

## Mg(II) and Zn(II) complexonates with a 1,3-diamino-2-propanol phosphorus-containing derivative as corrosion and scaling inhibitors

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### Abstract

Based on IOMS-1, an available, rather inexpensive and rather popular domestic scaling inhibitor used for stabilization treatment of water utilisation systems at industrial plants, small and large power plants and in utility systems, a new formulation has been developed that meets the requirements for phosphonate-based formulations of this type. In order to increase the scaling inhibition activity and ensure the ability to inhibit the corrosion of metals, rather small amounts of diaminopropanolmethylphosphonic acids (DPP) and their Zn(II) and Mg(II) complexes that showed high inhibitive capability were added to the formulation. Estimation of the effect of the DPP:metal molar ratio on the corrosion rate at various temperatures has shown that the maximum efficiency of corrosion inhibition is achieved at a DPP:Me molar ratio of 3:1–2:1 and with the DPP–Mg complexonate. In such case, the corrosion rate decreases with an increase in temperature, whereas it increases by about 8–10% per each 10°C in the absence of complexonates. Since the use of DPP alone is economically unjustified, the efficiency of formulations obtained at various IOMS-1:DPP–Mg molar ratios was studied. A high inhibitive activity both for scaling and corrosion was found at the molar ratio of the reagents of 3:1, respectively. The maximum scaling inhibition similar to that of DPP was achieved without lowering the cost efficiency of the new formulation compared to IOMS-1.

**Keywords:** formulation, IOMS-1, diaminopropanolmethylphosphonic acids (DPP), Zn(II) and Mg(II) complexes of DPP, ratio of components, scale inhibitor, corrosion inhibitor, efficiency estimation.

## Introduction

The issue of creating new reagents that can prevent metal corrosion and scale formation in pipelines of water distribution systems and processing equipment continues to be relevant [1, 2].

Priority in this field is given to well-known organophosphonates (OP) and formulations based on these compounds. Only a few publications deal with new reagents. For example, an ethylene diamine based inhibitor, which contains phosphono, sulfo and carboxy groups simultaneously, was shown to exhibit high efficiency. Phosphonoalkylsulfonic acids were also patented [3].

In our opinion, despite the high practical importance of such inhibitors, they cannot be used on a wide scale due to difficulties in the implementation of their production.

On the other hand, it is possible to use such reagents as additives to well-known formulations. In this case, they will be capable of providing not only an increase in their inhibitory activity but also a low price, owing to which their application seems appropriate [4].

Aliphatic amine derivatives containing both phosphono and hydroxy groups were also found to be of great interest [5].

Russian scientists synthesized a similar reagent based on 1,3-diamino-2-propanol [6], which was assigned the structure of 1,3-diamino-2-propanol-*N,N,N',N'*-tetra-(methylphosphonic acid) (DPTP) based on the results of IR spectroscopic studies. This reagent was found to be superior to foreign analogs in scale inhibition efficiency [7].

For the first time, we have found from NMR<sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} spectra that the resulting product, like in the case of aliphatic amine derivatives [8–11], is a mixture of diaminopropanolmethylphosphonic acids (DPP) that contains DPTP and its inner ester [12, 13].

The purpose of this work was to use DPP as well as Mg(II) and Zn(II) complexes of the acids contained in DPP, as part of a new formulation based on IOMS-1 scale inhibitor in order to enhance both the scale and corrosion inhibition performance.

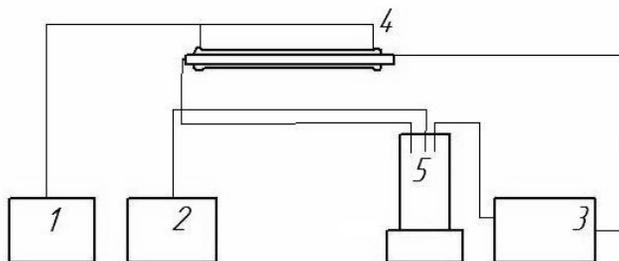
## Experimental

In this work we used an aqueous solution of DPP, which was prepared according to the procedure described in [14].

Diaminopropanolmethylphosphonic acids (DPP) and DPP-based formulations with IOMS-1 as the main active component were tested as inhibitors of both scale formation (CaCO<sub>3</sub>, CaSO<sub>4</sub>) and corrosion of structural steel St.3 and non-ferrous metals. It should be noted that many researchers have recognized IOMS-1 as an efficient scale inhibitor [15–19].

The efficiency of calcium sulfate scale inhibition in a supersaturated salt solution was estimated by determining the residual content of calcium ions *via* complexometric titration [20], which was carried out after salt crystallization in the presence of both DPP and DPP-based formulations.

Both corrosion inhibition and calcium carbonate precipitation inhibition were examined simultaneously as a function of the concentrations of DPP and DPP-based formulations using a setup developed in our research group. As shown in Figure 1, the setup consists of a thermostat (1), a corrosimeter (2), a peristaltic pump (3), a heat-exchange unit (4), and a container filled with water that was treated with a reagent (5).



**Figure 1.** The scheme of a setup for simultaneous determination of corrosion and scaling rates.

The corrosion rate was determined using an Expert-004 corrosimeter operating in a real-time mode, by measuring the polarization resistance with the use of electrodes made of St.3 steel and L60 brass that were immersed in the test solution. The amount of precipitated calcium carbonate was estimated by dissolving the precipitate formed on the tube of the heat exchanger in 0.1 N HCl solution followed by complexometric titration of calcium ions in the resulting solution by a standard method, as described in [20].

The model water environment for the tests was prepared by mixing equal volumes of solutions:

solution 1:  $\text{CaCl}_2 - 2.92 \text{ g/dm}^3$ ,  $\text{NaCl} - 40.6 \text{ g/dm}^3$ ,  $\text{MgSO}_4 - 4.26 \text{ g/dm}^3$ ;

solution 2:  $\text{NaHCO}_3 - 2.4 \text{ g/dm}^3$ .

The duration of the experiment was 3 h, and the temperature was within 70–90°C. The reagents were added as 0.1% solutions to concentrations of 2–6 mg/l (with respect to 100% product).

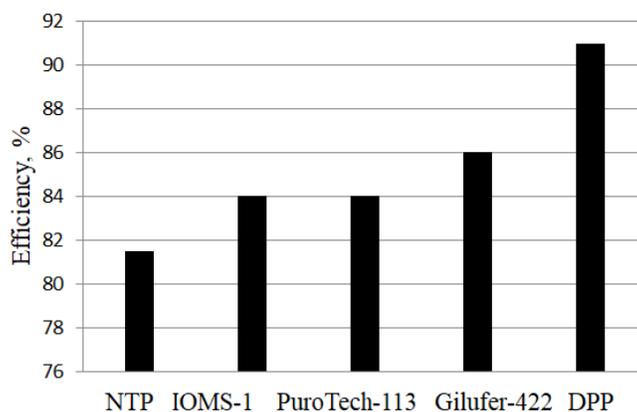
The test results for DPP were compared with the efficiency of foreign reagents intended for similar purposes.

To ensure anti-corrosion efficiency, we used the DPP complexonates with divalent Zn and Mg ions the components of the new formulations.

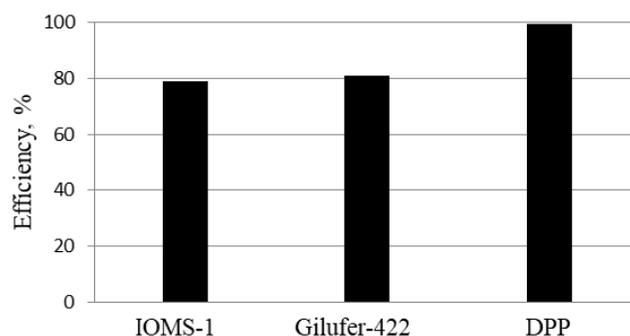
The efficiency of corrosion and scale inhibition was traditionally estimated through a decrease in the parameters indicated above in the blank experiments and in experiments with a reagent [21].

## Results and discussion

Figures 2 and 3 show the data on the efficiency of DPP as a scale inhibitor compared to domestic and foreign reagents for similar purposes.



**Figure 2.** Inhibitory efficiency against CaSO<sub>4</sub> precipitation in the presence of DPP and domestic and foreign inhibitors used for similar purposes.



**Figure 3.** Inhibitory efficiency against CaCO<sub>3</sub> precipitation in the presence of DPP and domestic and foreign inhibitors used for similar purposes.

An optimal DPP:Me molar ratio was determined by estimating the efficiency of DPP–Me (Zn, Mg) formulation as corrosion inhibitors, based on the anti-corrosion activity data obtained for a series of compounds containing various amounts of Me (Table 1).

**Table 1.** Anticorrosion activity of the DPP–Me formulation depending on the Me content.

Reagent	Molar ratio	Corrosion rate, $\mu\text{m}/\text{year}$	Efficiency, %
Control		201	0
DPP:Zn	5:1	140	30.3
	4:1	136	32.3
	3:1	63	68.7
	2:1	48	76.1
DPP:Mg	5:1	155	22.9
	4:1	130	35.3
	3:1	64	68.1
	2:1	48	76.1

The choice of Zn(II) is quite apparent: it is well known that Zn(II) as a component of the OP-based formulations makes them capable of corrosion inhibition [1, 2]. However, the use of Zn-containing reagents leads to some environmental stress. Recently, this problem has been successfully resolved by replacing Zn(II) with Ca(II) and Mg(II) [22, 23].

Table 2 summarizes data on the inhibitory efficiency against both corrosion and CaCO<sub>3</sub> precipitation in the presence of the DPP-Zn formulation and the Option 313-1 inhibitor (hydroxyethylidenediphosphonic acid (HEDP) – Zn) produced in Russia. The results indicated the efficiency of the DPP-Zn formulation as a corrosion inhibitor, which is higher than that of Option 313-3. Moreover, the DPP-Zn formulation was found to be a very efficient scale inhibitor.

**Table 2.** Dependence of inhibitory efficiency against corrosion and calcium carbonate precipitation on the working concentration of the DPP-Zn formulation and the Option 313-1 inhibitor used for similar purposes.

Reagent	Concentration of reagent, mg/L	Amount of precipitate, mg	Inhibitory efficiency against scaling, %	Corrosion rate, μm/year	Inhibitory efficiency against corrosion, %
Control	–	36	0	390	0
Option 313-1 (HEDP-Zn)	5	3.5	90.0	210	43.8
	10	4.0	88.8	135	65
	20	3.2	91.0	71	80.2
DPP:Zn (2.5:1 mol)	5	2.0	94.4	151	60.1
	10	1.5	95.8	109	70.2
	20	0.9	97.7	42	89.2

As follows from the test results, DPP used as a scale and corrosion inhibitor surpasses the domestic and foreign inhibitors for the similar purposes for the given chemical compositions of model aqueous solutions and experimental temperatures (Figures 2 and 3, Table 2). It should be noted that with an increase in the working concentration from 5 to 20 mg/l, the efficiency of the DPP formulation as a scale inhibitor increases from 94 to 97%, whereas the efficiency of HEDP–Zn remains almost unchanged (90–91%).

In our opinion, one of the reasons is probably the ability of DPP to form more stable complexes with iron ions compared to that formed by HEDP. Upon hydrolysis, these complexes reduce the efficiency of scaling inhibition. The high efficiency of this reagent makes it very promising for applications not only in “clean” recirculating water supply systems but also in “dirty” recirculating systems of metallurgical and oil industries that are characterized by a high content of salts, various forms of iron, and the presence of suspended impurities.

It should be noted that the corrosion rate decreases in the presence of the DPP–Me (Zn, Mg) formulation but increases by 8–10% with a temperature increase by each 10°C in the absence of the inhibitor. Moreover, the DPP–Mg formulation is not inferior to DPP–Zn in efficiency (the tests were carried out within a temperature range of 70–90°C in the model water environment, see Table 3).

**Table 3.** Effect of DPP–Me formulations as the reagents for stabilization treatment of model water medium on both the corrosion rate and scale formation.

Reagent	Temperature, °C	Concentration, mg/l	Corrosion rate, $\mu\text{m}/\text{year}$	Amount of precipitate, mg
Control	70	–	567.3	45.4
	80		612.1	47
	90		652.7	47.2
DPP:Mg	70	30	123.1	4.5
	80		100.9	4
	90		84	4.1
DPP:Mg	70	50	93.2	4
	80		83.1	4.3
	90		54	3.6
DPP:Zn	70	30	130.8	4.6
	80		105.9	4.1
	90		81.5	3.9
DPP:Zn	70	50	110	4.1
	80		91	4.0
	90		78	4.1

The efficiency of the IOMS-3 formulation as a scale and corrosion inhibitor was examined by varying the molar ratio of its components (IOMS-1:DPP–Mg) in order to determine the optimal composition of IOMS-3 (Tables 4 and 5).

The efficiency of IOMS-3 as the  $\text{CaSO}_4$  precipitation inhibitor was determined at reagent working concentration of 2(3) mg/l and 2.5 mg/l concentration of  $\text{CaCO}_3$  (with respect to 100% of the product).

As follows from Tables 4 and 5, both the IOMS-1 and DPP–Mg-based formulations exhibit high inhibiting activity against scale and corrosion. The IOMS-1:(DPP–Mg) molar ratio of (1–3):1 (respectively) in the IOMS-3-based formulation provides a high degree of inhibitory performance, which slightly decreases on passage to the 4:1 ratio, and increases at the ratio of 5:1.

**Table 4.** Inhibitory efficiency of IOMS-3 against precipitation of calcium salts depending on the molar ratio of its components.

IOMS-1:(DPP–Mg) molar ratio	Inhibitory efficiency of IOMS-3 against CaSO <sub>4</sub> precipitation, %	Inhibitory efficiency of IOMS-3 against CaCO <sub>3</sub> precipitation, %
1:0	84.0	79.0
1:1	93.0	70.0
	96.5	99.0
2:1	92.3	70.5
	96.0	98.5
3:1	92.0	68.0
	96.0	98.5
4:1	90.5	66.0
	94.0	98.0

**Table 5.** Inhibitory efficiency of IOMS-3 against corrosion and scaling (at 90°C) depending on the concentration of the working solution and molar ratios of its components.

IOMS-1:(DPP–Mg) molar ratio	Concentration of a 20% inhibitor solution, mg/L	Corrosion rate, $\mu\text{m}/\text{year}$	Amount of precipitate, mg	Inhibitory efficiency against corrosion, %	Inhibitory efficiency against scale, %
control	–	652.7	47.2	–	–
1:0	50	620.5	9.4	4.9	80.1
1:1	30	82.6	1.0	87	98.9
	50	52.0	0.6	92	98.7
2:1	30	83.2	1.1	87.3	97.7
	50	53.5	0.7	91.8	98.5
3:1	30	84	1.0	87.1	97.9
	50	54	0.7	91.7	98.5
4:1	30	102.3	1.9	84.3	96
	50	78	1.6	88	96.6
5:1	30	128.5	2.5	80.3	94.7
	50	95.2	2.0	85.4	95.8

## Conclusions

1,3-Diamino-2-hydroxypropanolmethylphosphonic acids, together with their Mg and Zn complexes, were suggested as synergistic additives in the new IOMS-3 formulation based on IOMS-1, an efficient commercial inhibitor of scaling.

We estimated the optimal molar ratios of the components of the new formulation that provide its maximum inhibitory efficiency against scaling and corrosion.

The high inhibiting performance of the IOMS-3 formulation is achieved at the DPP concentration of about 8% in the commercial inhibitor, which leads to a slight increase in the cost of the commercial product, but at low working concentrations of the reagent makes its application economically efficient.

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