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Investigation into the effects of phosphonic inhibitors on the formation of calcium sulfate scales

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ABSTRACT

The effects of several phosphonic additives on the formation of calcium sulfate scale on metal surface in a flow system were investigated thoroughly using multiple pipe flow system. Their chemical structure, concentration and run time are to be the main factors that influence the inhibitory capability of these anti-scalants. The relationships between these factors and the scale rate were established. The Langmuir adsorption isotherm is applied to predict the critical concentrations above which complete inhibition of scaling will occur. The inhibition efficiency order of the investigated organic additives is found as follows:EDTP > NTMP > NDPA > HEDP> NPDA, which corresponds to the number of phosphonate groups that the additives possess.

Keywords: Phosphonic inhibitors; Calcium sulfate scales; Pipe; Langmuir adsorption isotherm

1. Introduction

Scaling in piping systems and vessel surfaces is a serious problem in many industries. The problems of scale deposition are also associated with cooling systems and reverse osmosis water desalination. Gypsum or calcium sulfate dihydrate is a dominant scalant in most industrial water systems and measures have been sought to prevent the formation of gypsum scale. Nucleation rate is influenced by many factors such as levels of supersaturation [1–3], velocity [3–6], Reynolds number [2,7] and temperature [8]. It is well-known that many additives and impurities strongly influence the crystallisation processes. The effects of additives on induction period were investigated by Sarig and Mullin [9], and Prisciandaro et al. [10] who measured the induction period for gypsum nucleation when additives were added to estimate the interfacial tension values and compared them with those obtained in the absence of additives [11]. Various models have been proposed for the adsorption of additives and impurities onto crystal surfaces [12–15]. The addition of polyphosphates such as sodium hexametaphosphate (SHMP) in small amounts apparently showed an increase in solubility of gypsum in brackish waters, but raising the additive concentration did not result in a comparative increase in solubility [16]. Although polyphosphates exhibit excellent inhibition against certain scale formation, they can hydrolyze in a short time to form orthophosphate, which is inactive when used as an antiscalant and leads to the deposition of insoluble calcium phosphate [17]. A study by Amjad [18] revealed that pyrophosphate, an effective growth inhibitor for calcium phosphate, calcium oxalate, barium sulphate and calcium carbonate, exhibits only a slight inhibitory effect on gypsum growth. He et

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al. [19] investigated the inhibition of gypsum and barium sulphate nucleation by polyphosphonates and polycarboxylates at temperatures from 25 to 90°C. They found that the most effective inhibitor against gypsum was hexamethylenediamine-tetramethylenephosphonic acid (HDTP) and the most effective inhibitor against barium sulphate was 1-hydroxyethylidine 1,1-diphosphonic acid (HEDP). In addition, HEDP, HDTP and nitrilo-trimethylenephosphonic acid (NTMP) are also very effective for inhibiting the growth of calcium carbonate crystals [20–22]. However, the effect of HEDP on gypsum control is rather poor as compared with other polyphosphonic acid such as NTMP, ethylenediaminetetramethylenephosphonic acid (EDTP) and (diethylenetriaminepentamethylenephosphonic acid (DTPP) [12,15]. Prisciandaro et al. also found that the retarding effectiveness of NTMP on gypsum nucleation is much greater than citric acid and 2-phosphonobutane-1,2,4-tricarboxylic acid [10].

This article investigates the relationship between the chemical structure of several phosphonic additives and their inhibitory effect on calcium sulphate scaling in water pipes. The influence of time and inhibitor concentration is closely scrutinized and the Langmuir adsorption isotherm is applied in an attempt to predict the performance of the inhibitors.

2. Experimental

2.1. Equipment setup

A multiple pipe flow system previously designed at Curtin University of Technology, WA, Australia, was used for the experiments (Fig. 1). The test section consists of four vertical tubular units placed parallel to one another. A manifold placed at the bottom close to the mixing section is used to distribute the solution evenly to the four tubular units. Another manifold on the top is used to collect the solution coming out from the test section. The calcium chloride solution and the sodium sulphate–additive solution from separate glass vessels were pumped into the test section, mixed in the bottom manifold and distributed equally to four identical vertical tubular units before exiting through the top manifold to waste container.

2.2. Operating conditions

The operating conditions are listed in Table 1.

The supersaturation ratio S was calculated using an extended Debye Huckel equation with addition of linear and quadratic terms.

$$\log K_{sp}(P) = \log K_{sp}^{o} + 8\alpha \frac{\sqrt{I}}{1 + A_{sp}\sqrt{I}} + B'I - C'I^2 \tag{1}$$

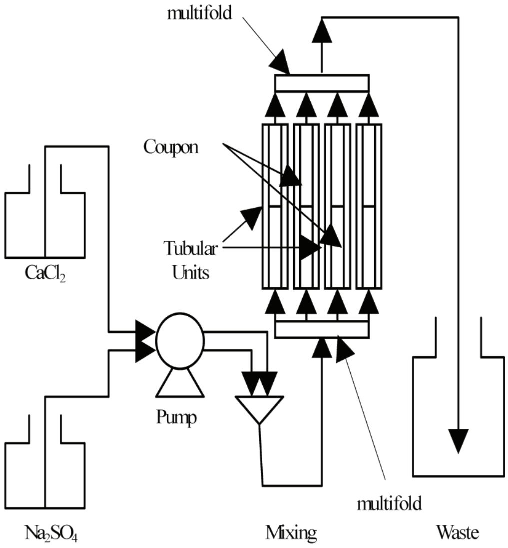


Fig. 1. Diagram of a multiple pipe flow system.

Table 1
Operating conditions

Calcium chloride concentration	0.15 M
Sodium sulphate concentration	0.15 M
Calcium sulphate concentration	0.075 M
Supersaturation	3.0503
pH	5.4 ± 0.2
Temperature	20°C
Flow rate	2 mL.s^{-1} (7.20 L h^{-1})
Coupon	Stainless steel
Coupon length	0.03 m
Coupon diameter	0.013 m
Run time	4 h
Break intervals	every hour

where K_{sp} (P) = [Ca^{2+}] [SO$_4^{2-}$] = practical solubility product; K_{sp}^{o} is solubility product at zero ionic strength, α is Debye–Huckel limiting slope, I is ionic strength and A_{sp}, B', $C'$are adjustable parameters.

Since [Ca^{2+}] = [SO$_4^{2-}$] = s

$$\log s = \log s_o + 4\alpha \frac{\sqrt{I}}{1 + A_{sp}\sqrt{I}} + \frac{B'}{2} I - \frac{C'}{2} I^2 \tag{2}$$

where s is the molality solubility of $CaSO_4.2H_2O$ (mol/kg) and s_o is the hypothetical solubility at $I = 0$.

The value of s_o can be calculated using experimental values of the molal solubility of $CaSO_4.2H_2O$in water and parameters A_{sp}, B', C' attained by Marshall and Slusher [23].

Thus,

$$S = \frac{C_m}{s} \tag{3}$$

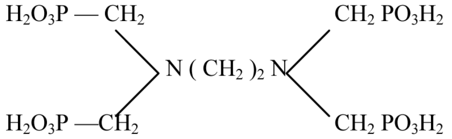
where C_m is initial molal concentration of $CaSO_4$ (mol/kg).

2.3. *Additive selection*

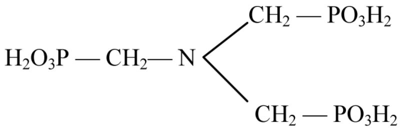
Additives of interest should affect the surface processes of the crystals at concentrations much lower than those of the scale forming materials. A general rule is that the additive must be capable of attaching to the surface and block active sites or enter a growing surface and disrupt further crystal growth. To be effective, the additive should usually have a molecular structure similar to the crystallising substance [24].

The additives used in this work were the following phosphonic acids:

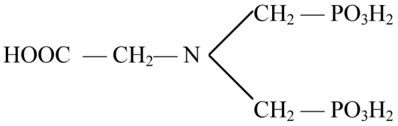
(a) EDTP (N,N,N′,N′-ethylenediaminetetra-methylene phosphonic acid)



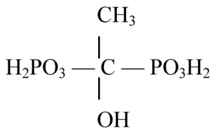
(b) NTMP (nitrilotrimethylenephosphonic acid)



(c) NDPA (nitrilodimethylenephosphonicacetic acid)

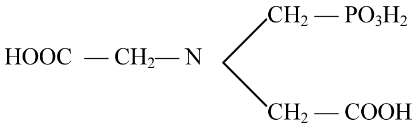


(d) HEDP (hydroxyethylidene-1,1-diphosphonic acid)



$$H_2PO_3 - \underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - PO_3H_2$$

(e) NPDA (nitrilomethylenephosphonicdiacetic acid)



These additives contain at least one functional groups that is phosphonic acid. The additive concentrations in the test solution ranged from 10^{-7} to 10^{-5} mol/L. Such concentrations were from four to six orders of magnitude below the calcium concentration, thus would not affect the ionic strength and supersaturation level of the test solution.

The additives were kindly supplied by Dr. Franca Jones of the Nanochemistry Research Institute, Curtin University of Technology, WA, Australia. HEDP (60% in aqueous solution) was purchased from Aldrich (Sigma-Aldrich Australia). The four other phosphonic acids with purity ≥ 97% were home synthesized and tested by spectrometric methods.

2.4. *Procedures*

Before each run a pre-calculated amount of the investigated additive was accurately weighed and then diluted with the 0.15 M sodium sulphate solution so that its concentration achieved after mixing with the 0.15 M sodium sulphate solution would be exactly as designed. The mixture was stirred well and put into the Na_2SO_4 container. The pump was started and experiment was monitored carefully. After each hour, the pump was switched off, a bottom coupon from one of the four test units was withdrawn out and replaced by a new one. When the experimental run was completed, the coupons were placed in an oven at 60°C overnight, then cooled down to room temperature and weighed to find the mass of scale deposited.

3. Results and discussion

3.1. *Inhibiting effects of the additives*

Percentage of inhibition is defined by the following equation:

$$\%\ \text{inhibition} = 100 \cdot \left(\frac{m_0 - m_a}{m_0} \right) \tag{4}$$

where m_0 = scale mass in experiment without additive, m_a = scale mass in experiment with additive.

Results show that the scale formation is obviously influenced by the additives at different levels. At the same additive concentration, the degree of inhibition depends on the chemical structure of the inhibitor. For each inhibitor the degree of inhibition depends on its concentration.

3.2. *Effects of time on inhibition*

In general, the amount of scale significantly increases when the time increases (Fig. 2). The relationship between scale mass and time in the absence of additives has been previously discussed by Hoang et al. [25]. The paper reported that in the absence of inhibitors, the curves of scale mass against time after the induction period needed for nucleation indicates a polynominal relationship between scale mass and time. In the presence of inhibitors, the scale deposition seems to have the same trend for all additives. Namely, the scaling rate of calcium sulphate increases with time even though an inhibitor is used. This trend can also be seen in the inhibiting effects of the additives (Fig. 3). Since the growth retardation results from the additive molecules blocking active sites of the crystal surface, the inhibition reduction can be attributed to the decrease in surface coverage by the inhibitor. Although the concentrations of calcium sulphate and inhibitor in the supersaturated solution are almost constant over time, the

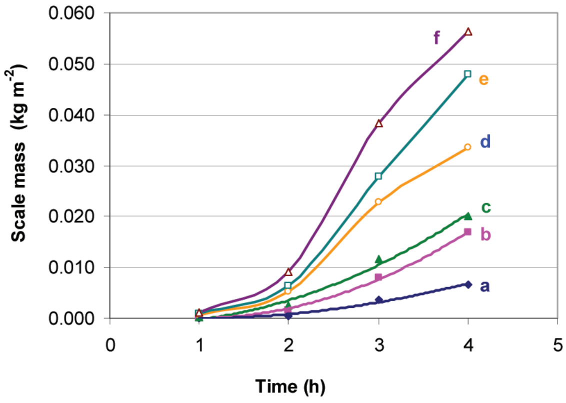


Fig. 2. The deposition of scale over time in the presence of phosphonic additives. Calcium sulphate concentration = 0.075 M, flow rate = 2×10^{-6} m^3 s^{-1}, coupon: stainless steel, length = 0.03 m, diameter = 0.013 m; temperature = 20°C; Additive concentration: (a) EDTP 2×10^{-6} M; (b) NTMP 2×10^{-6} M; (c) NDPA 10^{-5} M; (d) HEDP 10^{-5} M; (e) NPDA 10^{-5} M; (f) no additive.

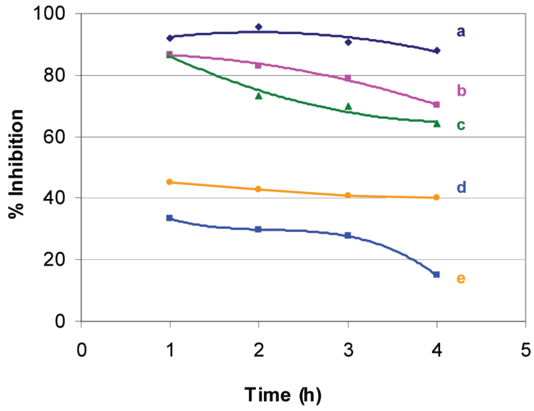


Fig. 3. The change of inhibiting effects over time. Calcium sulphate concentration = 0.075M; flow rate = 2.10^{-6} m^3 s^{-1}; temperature = 20°; Coupon: stainless steel, length = 0.03 m, diameter = 0.013 m. Additive: (a) EDTP 2×10^{-6} M; (b) NTMP 2×10^{-6} M; (c) NDPA 10^{-5} M; (d) HEDP 10^{-5} M; (e) NPDA 10^{-5} M.

number of nuclei and the growth rate increase, possibly leading to the concentration of inhibitor to be insufficient to cover the surface. As a result, a higher concentration of inhibitor is needed to maintain complete inhibition.

3.3. Relationship between scale mass and additive concentration

Fig. 4 shows the effect of additive concentration on the scale formation. Each curve seems to be linear within the range of EDTP concentrations from 0 to 10^{-6} mol /L. Beyond this range the curves are non-linear. The best fit equation for the whole range should be an exponential function, excluding all the points where the scale mass values are equal to zero. Similar behaviour can be observed from the curves of NTMP and NDPA (Fig. 5).

Thus, the logarithm of the scale mass formed at various time periods are plotted against EDTP concentration (Fig. 6). The points fitted a linear relationship between log (scale mass) and the additive concentration ranging from 0 up to 2.5×10^{-6} mol dm^{-3}. At higher concentrations the logarithmic values became indeterminate due to the very low values of the scale mass. Similarly, the plots of log (scale mass) against NTMP and NDPA are shown in Fig. 7. The equations describing the relationship between

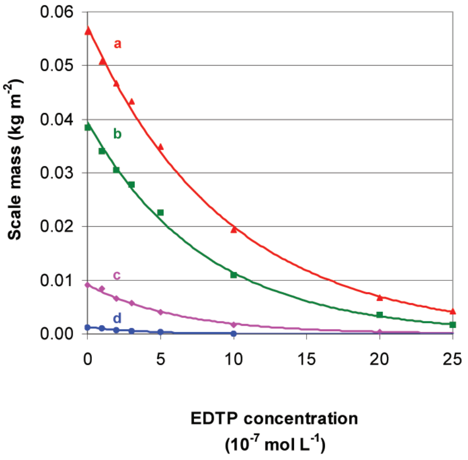


Fig. 4. Relationship between scale deposit and concentration of EDTP. Calcium sulphate concentration = 0.075M; flow rate = 2×10^{-6} m^3 s^{-1}; temperature = 20°C. Coupon: stainless steel, length = 0.03 m, diameter = 0.013 m. Run time: (a) 4 h, (b) 3 h, (c) 2 h, (d) 1 h.

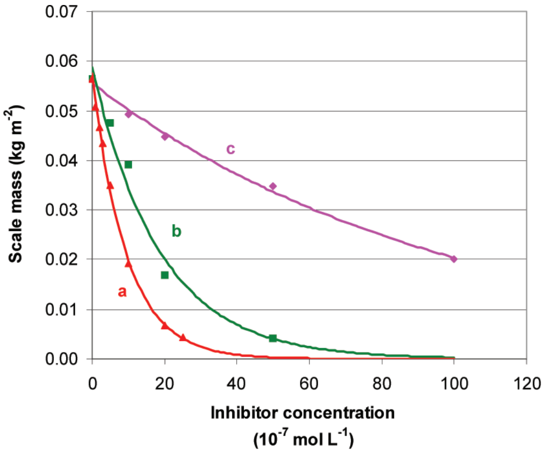


Fig. 5. Relationship between scale deposit and concentration of inhibitor. Calcium sulphate concentration = 0.075 M; flow rate = 2×10^{-6} m^3 s^{-1}; temperature = 20°C. Coupon: stainless steel, length = 0.03 m, diameter = 0.013 m. Inhibitor: (a) EDTP, (b) NTMP, (c) NDPA. Run time = 4 h.

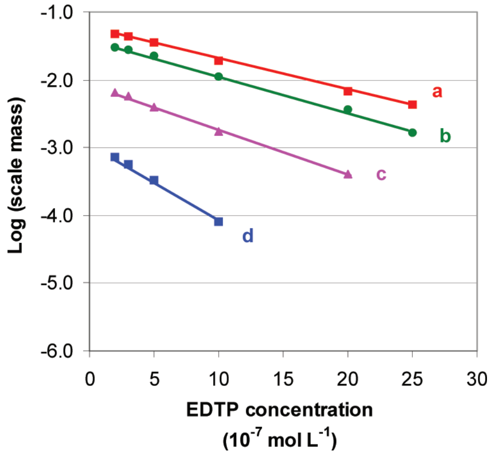


Fig. 6. Relationship between log (scale mass) and EDTP concentration. Supersaturation level = 3.05; flow rate = 2×10^{-6} m^3 s^{-1}; temperature = 20°C. Stainless steel coupon, length = 0.03 m, diameter = 0.013 m. Run time: (a) 4 h, (b) 3 h, (c) 2 h, (d) 1 h.

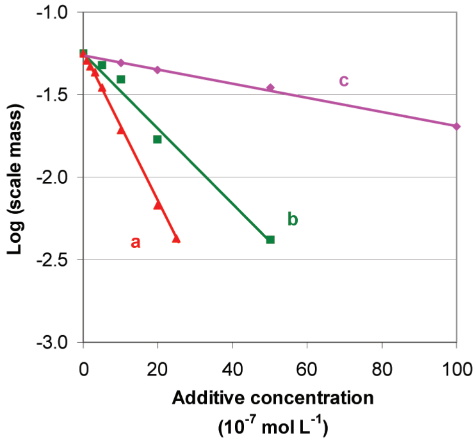


Fig. 7. Relationship between log (scale mass) and additive concentration. Calcium sulphate concentration = 0.075M; flow rate = 2×10^{-6} m^3 s^{-1}; temperature = 20°C. Coupon: stainless steel, length = 0.03 m, diameter= 0.013 m. Additive: (a) EDTP, (b) NTMP, (c) NDPA.

scale mass and concentration for some additives are listed in Table 2, where m represents scale mass (kg/m^2) and Ca is additive concentration (10^{-7} mol/L).

3.4. Langmuir adsorption isotherm

In a process of growth or dissolution of a crystal, three important steps should be considered:
(a) diffusion of ions or ion pairs to or from the surface
(b) formation of nuclei and their subsequent growth or dissolution by spread mechanism
(c) surface diffusion and incorporation or release at the crystal dislocations.

It is generally accepted that step (a) is fast enough that the crystallisation of the majority of sparingly soluble salts is controlled by surface reaction. The additives inhibit the process through adsorption at active growth sites on the crystal surface. The adsorption of inhibitor molecules on the surface of the crystals may be interpreted by an equilibrium adsorption isotherm. The theoretical basis of Adsorption Isotherms is customarily described in terms of a balance of rates of adsorption and desorption [26]. Three important assumptions are made:

1. The adsorbate covers the surface up to complete coverage as a monolayer on the substrate (adsorbent).
2. There are no adsorbate–adsorbate interactions on the surface of the host substrate.
3. On the substrate all binding sites are equivalent.

Assuming the constraints of the Langmuir isotherm including the absence of interaction between adsorbed molecules, the rate of crystal growth in the presence of inhibitor is given by [27]:

$$R_i = R_0 - \theta R_0 (1-b) \tag{5}$$

where θ is the fraction covered by inhibitor, R_o is the rate in the absence of inhibitor and bR_o is the limiting rate in the presence of inhibitor ($0 < |b| \le 1$). The parameter b measures the effectiveness of an inhibitor, when present at infinite concentration, at monolayer coverage, or at a concentration less than that for monolayer coverage [28]. If $b = 0$, the inhibitor is capable of completely inhibiting the rates of growth or dissolution at concentrations approaching infinity [27].

$$\theta = \frac{1}{1+K^{-1}C_i^{-1}} \tag{6}$$

where K is the affinity of the inhibitor for the surface and C_i is the concentration of the inhibitor in solution

$$R_i = R_0 - \left(\frac{1}{1+K^{-1}C_t^{-1}}\right)\cdot R_0 \cdot (1-b) \tag{7}$$

Table 2
Equations expressing relationship between scale mass and additive concentration derived from the curves

Additive	Equation	R^2
EDTP	$m = 0.0574 \exp(-0.1055\ \mathrm{Ca})$	0.9990
EDTP	$\log m = -0.0458\ \mathrm{Ca} - 1.2414$	0.9990
NTMP	$m = 0.0588 \exp(-0.0536\ \mathrm{Ca})$	0.9878
NTMP	$\log m = -0.0233\ \mathrm{Ca} - 1.2304$	0.9878
NDPA	$m = 0.0555 \exp(-0.0100\ \mathrm{Ca})$	0.9969
NDPA	$\log m = -0.0044\ \mathrm{Ca} - 1.2553$	0.9969

The Langmuir adsorption isotherm can be written as:

$$\frac{R_0}{R_0 - R_i} = \frac{1 + K^{-1}C_i^{-1}}{1-b} \tag{8}$$

$$\frac{R_0}{R_0 - R_i} = \frac{1}{1-b} + \frac{1}{K(1-b)} \cdot C_i^{-1} \tag{9}$$

The plot of $R_o/(R_o - R_i)$ against C_i^{-1} is a straight line, whose extrapolation meets the y-axis at $1/(1 - b)$. The ideal Langmuir behaviour is represented by $b = 0$ (line A), thus complete inhibition ($R_i = 0$) exists at infinite additive concentration. If $b > 0$, the curve crosses the y-axis at a point higher than 1 (line B), indicating that the inhibitor is not capable of complete inhibition on growth or dissolution. In contrast, a y-axis intercept less than 1 (line C) implies that the additive can suppress the crystal growth completely at concentrations below those required for a complete monolayer coverage [27].

Experimental results show that the curves of $R_o/(R_o - R_i)$ vs. C_i^{-1} for the phosphonate inhibitors are straight lines as expected (Fig. 8). It indicates that the Langmuir isotherm satisfactorily describes the inhibiting effects of these additives in terms of a monomolecular blocking layer of adsorbate at the crystal surface.

The curves corresponding to the two first inhibitors (a) and (b) have the form of line C while the third one (c) is closer to the ideal line A. Therefore, EDTP and NTMP are much more effective than NDPA, which is unable to completely inhibit the crystal growth unless a much higher concentration is used. The curves (d) and (e) have the form of line B, indicating that the two corresponding chemicals do not have the capability of completely suppressing the growth of gypsum at any concentration in the conditions of the experiments currently used.

The coefficient b calculated from Table 3 has a negative value for the first three additives, which indicates that the crystal growth can be suppressed completely at the additive concentrations below those required for a total coverage of the crystal surface. When $R_o/(R_o - R_i) = 1$, the corresponding concentrations of EDTP, NTMP and NDPA are $3{\times}10^{-6}$, $7.0{\times}10^{-6}$ and $6.0{\times}10^{-5}$ mol L^{-1}, respectively. At additive concentrations higher than these critical concentrations, complete inhibition of scaling will occur. These values are consistent with the experimental results. In all the investigated concentrations, EDTP was capable to completely inhibit the scale formation of calcium sulphate at concentrations of $5{\times}10^{-6}$ and $1{\times}10^{-5}$ mol L^{-1}. Similarly, NTMP could exert a complete inhibition at concentration of $1{\times}10^{-5}$ mol L^{-1} only, and NDPA was unable to inhibit the scaling completely at any of the concentrations employed, which were well lower than its critical concentration. On the other hand, HEDP and NPDA with positive b values are not capable of complete inhibition on the growth of calcium sulfate scales regardless how much the concentration is used.

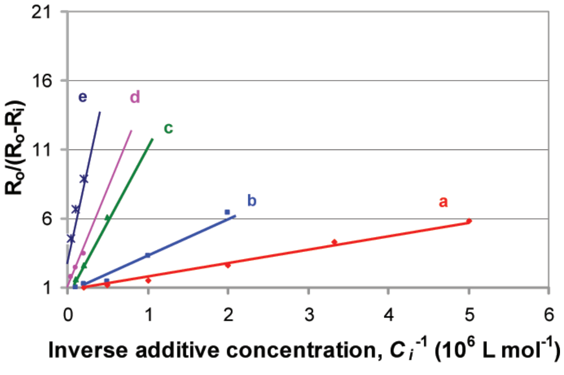


Fig. 8. Experimental plots of $R_o/(R_o - R_i)$ against inverse additive concentration. Additive: (a) EDTP; (b) NTMP; (c) NDPA; (d) HEDP; (e) NPDA.

Table 3
Langmuir isotherm constants for the phosphonic additives

Additive	$1/(1 - b)$	$1/[k(1 - b)]$	b
EDTP	0.6386	0.6386	–0.5659
NTMP	0.6461	2.8276	–0.5477
NDPA	0.8668	8.0033	–0.1536
HEDP	1.0154	14.598	0.0154
NPDA	3.4640	27.987	0.7113

3.5. Effects of chemical structure

The inhibition efficiency order of the investigated organic additives is found as follows:

EDTP > NTMP > NDPA > HEDP> NPDA

It is found that this order corresponds to the number of phosphonate groups that the additives possess. EDTP with four phosphonate groups at low concentrations completely suppresses the scaling of calcium sulfate from a 0.075 M supersaturated solution during four hours. The excellent performance of EDTP in preventing calcium sulphate precipitation has been reported by several authors [12,13,15,28]. NTMP having three phosphonate functional groups, at the concentration of $1{\times}10^{-5}$ mol L^{-1}, suppresses calcium sulfate scale formation as does EDTP; however, it is much less effective at lower concentrations. For instance, $1{\times}10^{-6}$ mol L^{-1} NTMP exhibits only a 30.43% inhibition compared with 65.70% inhibition given by EDTP at the same concentration. NDPA with two phosphonate groups is even less effective, giving only 64.20% inhibition at a concentration of $1{\times}10^{-5}$ mol L^{-1}. HEDP possesses two phosphonate groups and one hydroxyl group. In the same conditions it suppresses only 40.3% of total growth and therefore is much less effective than NDPA which also carries two phosphonic groups and one carboxylic group. The data well agrees with a report by Klepetsanis and Koutsoukos [12] who found a rate reduction of 40% of gypsum precipitation in the presence of 1×10^{-5} mol L^{-1} HEDP. Bosbach and Hochella [29] reported a total blocking of monolayer steps of gypsum and crystal growth stopped when increasing the HEDP concentration to 20×10^{-5} M in a supersaturated solution containing 0.023 M Ca^{2+} and SO_4^{2-}, but results from Wilson [15] showed only 24–28 % of inhibition at HEDP concentrations of $1–5\times10^{-5}$ M for a 0.035 M $CaSO_4$ solution. Actually, although HEDP is very effective in inhibiting the crystallisation of barium sulfate and calcium carbonate [14,19–22] the effect of HEDP on gypsum control is rather poor as compared with other polyphosphonic acid such as NTMP and EDTP [12,15,30]. The better performance of NDPA can be attributed to the flexible structure of NDPA which has a three-atom chain from the nitrogen atom to the oxygen atom while HEDP possesses a more rigid structure with only a two atom chain from the carbon atom to the oxygen atom. It was suggested that an effective inhibitor should contain at least two phosphonate groups and a "two atom chain" — the chain from the centre of the molecule to the phosphorus atom on the phosphonate group [31]. The inhibiting capability of the phosphonates is attributed to the fact that the phosphonate groups closely match the sulphate lattice positions [15]. The size and geometric structure of methylene phosphonate group ($–CH_2PO_3^{2-}$) is similar to those of hydrogenphosphate (HPO_4^{2-}). On the other hand, brushite ($CaHPO_4.2H_2O$) is isostructural with gypsum ($CaSO_4.2H_2O$). They have very similar unit cell size and anionic tetrahedral orientation with a layered structure containing sheets of water and, in fact, it is known that gypsum can grow epitaxially on brushite [32]. Therefore, it is suggested that sulphate ions in the gypsum lattice can be easily replaced by hydrogenphosphates and similar species.

4. Conclusion

Phosphonic additives have a great impact on the deposition of gypsum on the pipe walls. EDTP and NTMP are the most effective to prevent calcium sulphate scaling on the pipe walls, while HEDP and NPDA shows a low capability of inhibition. Since data from extensive literature using stirred crystallisers is correlated well to those of the pipe system studied here, it is concluded that moving from a stirred reactor to a pipe reactor does not change the effectiveness of the inhibitors.

The best fit equation of scale deposition for the whole range of additive concentration is an exponential function, excluding all the points where the scale mass values are equal to 0. The inhibiting effects of the organic additives are described satisfactorily with the Langmuir isotherm, which can be used to estimate the critical concentration of additives, under which the inhibition of scale formation would be incomplete.

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