

## Magnesium and zinc organophosphonate complexonates as scaling and corrosion inhibitors

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### Abstract

This work deals with the creation of multipurpose formulations based on organophosphonates (OP) for simultaneous inhibition of scaling and corrosion in water consumption systems. Comparative analysis of OP-based scaling and corrosion inhibitors of various chemical composition and structure and with formulations based on the above containing OP-based zinc and magnesium complexonates was carried out. It was found that with an increase in the number of functional groups in the reagent molecule and the length of the hydrocarbon radical connecting the aminomethylenephosphonate groups, an increase in the kinetic parameters of nucleation occurs. Accordingly, the efficiency of the reagent increases, thereby working concentration can be decreased. Under the selected experimental conditions (water composition, mg/dm<sup>3</sup>: Ca<sup>2+</sup> – 526, Mg<sup>2+</sup> – 426, Na<sup>+</sup> – 1127, HCO<sub>3</sub><sup>-</sup> – 871, SO<sub>4</sub><sup>2-</sup> – 1704, Cl<sup>-</sup> – 2166; temperature – 70–90°C; material: St.3), zinc and magnesium complexonates obtained at a molar ratio of 2.5:1 (OP:Me) were tested as scaling and corrosion inhibitors. It has been found that magnesium complexonates are not inferior to zinc complexonates in efficiency. With an increase in temperature, the corrosion rate in the presence of complexonates decreases due to the formation of a “protective film” on the metal surface. The formation of a such a film is confirmed by the results of ellipsometric studies (with a SPEL-7LED spectral LED ellipsometer) and elemental analysis (an iCAP 6300 Duo atomic emission spectrometer with inductively coupled plasma). Depending on the experimental conditions, the film is 30–400 nm thick. The composition of the “protective film” includes an iron complexonate (with a molar ratio close to 1.5:1) and magnesium hydroxide.

Received: March 15, 2022. Published: May 17, 2022

doi: [10.17675/2305-6894-2022-11-2-17](https://doi.org/10.17675/2305-6894-2022-11-2-17)

**Keywords:** *composition, scaling inhibitor, corrosion inhibitor, efficiency evaluation.*

## Introduction

The technical overhaul of production facilities, such as replacement of obsolete processes with new ones that allow reducing the production costs, including power consumption, mitigation of environmental impact, *etc.*, remains an urgent task. The buildup of mineral deposits and metal corrosion in water utilization systems and process equipment are among the negative phenomena that hinder the resource and energy conservation.

The problem of scaling prevention is solved by treatment of water that is used as a cooling agent, heat-transfer medium or hydraulic transportation medium with reagents that inhibit the scaling process and are widely used in international and domestic practice. Of these, the most interesting agents include polyphosphates, organic phosphonates (OP) with various chemical compositions and structures, polycarboxylates, polyacrylates, and polymethacrylates (with a molecular weight of up to 10000) [1–4]. The mechanism of action of such reagents involves the adsorption of micro-nuclei of the crystallizing salt on the surface, which prevents their further growth. The reagent consumption depends on the water quality and operating conditions but does not exceed 5 mg/dm<sup>3</sup>.

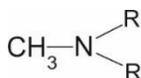
OP can also be used to inhibit corrosion. In this case, formulations containing their complexonates, in particular with zinc, are used. Corrosion prevention is due to the formation of a “protective film” on the metal surface. However, the consumption of reagents with respect to an OP increases by an order of magnitude and amounts to 15–100 mg/dm<sup>3</sup> [5–11]. This circumstance limits their possible use, taking into account the fact that the MPC for zinc in recreational and household purpose water bodies is 1 mg/dm<sup>3</sup>, and that for fishery water bodies is 0.01 mg/dm<sup>3</sup>.

The creation of OP-based inhibitors and formulations that do not contain environmentally hazardous additives and can efficiently prevent scaling and corrosion at lower concentrations, which would allow them to be used in compliance with stricter quality requirements for consumed and discharged water, is an urgent task.

The purpose of this study is to study the possibility of creating efficient OP-based formulations containing magnesium complexes and perform their comparative analysis with zinc analogues for simultaneous inhibition of scaling and corrosion that would also meet the environmental and economic requirements.

## Experimental

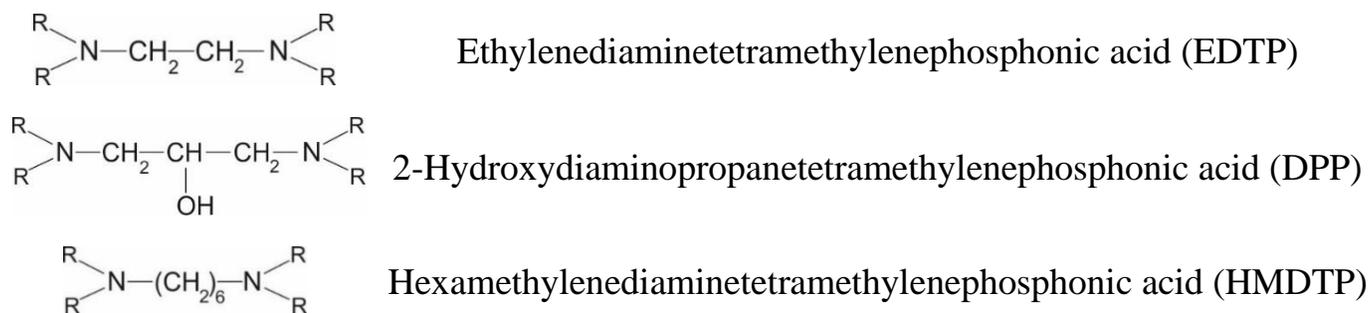
OP differing in the number of functional groups in the reagent molecule and the length of the hydrocarbon radical linking the aminomethylenephosphonic groups were used as the objects of this study:



Methyliminodimethylenephosphonic acid (MDP)



Nitriлотrimethylenephosphonic acid (NTP)



where R is  $\text{CH}_2\text{PO}_3\text{H}_2$ , as well as their composite formulations containing zinc and magnesium complexonates with a molar ratio of OP:Me=2.5:1.

A comparative evaluation of OP efficiency was performed by studying their effect on the kinetic parameters of calcium sulfate nucleation ( $Re_c=12500$ ,  $t=40^\circ\text{C}$ ), thus allowing them to be compared with a high degree of probability [12].

The values of nucleation kinetic parameters ( $\sigma$  is the specific surface energy,  $r$  is the critical nucleation radius,  $n$  is the order of the nucleation reaction) were calculated using the following equations.

Gibbs–Volmer equation:

$$\beta = A \exp \left[ - \frac{16\pi \cdot \sigma^3 \cdot M^2}{3R^3 \cdot T^3 \cdot \rho^2 \cdot \ln^2 S} \right],$$

where  $\sigma$  is the specific work for the formation of a critical-size nucleus (specific surface energy),  $\text{mJ}/\text{m}^2$ ;  $M$  is the molecular weight of the crystallizing salt;  $R$  is the universal gas constant,  $\text{J}/\text{mol} \cdot \text{K}$ ;  $T$  is the temperature,  $\text{K}$ ;  $\rho$  is the salt density,  $\text{g}/\text{cm}^3$ ;  $S$  is the relative supersaturation equal to the ratio of the initial concentration to the equilibrium one;

Ostwald–Freundlich equation:

$$r = \frac{2\sigma \cdot M}{R \cdot T \cdot \ln S},$$

Christiansen-Nielsen equation:

$$\beta = k \cdot \Delta C^n,$$

where  $\Delta C = C_{\text{ini}} - C_{\text{sol}}$ ,  $n$  is the reaction order, and  $k$  is the rate constant.

The relationship between the nucleation rate ( $\beta$ ) and induction period ( $t_{\text{ind}}$ ) can be represented as:

$$\beta = \frac{1}{t_{\text{ind}}}$$

After substituting into the equations and logarithmation, we obtain:

$$\ln t_{\text{ind}} = \ln A + \frac{16\pi \cdot \sigma^3 \cdot M^2}{3R^3 \cdot T^3 \cdot \rho^2 \cdot \ln^2 S}$$

$$\ln t_{\text{ind}} = \ln k + n \ln C_1.$$

NTP and DPP are complexonates obtained with a molar ratio of OP:Me=2.5:1 by dissolving the corresponding oxides in NTP and DPP complexones, followed by adjusting the solution pH to 5.5–6.0. The studies were performed at a 70–90°C with stirring ( $Re_c=12500$ ) in water with mineral composition, mg/dm<sup>3</sup>: Ca<sup>2+</sup> – 526, Mg<sup>2+</sup> – 426, Na<sup>+</sup> – 1127, HCO<sub>3</sub><sup>-</sup> – 871, SO<sub>4</sub><sup>2-</sup> – 1704, Cl<sup>-</sup> – 2166, corresponding to the average water quality in water usage systems. The pH of the solutions was 7.2–7.5. The efficiency of the reagents in the simultaneous inhibition of scaling and corrosion was tested using a set-up reported previously [7].

The linear polarization resistance method was used to determine the corrosion rate. Measurements were taken using an Expert-004 corrosion meter [13] (the relative error of the method is 7%) at 20 min intervals on electrodes made of St.3, with a total exposure of 180 minutes. The scaling inhibition efficiency was determined by the amount of calcium carbonate built up on the “reference pipe” by the standard procedure (the relative error of the method is 3%).

The formation of a “protective film” on the metal surface depending on the experimental conditions was determined by ellipsometry (using a SPEL-7LED spectral LED ellipsometer). The absolute error is 1 nm. Depending on the experimental conditions, the film thickness was 30 to 400 nm. The composition of the resulting film was analyzed using an iCAP 6300 Duo atomic emission spectrometer with inductively coupled plasma. The scale with a weight of 5–6 mg was dissolved in a mixture of concentrated nitric (2 cm<sup>3</sup>) and hydrochloric (0.5 cm<sup>3</sup>) acid solutions (with a volume-to-volume ratio of 4:1). The volume was adjusted to 10 cm<sup>3</sup> with distilled water.

## Results and Discussion

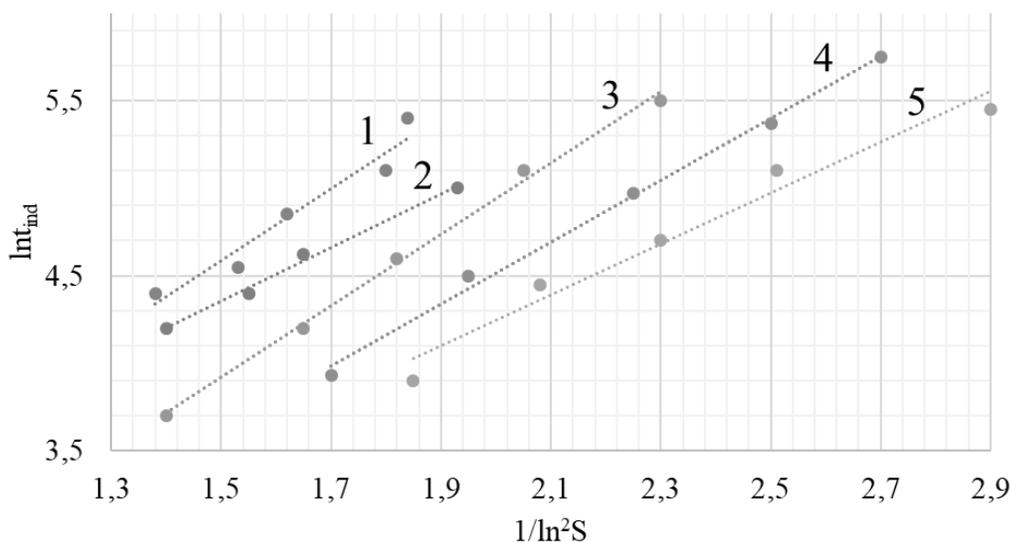
Based on the  $\ln t_{\text{ind}} - 1/\ln^2 S$  plots at various concentrations of supersaturated solutions (Figure 1), the values of  $\sigma$  and  $n$  were determined. The  $\sigma$  value was subsequently used to calculate the critical nucleation radius  $r$ .

Table 1 shows the calculated values of nucleation parameters for the reagents studied.

One can see from the data presented in Table 1 that with an increase in the number of functional groups in the reagent molecule (MDP–NTP–EDTP) and the length of the hydrocarbon radical linking the aminomethylenephosphonic groups (EDTP–DPP–HMDTP), the kinetic parameters of nucleation increase and, accordingly, the consumption of the reagent goes down.

This circumstance can be considered as an opportunity to reduce the OP consumption for the simultaneous inhibition of scaling and corrosion. It should be noted that, due to the structure of HMDTP, it forms a binuclear complex containing two independent

iminodimethylenephosphonic acid moieties separated by a hexamethylene bridge. In view of this, there is no trend for an increase in the efficiency of the HMDTP complexonate as a corrosion inhibitor as compared to the corresponding NTP complexonate. In addition, at OP concentrations of 15–100 mg/dm<sup>3</sup> used for the simultaneous inhibition of scaling and corrosion, the efficiency of their use depending on the composition and structure levels off.



**Figure 1.** Determination of the specific surface energy of calcium sulfate nucleation in the presence of: 1 – HMDTP; 2 – DPP; 3 – EDTP; 4 – NTP; 5 – MDP ( $t=40^{\circ}\text{C}$ ).

**Table 1.** Effect of organophosphonates on kinetic parameters.

Reagent	Reagent concentration, mg/dm <sup>3</sup>	Nucleation reaction order, $n$	Specific surface energy, $\sigma$ , mJ/m <sup>2</sup>	Critical nucleus radius, $r$ , nm
–	–	5.5	7.3	3.8–6.0
MDP	1.0	5.7	7.9	4.2–6.0
NTP	1.0	6.0	8.3	4.3–6.2
EDTP	1.0	8.2	9.8	5.1–6.4
DPP	0.7	13.3	12.8	6.7–8.0
HMDTP	0.25	14.1	13.3	6.8–8.3

Table 2 shows comparative results of scaling and corrosion inhibition by magnesium and zinc complexonates of NTP and DPP in the temperature range of 70–90°C.

**Table 2.** Inhibition of scaling and corrosion.

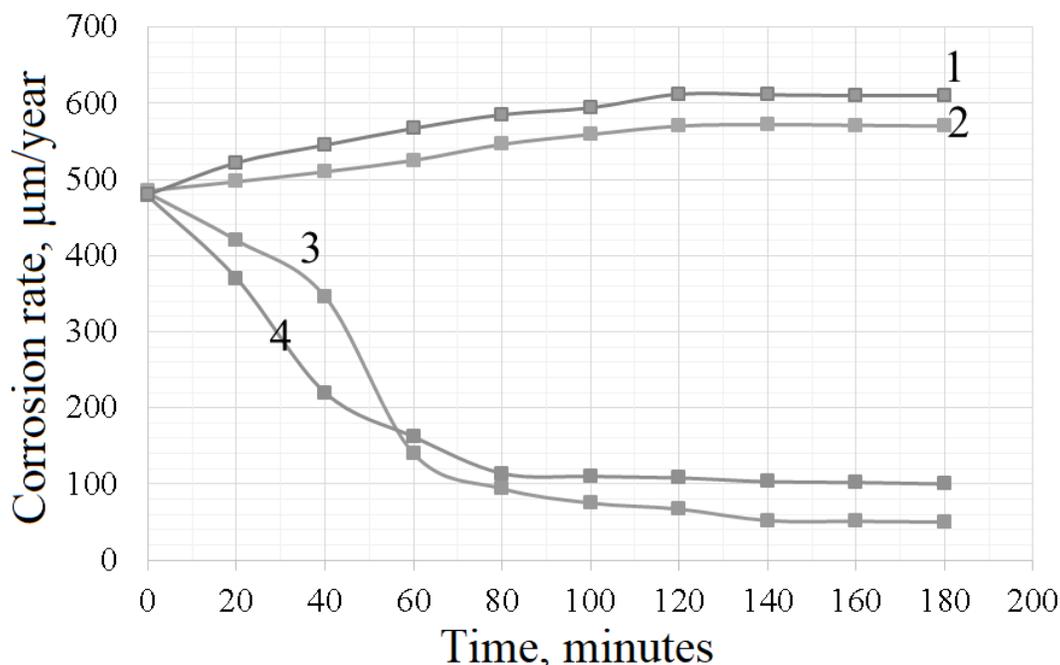
	Temperature, °C	Concentration, mg/dm <sup>3</sup>	Corrosion rate, µm/year	Corrosion inhibition efficiency, %	Amount of deposits, mg	Scaling inhibition efficiency, %
Reference experiment	70		570	–	45.4	–
	80	–	610	–	47	–
	90		650	–	47.2	–
NTP:Mg	70		100	82.46	3.4	92.51
	80	30	60	90.16	3.3	92.98
	90		50	92.31	3	93.64
	70		50	91.23	3.4	92.51
	80	50	50	91.8	3.5	92.55
	90		40	93.85	3.6	92.37
NTP:Zn	70		130	77.19	4.4	90.31
	80	30	120	80.33	4	91.49
	90		90	86.15	4	91.53
	70		80	85.96	4	91.19
	80	50	80	86.89	4.1	91.28
	90		80	87.69	4	91.53
DPP:Mg	70		120	78.95	4.5	90.09
	80	30	100	83.61	4	91.49
	90		80	87.69	4.1	91.31
	70		90	84.21	4	91.19
	80	50	80	86.89	4.3	90.85
	90		50	92.31	3.6	92.37
DPP:Zn	70		130	77.19	4.6	89.87
	80	30	110	81.97	4.1	91.28
	90		80	87.69	3.9	91.74
	70		110	80.70	4.1	90.97
	80	50	90	85.25	4	91.49
	90		80	87.69	4.1	91.31

One can see from the data in Table 2 that the use of both zinc and magnesium complexonates in the temperature range studied results in a more than tenfold reduction in the amount of deposits (inhibition efficiency >90%) due to the presence of free OP in the formulation, which provides scaling inhibition.

In the concentration range studied, the total corrosion rate decreases, especially noticeably with an increase in concentrations to 50 mg/dm<sup>3</sup> and temperature to 90°C. At the same time, the decrease in the corrosion rate in the presence of zinc and magnesium complexonates is 4–6% per 10°C, while the corrosion rate in the reference experiments increases by 6.3% per 10°C on average.

A decrease in the corrosion rate with an increase in the concentration of reagents and temperature can serve as an indirect confirmation of the formation of a “protective film” on the metal surface, which, according to [14], consists of heterocomplexes of organo-inorganic coordination polymers. Obviously, the rate of its formation depends on the initial concentration, exposure time and temperature.

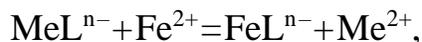
In order to confirm this assumption, Figure 2 presents the results of measuring the corrosion rate in the reference experiments and in the presence of the magnesium NTP complex at temperatures of 70–90°C and an exposure time of up to 180 minutes.



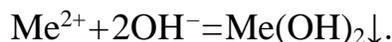
**Figure 2.** Change in the corrosion rate. Concentration of reagents – 30 mg/dm<sup>3</sup>. 1 – reference (90°C), 2 – reference (70°C), 3 – Mg-NTP (70°C), 4 – Mg-NTP (90°C).

Figure 2 shows that while in the reference experiments a steady increase in the corrosion rate is observed during the entire exposure, the corrosion rate decreases from the beginning of exposure in the presence of the NTP magnesium complex (the equilibrium values of the corrosion rate are reached within 100–120 minutes). This confirms the

assumption made by Yu.I. Kuznetsov *et al.* [15] about the possible inhibition of corrosion due to electrophilic substitution of the metal in the complexonate by iron cations:



with subsequent binding of the metal cation into the hydroxide:



Taking into account the suggested mechanism, the efficiency of metal corrosion inhibition by zinc and magnesium complexonates (Table 2) may be due to the very low solubility of their hydroxides:

$$SP_{\text{Zn}(\text{OH})_2} = 1.4 \cdot 10^{-17}, SP_{\text{Mg}(\text{OH})_2} = 7.1 \cdot 10^{-12}.$$

The formation of an iron complexonate is also confirmed by the analysis of the deposit (using the magnesium-NTP complex in a solution that does not contain magnesium) built up on the electrodes, %: P – 15.72 (50.54 in NTP), Fe – 14.52, Mg – 0.11, which corresponds to the molar ratio NTP:Fe=1.5:1.

## Conclusions

A comparative analysis of scaling and corrosion inhibitors based on OP with various chemical compositions and structures and their formulations containing complexonates of the same OP with zinc and magnesium has been carried out.

It has been found that with an increase in the number of functional groups in the reagent molecule and an increase in the length of the hydrocarbon radical linking the aminomethylenephosphonic groups, an increase in the kinetic parameters of nucleation and, accordingly, in efficiency is observed, which leads to a decrease in the working concentration of the reagent.

Under the selected experimental conditions (water composition, mg/dm<sup>3</sup>: Ca<sup>2+</sup> – 526, Mg<sup>2+</sup> – 426, Na<sup>+</sup> – 1127, HCO<sub>3</sub><sup>-</sup> – 871, SO<sub>4</sub><sup>2-</sup> – 1704, Cl<sup>-</sup> – 2166; temperature 70–90°C; material: St.3), zinc and magnesium complexonates obtained at a molar ratio of 2.5:1 (OP:Me) have been tested as scaling and corrosion inhibitors. It has been found that magnesium complexonates are not inferior to zinc complexonates in efficiency. In the presence of complexonates, the corrosion rate decreases with an increase in temperature. This is due to the formation of a “protective film” on the metal surface.

The formation of a “protective film” is confirmed by the results of ellipsometric studies (with a SPEL-7LED spectral LED ellipsometer) and elemental analysis (an iCAP 6300 Duo atomic emission spectrometer with inductively coupled plasma). Depending on the experimental conditions, the film thickness ranges from 30 to 400 nm, while the “protective film” comprises an iron complexonate (with a molar ratio close to 1.5:1) and magnesium hydroxide.

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