industry due to corrosion processes amount to about USD 1.3 billion, more than USD 460 million of which are associated precisely with the processes of downhole equipment corrosion [1].

Application of toxic compounds of arsenic, ammonia, formaldehyde, and others acting as corrosion inhibitors for acid treatments has been reported, the use of which is now limited. In general, film-forming corrosion inhibitors are most widely applied in oil production processes, such as various nitrogen compounds, phosphoric acid esters, mercaptocarboxylic acids, sulfur-containing carboxylic acid esters, and others [2]. There is data on the corrosion-protective properties of complex structure substances containing nitrogen [3], sulfur, oxygen and phosphorus [4, 5], plant extracts [6, 7], for example, the use of phosphonates (organophosphorus compounds) as a new class of corrosion inhibitors is known [8]. Despite all the advantages (low toxicity, ability to protect steel in hard waters), phosphorus-containing complexones under certain conditions may be insufficiently effective and expensive. Thus, recently there has been a significantly increasing interest in the use of organophosphorus compounds and reagents from plant origins as carbon steel corrosion inhibitors. One of the natural sources of organic phosphorus compounds is phosphatide concentrate, which is a by-product of the oil and fat industry. For oil subjected to hydration, the rate of phosphatide concentrate formation is 0.8-1% per ton. Currently, phosphatide concentrate is used for the production
of lecithin aimed at using in perfumery and medical industries. Soybeans, sunflowers, and canola are the main sources of plant-based lecithin. In general, phospholipids are excellent surfactant amphiphilic molecules that are widely used as a wetting agent. Phospholipids (PL) are a subclass of lipids that usually consist of a glycerol backbone with positions 1, 2 linked to two fatty acyl groups via ester bonds. The third position of glycerol is associated with a phosphate group. The phosphate group carries two ester bonds with the main chain of glycerol and a polar head group such as choline, ethanolamine, inositol, serine, and glycerol [9]. PLs are surfactant wetting agents that can coat the surface of crystals to increase hydrophilicity. Depending on terms of use, PLs can act as cationic or anionic surfactants. Thus, the use of PL-based corrosion inhibitors will contribute to the creation of a hydrophilic protective film on the metal surface, which prevents the deposition of wax crystals and the formation of a deposits layer firmly attached to the surface of the metal to be protected.

2. Materials and methods.
Phosphatide concentrate of the Biysk Oil Extraction Plant was used as an object of research. PL from the phosphatide concentrate was isolated by sequential extraction with acetone, filtration, centrifugation, and distillation.

Surfactants (SAA) of various mechanisms of action were used as additives to PL: acetam C.70 (C12-C14 alkyltrimethylammonium chloride, cationic SAA, catapav (C16-C18 alkyldimethylbenzylammonium chloride, cationic surfactant), oxypav (tertiary amine oxides, nonionic surfactant), CP-20 (condensation products of mono- and dialkylphenols with ethylene oxide, nonionic surfactant), oleylamidopropyldimethylamine (a mixture of zwitterionic surfactant, oleylamidopropyldimethylamine and sodium chloride).

The corrosion intensity was determined on carbon steel plates (wt%: carbon - 0.2, silicon - 0.05-0.17, manganese - 0.5, nickel, copper, chromium - up to 0.2, arsenic up to 0.08, sulfur and phosphorus - up to 0.05 and 0.04, respectively, iron 98.3) sized 30x50x3 mm. Before testing, steel samples were subjected to cleaning, grinding, and degreasing. Experiments to assess the intensity of corrosion were carried out in a 15% aqueous solution of hydrochloric acid at 60 °C. The corrosion rate (V, g / cm²) was determined from the samples weight loss.

The rate of metal electrochemical corrosion was determined on similar steel plates by the value of the corrosion current density (I, A / m²) and the rate of electrochemical corrosion (K, g / m² * h). The model of the microelement was a galvanic cell that allows fixing the current strength and potentials of each electrode. The degree of inhibitors protection (Z, %) was calculated as the ratio of the difference in the corrosion rate of the sample series without an inhibitor and with an inhibitor to the corrosion rate of the sample series without an inhibitor.

3. Results
The dependence of the corrosion rate in 15% hydrochloric acid on the PL concentration is shown in figure 1, from which it follows that the optimal protective capacity at 60 °C is observed under inhibitor concentration of 300 mg / l and equals 86.44%.
Figure 1. Steel corrosion rate in 15% HCl solution added with phospholipids

For comparison, Table 1 presents the results of measuring the corrosion-protective properties of phospholipids and commercial surfactants in 15% HCl at 60 °C.

| Inhibitor                  | V (g/cm²*h) | Z (%)  |
|----------------------------|-------------|--------|
| PL                         | 0.0018      | 86.44  |
| acetam C.70                | 0.0020      | 85.64  |
| catapav                    | 0.0006      | 92.65  |
| oxypav                     | 0.0018      | 81.92  |
| CP-20                      | 0.0040      | 64.45  |
| leylamidopropyldimethylamine | 0.0031    | 75.01  |

It is known that the combined use of several individual substances can lead to a synergistic increase in efficiency. Consequently, synergistic mixed surfactant systems at the proper ratios have greater corrosion-protective efficacy and stability than individual surfactants. Thus, they can be a suitable tool for inhibiting corrosion processes. A number of experiments were carried out to assess the anticorrosive effectiveness of binary mixtures of surfactants and phospholipids as corrosion inhibitors. It has been observed that mixtures of surfactants exhibit significantly different characteristics from individual surfactants. Moreover, for binary surfactant systems, less active foaming is observed, and for some binary systems, complete absence of foaming, compared to individual ones when they are used in combination with phospholipids. During the experiment, it was found that in the ratio of 25/75%, the most effective were the binary systems PL / acetam C.70 (Z = 93.85%), PL / catapav (Z = 94.57%). It was found that in the PL / oleylamidopropyldimethylamine and PL / CP-20 systems, weak foaming is observed. In a 50:50% ratio, the most effective systems are PL / catapav (Z = 94.78%), PL / oxypav (Z = 86.69%). It was also revealed that in the PL / oleylamidopropyldimethylamine and PL / CP-20 systems, no foaming is observed at this ratio. In the ratio of 75:25%, the PL / catapav systems (Z = 93.74%), PL / acetam C.70 (Z = 90.18%) showed the highest protective ability. Foaming is not observed in PL / oleylamidopropyldimethylamine and PL / CP-20 systems. It was found that in the presence of 50% PL in systems with active foaming, foaming is absent. Thus, PLs have antifoam properties. When determining the anticorrosive efficiency of binary systems containing phospholipids
applying a microelement model it was found that the introduction of phospholipids into the system leads to a decrease in the density of the corrosion current and a slowdown in the rate of electrochemical corrosion (table 2).

Table 2. Results of measurements of electrochemical corrosion rate in 15% HCl added with the binary mixtures of surfactants and PL.

| Content                                   | Ratio, wt%: | I, A/m² | K, g/m²*h |
|-------------------------------------------|-------------|---------|-----------|
| PL / acetam C.70                          | 25/75       | 0.176   | 0.362     |
| PL / acetam C.70                          | 50/50       | 0.156   | 0.321     |
| PL / acetam C.70                          | 75/25       | 0.160   | 0.328     |
| PL / catapav                              | 25/75       | 0.159   | 0.328     |
| PL / catapav                              | 50/50       | 0.156   | 0.321     |
| PL / catapav                              | 75/25       | 0.169   | 0.351     |
| PL / catapav                              | 25/75       | 0.179   | 0.371     |
| PL / catapav                              | 50/50       | 0.177   | 0.370     |
| PL / catapav                              | 75/25       | 0.175   | 0.362     |
| PL / CP-20                                | 25/75       | 0.173   | 0.355     |
| PL / CP-20                                | 50/50       | 0.169   | 0.348     |
| PL /CP-20                                 | 75/25       | 0.166   | 0.341     |
| PL / oleylamidopropyl(dimethyl)amine      | 25/75       | 0.173   | 0.410     |
| PL / oleylamidopropyl(dimethyl)amine      | 50/50       | 0.166   | 0.341     |
| PL / oleylamidopropyl(dimethyl)amine      | 75/25       | 0.183   | 0.376     |

4. Conclusion
As a result of gravimetric measurements and anti-corrosion tests carried out on the model of a microelement, it was shown that phospholipids isolated from oil production waste possess corrosion protective properties. It was found that the maximum protective properties are observed at a PL concentration of 300 mg/l. It has been shown that when using binary systems of phospholipids with surfactants at 60 °C in a 15% hydrochloric acid aqueous solution, the highest degree of protection is observed up to 95% (PL: catapav in the ratio of 50:50 wt%), which is much higher than protective ability of individual components. In some cases, the introduction of phospholipids into the system reduced foaming or completely eliminated it.

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