Study of various organophosphonate additives as calcium carbonate inhibitors for reverse osmosis

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Abstract. Various chemical additives are used in water treatment industry, among them – precipitation inhibitors for reverse osmosis membrane facilities. The development and synthesis of new inhibitor formulas and the study of their effectiveness is still an urgent task for many researchers working in this field. The relationship between the structure of phosphonate scale inhibitors and their effectiveness in preventing of calcium carbonate precipitation was studied. Two classes of tetraphosphonate and diphosphonate inhibitors that possess systematic structural similarities and differences have been tested on the laboratory membrane unit. All chemicals were tested at doses of 1 and 5 mg/L. The results showed that the antiscalant efficiency for both groups of inhibitors increases with elongation of methylene chain, but the longest compounds have a sharp drop in inhibition efficiency.

1 Introduction

Nowadays antiscalant dosing is assigned a leading role in the prevention of low-soluble salts sedimentation on reverse osmosis membranes [1, 2]. Every year new inhibitors are synthesized and tested in laboratory or industrial conditions. In the last 10–15 years environmentally-friendly polymers have been developed to escape environmental concerns and discharge limitations for RO concentrate [3–5]. In addition to inhibiting efficiency, it is likely that low cost, usability and availability are required for widespread industrial use. Sometimes this is a reason to the limited use of new inhibitors. Therefore sodium hexametaphosphate (HMPT) as well as antiscalants based on phosphonic acid are used widely at RO water treatment facilities. Among them the organophosphonates are dominating the global market [6–9]. They are readily soluble in water, non-toxic and effective at low treatment concentrations [10].

In addition to traditional phosphonates, more complex compounds, such as diphosphonate or tetraphosphonates, are synthesized and studied [6, 11]. Ongoing interest in the application of phosphonates is due its high efficiency in preventing the nucleation

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and crystallization of many sparingly soluble inorganic salts [12, 13]. They can also affect the adhesion of inorganic crystals to critical surfaces of the water treatment system [14].

It is known that phosphonates are most effective in inhibiting the crystal growth of calcium sulfate dehydrate, but also can influence on calcium carbonate crystallization. In this work we investigate a relative effectiveness in inhibiting the crystal growth of calcium carbonate in reverse osmosis membrane element of a family of polyphosphonate additives with various length of the organic polymethylene chain.

2 Materials and methods

Two classes of phosphonate inhibitors, namely, diphosphonates (6 additives) (Table 1) and tetraphosphonates (5 additives) (Table 2), were synthesized and supplied by the Crystal Engineering, Growth & Design Laboratory, University of Crete (Greece). These two families of additives possess the same functionality, amino-*bis*(methylenephosphonic acid). Tetraphosphonates have two of these (one on each end) and diphosphonates have one (only on one end). These compounds differ in the length of the polymethylene chain. Tetraphosphonates have a $–(CH_2)_x–$ (x = 2, 4, 6, 8, 12) chain bridging the two N atoms and diphosphonates have a $–(CH_2)_xCH_3$ (x = 0, 1, 3, 5, 7, 11) non-polar side-chain [11].

Table 1. Diphosphonate scale inhibitors.

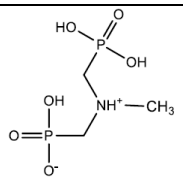
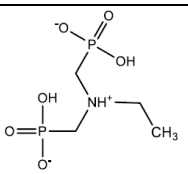
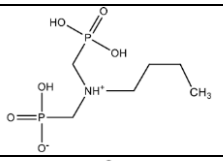
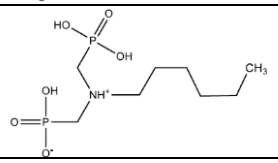
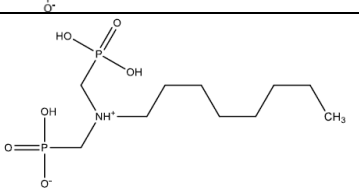
Additive abbreviation	Additive Name	Additive Schematic Structure
MBMP (C_1-D)	Methylamine-*bis* (methylenephosphonic acid)	
EBMP (C_2-D)	Ethyleneamine-*bis* (methylenephosphonic acid)	
BBMP (C_4-D)	Butyleneamine-*bis* (methylenephosphonic acid)	
HBMP-D (C_6-D)	Hexamethyleneamine-*bis* (methylenephosphonic acid)	
OBMP-D (C_8-D)	Octamethyleneamine-*bis* (methylenephosphonic acid)	

Table 1 (continuation)

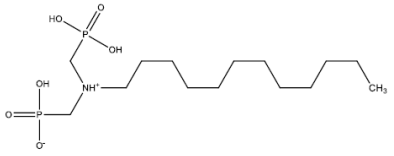
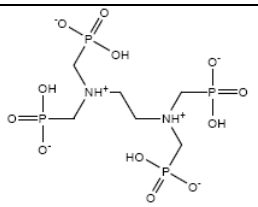
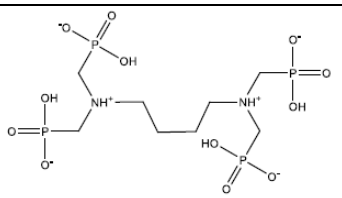
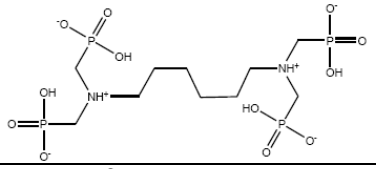
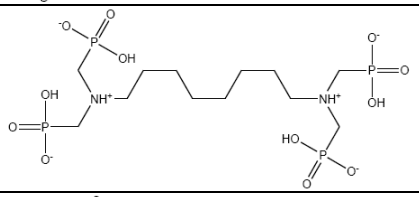
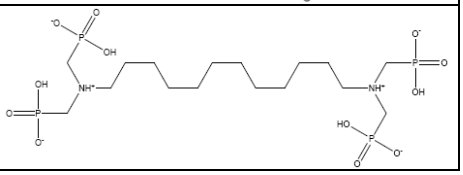
DABMP (C_{12}-D)	Dodecamethyleneamine-*bis* (methylenephosphonic acid)	

Table 2. Tetraphosphonate scale inhibitors.

Additive abbreviation	Additive Name	Additive Schematic Structure
EDTMP (C2)	Ethylenediaminetetrakis (methylenephosphonic acid)	
TMTMP (C4)	tetramethylenediamine-tetrakis (methylenephosphonic acid)	
HDTMP (C6)	hexamethylenediamine-tetrakis (methylenephosphonic acid)	
ODTMP (C8)	Octamethylenediamine-tetrakis (methylenephosphonic acid)	
DDTMP (C12)	Dodecamethylenediamine-tetrakis (methylenephosphonic acid)	

The antiscalant behavior of phosphonate compounds was investigated using lab membrane unit (Fig. 1) equipped with the spiral wound module TW 30-1812-50 (DOW Filmtec, USA) with reverse osmosis polyamide membranes with selectivity up to 98%. Scaling experiments were conducted in circulation mode whereby reject flow (concentrate) was returned to the feed water tank and permeate was collected in a separate tank. Continuous concentration of calcium and bicarbonate ions in the circulated solution provides supersaturation conditions to initiate and sustain calcium carbonate scaling throughout the experiment. Transmembrane pressure was maintained at 6 bar (the maximum pressure provided by the existing RO pump).

A model solution was prepared by careful adding and mixing of 1 M $MgSO_4$, $NaHCO_3$ and $CaCl_2$ solutions in distilled water. Final composition of feed solution had total hardness 7 mEq/L, calcium 6 mEq/L, pH = 9 and TDS was about 850 ppm. pH of feed solution was adjusted by addition of HCl aqueous solution.

Calcium carbonate scaling experiments was carried out in series for all new phosphonate scale inhibitors. Two additive concentrations were chosen: 1 ppm (low, only for tetraphosphonates) and 5 ppm (typical).

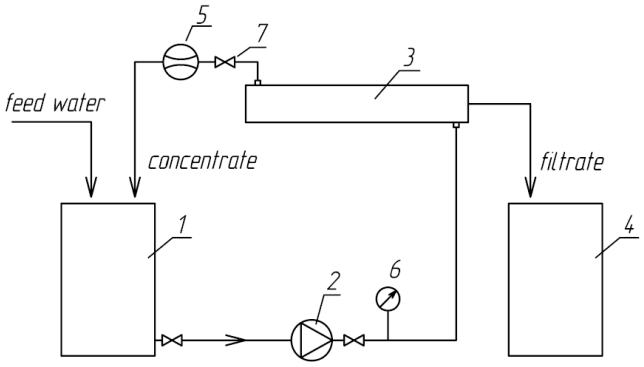


Fig. 1. Schematic diagram of laboratory membrane RO unit for membrane scaling tests:
1 – feed water tank; 2 – pump; 3 – spiral wound membrane module; 4 – permeate tank;
5 – concentrate rotameter; 6 – pressure-gauge.

The samples were taken from initial feed solution and circulated solution (for various concentration ratios) – from tank 1 (Fig. 1), and for permeate – from tank 4 (Fig. 1) (one sample characterized the average quality of product water). In all samples the following parameters are determined: temperature, TDS (conductivity), pH, total hardness, total alkalinity, and calcium. Conductivity and temperature are controlled by a laboratory conductivity meter Cond 730 (WTW inoLab®); pH value – using laboratory pH meter HI 2215 (Hanna Instruments); total alkalinity – by titration with HCl; and total hardness and calcium – by complexometric EDTA titration.

To restore the membrane element's productivity and to remove accumulated scales, chemical washing was conducted between series of experiments using a 2% solution of citric acid.

The amount of $CaCO_3$ scales accumulated in the membrane module was calculated as a difference between initial amount of calcium in the feed solution and total amount of calcium in concentrate (circulating solution) and permeate. Antiscalant performance was evaluated by comparison of scaling rate values determined throughout experiments with, and without antiscalant dosing. Antiscalant efficiency as a calcium carbonate and calcium sulphate inhibitor was calculated by using the following equation:

$$E(\%) = \frac{M_{Ca}^{blank} - M_{Ca}^{antiscalant}}{M_{Ca}^{blank}} \cdot 100 \quad (1)$$

where M_{Ca}^{blank} and $M_{Ca}^{antiscalant}$ are the mass of calcium accumulated in membrane module in the absence of antiscalant and with antiscalant dosing respectively, mg.

Scaling test for each reagent was repeated 2–3 times and the average antiscalant efficiency was calculated.

3 Results and discussion

The results show that changes in the chemical structure of an inhibitor molecule have an effect on inhibitory efficiency. Most additives improved the process and prevented scale formation in the membrane module.

Tetraphosphonates at high concentration (5 mg/L) revealed a systematic antiscaling efficiency that dependents on the length of the bridging units $–(CH_2)_x–$ (x = 2, 4, 6, 8, 12) (Fig. 2, Table 3). Specifically, the scale inhibition efficiency ranking was $2 < 4 < 6 < 8$. These results reveal the tendency of decreasing of inhibition effect is proportional to the number of methylene groups on the side-chain. However the inhibitor DDTMP (C12) with x = 12 showed reduced efficiency (between EDTMP and TMTMP). Tests conducted with inhibitor concentration of 1 mg/l showed similar tendency, but not so systematic that can be partially explained by low doses of additives. In general, the experimental results with tetraphosphonates show a similar tendency obtained in [11] for calcium sulphate crystallization (with the exception of DDTMP performance).

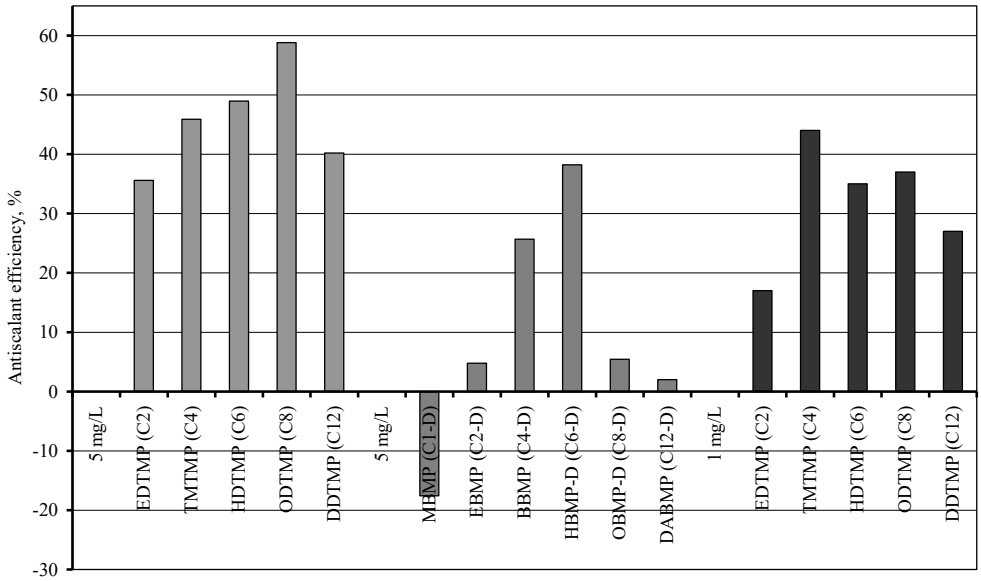


Fig. 2. Tetraphosphonate and diphosphonate scale inhibitors performance.

The similar trend was observed for diphosphonates, *i.e.* the longer the side-chain length, the higher the efficiency, but extremely long chain causes the deterioration of antiscalant efficiency (Fig. 2, Table 3). Lower antiscalant efficiency was coupled with lower RO membrane flux. Decrease in efficiency, that is an increase in the amount of calcium carbonate scale on the membrane, can be explained by a longer duration of the experiment (from 2 to 4.5 hours against 0.8–1.3 hours for other additives), which is caused by a lower flow through the membrane during these tests. Perhaps the effectiveness of OBMP and DABMP as inhibitors are high, but the reagents themselves were deposited on the membrane and reduced its productivity. This phenomenon requires verification – further scaling experiments with the SEM examination of the membrane surface. It is interesting that the first diphosphonate MBMP (C1-D) demonstrated negative efficiency – on the contrary, it increased the formation of calcium carbonate sediment on the membrane surface. At the same time, this did not cause a noticeable increase in the duration of the scaling tests as for OBMP and DABMP additives.

Since the antiscalant dosing was carried out according to the total weight of chemicals, but not the molar mass, the concentrations were recalculated to -$PO(OH)_2$, (see Table 3). Correlating corrected doses and antiscalant efficiency, it can be concluded that a decrease in the concentration for higher molecular weight compounds does not change the revealed general trends of its antiscaling behavior.

Table 3. Antiscalant efficiency in reverse osmosis tests.

Antiscalant	Dosage, mg/L	Dosage as -$PO(OH)_2$, mg/L	Average test duration, hours	Inhibitor efficiency, %
EDTMP (C2)	1.0	0.74	1.00	17
TMTMP (C4)	1.0	0.70	0.90	44
HDTMP (C6)	1.0	0.66	0.75	35
ODTMP (C8)	1.0	0.62	1.00	35
DDTMP (C12)	1.0	0.55	1.25	27
EDTMP (C2)	5.0	3.7	1.25	36
TMTMP (C4)	5.0	3.5	1.33	46
HDTMP (C6)	5.0	3.3	0.93	49
ODTMP (C8)	5.0	3.1	0.93	59
DDTMP (C12)	5.0	2.8	1.34	40
MBMP (C1-D)	5.0	3.8	1.10	-18
EBMP (C2-D)	5.0	3.6	1.07	5
BBMP (C4-D)	5.0	3.2	0.75	26
HBMP-D (C6-D)	5.0	2.9	0.84	38
OBMP-D (C8-D)	5.0	2.6	1.90	5
DABMP (C12-D)	5.0	2.1	4.50	2

Generally, diphosphonates demonstrated a much lower inhibitory efficiency in comparison with tetraphosphonates. It has been reported that the number of adsorption active centers in the molecule directly promotes inhibition process [13, 15]. Tetraphosphonates can interact by one amino-bis(methylenephosphonate) moiety with a calcium ion on the crystal surface or by two aminobis(methylenephosphonate) groups with neighboring surface calcium ions [11]. However, it is important to note that in the diphosphonate family of inhibitors, the number of active centers i.e. the phosphonate centers on the molecule backbone is the same for all diphosphonates. The polymethylene non-polar side-chain certainly does not contribute to the inhibition process, because it cannot interact with the mineral surface. Hence the systematic elongation of the side-chain undoubtedly is related to the mobility of the inhibitor molecule. Apparently, as the molecule becomes larger (due to elongation), its access to the surface of the forming nuclei becomes profoundly restricted. This is confirmed by the fact that the “longest” diphosphonates OBMP (C8-D) and DABMP (C12-D) and tetraphosphonate DDTMP (C12) are the least efficient.

4 Conclusions

Calcium carbonate scaling tests carried out on the RO unit demonstrate acceptable efficiency of most diphosphanate and tetraphosphonate inhibitors. It was found that among

the family of organophosphonates the inhibitor efficiency increases with elongation of polymetylene bridging chain, but up to a certain limit. For tetraphosphonates this is a longest compound – dodecamethylenediamine-tetrakis(methylenephosphonic acid) that has a reduced efficiency. For diphosphonate family the inhibitor efficiency starting with the octamethylenediamine-tetrakis (methylenephosphonic acid) has a sharp drop. These results can be helpful for developing new classes of reagents for reverse osmosis application.

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