

Investigation into the effect of phosphonate inhibitors on barium sulfate precipitation

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Abstract

The effect of a series of phosphonate molecules on barium sulfate precipitation was tested. While an increase in the number of phosphonate groups generally resulted in increased inhibition of barium sulfate precipitation, two notable exceptions showed that a relatively high number of phosphonate groups does not guarantee inhibition while a relatively low number of phosphonate groups does not imply no inhibition. Increasing the pH showed an increased effect of additives on barium sulfate precipitation up to pH 8. However, on increasing from pH 8 to 12, a loss of inhibition in the additives was observed which appears to be due to the barium sulfate surface changing with pH.

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1. Introduction

Scale occurs in many processes ranging from desalination to oil production and results in costs associated with its removal. Barium sulfate is a known scale that is particularly prevalent in oil production [1, 2]. The solid has a low solubility product [3],

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$K_{sp} \sim 10^{-9.99}$ but solubility is found to increase when electrolytes are present. Since much literature exists on barium sulfate and since it is an industrial scale problem, barium sulfate appears to be a suitable choice as a model compound to investigate the factors which affect scale formation. To this end, isostructural compounds were selected to ascertain the effects of chemical factors and shape factors on precipitation inhibition behavior. For this purpose, the effect of various phosphonate based organics on the precipitation of barium sulfate was experimentally determined. These experimental results will be combined with molecular modelling studies in the future as part of a holistic approach to determining how scale inhibitors function.

The following organics were investigated (Fig. 1): EDTP = ethylenediaminetetraphosphonic acid, HEDP = hydroxyethylenediphosphonic acid, MNDP = N-methyl-nitrilodimethylene phosphonic acid, NDP = nitrilodimethylenephosphonic acid, NTMP = nitrilotrimethylenephosphonic acid, and DOTP = teraazocyclododecanetetramethylenephosphonic acid. In these compounds, the number of phosphonate groups increases from 2 up to 4. It is hoped the differences between these molecules, as well as their similarities, will shed some insight into their mode of behavior on crystallization.

2. Experimental

Solids ($BaCl_2$, NaOH and Na_2SO_4), made to the required concentrations using MilliQ water, were of analytical grade from Ajax and BDH. HCl was diluted from 32% (AR grade) concentrated solution obtained from Ajax. Filtered MilliQ water, having a resistance of 18 M Ω , was used throughout. Organic additives were either AR grade from Aldrich or synthesized in-house.

The experiments conducted were non-seeded precipitation runs in a thermostatted reaction vessel, monitored using conductivity. The value quoted as S (supersaturation) is defined as $S = c/c_0$, where c is the initial concentration of the barium sulfate in solution and c_0 is the equilibrium solubility concentration at 25°C. The method consisted of equilibrating 200 mL MilliQ water with 0.5 ml BaCl₂ (100 mM, final Ba²⁺ concentration 0.249 mM). The conductivity meter was then set to record and the values logged onto a computer. Equivalent Na₂SO₄ (0.5 ml, 100 mM) was added to commence the reaction. The graph of conductivity versus time was used to calculate k_{obs} by fitting the linear region of the de-supersaturation curve [4]. The natural pH was found to be 5.6 and this was altered by addition of either dilute HCl or NaOH to achieve pH values from 3-12.

The solutions from conductivity measurements were either placed into clean polyethylene containers at the bottom of which were cleaned, round glass microscope cover slips to collect the solids (when precipitation was not seen to occur during the conductivity run) or the solution was directly filtered through a 0.2 μm filter and the solids collected.

The solutions with the cover slips were allowed to stand for a couple of days. The cover slips were removed with tweezers, filter paper was used to adsorb any remaining electrolyte and then the slip was placed onto carbon tape which was fixed to the SEM stub. The filtered solids were placed into a small amount of MilliQ water, pipetted onto the Scanning Electron Microscope (SEM) stub directly and allowed to dry. The cover slip was also allowed to dry thoroughly before all samples were sputter coated with gold. Images were obtained on a Philips XL30 machine.

3. Results and discussion

Reproducibility of the experiments was assessed by performing 7 control runs. They showed a rate of change in conductivity in the linear regime of $(3.34 \pm 0.25) \times 10^{-5} \mu\text{S s}^{-1}$ and an induction time of 154 ± 30 s. The reproducibility was confirmed by running a control before starting the next series of experiments with a new additive.

NDP showed no inhibition of barium sulfate precipitation (see Fig. 2a). The SEM image shows that the overall morphology remains unaffected by the addition of this additive, even at 10 ppm (4.9×10^{-5} M; Fig. 3b) though some rounding of the corners is observed. This high level corresponds to about 1 molecule of additive per 5 barium atoms and when the phosphonate groups are taken into account this equates to about one phosphonate functional group per 2.5 barium atoms. The MNDP behaved similarly to the NDP (Fig. 2a). The morphology of the barium sulfate was completely unaltered in the presence of up to 10 ppm (4.6×10^{-5} M) of this additive (again, roughly 1 phosphonate functional group to 2.5 barium atoms). Phosphonate inhibitors are known to be good inhibitors and it was found that the lack of inhibition for these molecules is most likely related to the pH. This suggests that the species present at the natural pH of 5.6 was not the optimal species for interaction with the barium sulfate surface. The lack of interaction at this pH is reflected in the negligible effect on the resultant barium sulfate morphology.

Barium sulfate precipitated in the presence of NTMP was inhibited (Fig. 2b). At 5 ppm NTMP (1.6×10^{-5} M), the barium sulfate particles are round and thin (Fig. 3c) and the de-supersaturation rate is about 50% of the control. This level of NTMP is equivalent to 1 phosphonate molecule per 15 barium atoms or 1 phosphonate functional group per 5 barium atoms.

Interestingly, the macrocyclic DOTP molecule increases the rate of precipitation of barium sulfate (Fig. 2b). The morphology was rather insensitive to increasing DOTP concentration (up to 10 ppm $\equiv 1.8 \times 10^{-5}$ M), being similar in all cases. The particles were almost identical to the control sample except that a new edge appeared which rounded the ends (Fig. 3b). Again a lack of inhibition resulted in minor morphological changes.

HEDP had a significant effect on the de-supersaturation rate (Fig. 2c). The morphology of barium sulfate in the presence of 5 ppm HEDP was significantly altered such that thin round particles were formed (Fig. 3f). At this level of HEDP, the effect on barium sulfate de-supersaturation was almost complete inhibition. The amount of HEDP required to achieve 50% inhibition relative to the control corresponds to 0.24×10^{-5} moles per litre. This is roughly 1 phosphonate molecule per 100 barium atoms or 1 phosphonic acid functional group per 50 barium atoms. It should be noted that the increase in the number of phosphonate groups on going from HEDP to NTMP does not result in better inhibition for NTMP. While both inhibit at this pH, HEDP is better both on the basis of per molecule and per phosphonate functional group and this may be associated with the OH group bonding with the surface as suggested by van der Leeden [5].

EDTP was found to be very effective in inhibiting barium sulfate precipitation (Fig. 2c). Only 0.5 ppm (0.1×10^{-5} moles per litre) is required to effectively suppress precipitation (this corresponds to roughly 1 phosphonate molecule per 200 barium atoms). Even if each of the phosphonate molecules were able to complex 4 barium atoms this is still a ratio of 1:50 for complete inhibition. The SEM image shows that at 0.5 ppm,

where total inhibition is observed, thread-like particles in the 5-10 μm range eventually appear when the solution is allowed to stand for two days (Fig. 3e).

While it is tempting to say the difference between DOTP and EDTP is due to structural differences, preliminary molecular modelling studies on the (001) face showed that DOTP and EDTP (both fully de-protonated) can form similar adsorbed structures. The difference in inhibition, therefore, appears to be more complex and is perhaps due to hydration and/or complexation effects with the solution. If HEDP and DOTP are excluded, the trend is that inhibition increases with increasing number of phosphonate groups. However, with the inclusion of these two additional molecules it is clear that this trend is not general. When significant inhibition of barium sulfate precipitation occurs, this dramatically alters the morphology of the barium sulfate particles. While the conductivity results suggest that the morphological change is due to changes in the growth rate (caused by adsorption onto particular faces) of barium sulfate, the possibility of nucleation inhibition by these compounds cannot be excluded.

10 ppm NDP , 2 ppm HEDP, 0.2 ppm EDTP and 2 ppm NTMP were then selected to assess the effect of pH. Controls at each pH were conducted and runs were then performed with a phosphonate additive present. The linear de-supersaturation rate in the presence of the phosphonate additives at each pH was normalized by dividing by the linear de-supersaturation rate of the control at the same pH. These data are plotted versus pH in Fig. 4; a low ratio implies good inhibition. Clearly, maximum inhibition occurs at a pH of about 8 for all of the additives. Deterioration in the inhibition activity is noted on further increasing the pH to 12. The control morphology at each pH was equivalent to the control at pH 5.6 (see Fig. 3a) except at pH 12 where the morphology was more

rhombohedral. The morphology of the barium sulfate particles formed in the presence of all the additives at pH 3 were equivalent to the control at pH 5.6.

Inhibition by the NDP molecule improved with increasing pH and the particles formed at pH 8 are consistent with those obtained by Black *et al.* [6]. We would predict that the MNDP would also inhibit at the higher pHs given that the most likely cause for NDP inhibiting at the higher pHs is the dissociation state of the molecule. The dissociation constants for NDP would be expected to change, but not substantially, with the addition of a methyl group.

As a first approximation to understanding this behavior, speciation curves for HEDP and NTMP using literature dissociation constants were obtained [7]. Firstly, it appears that on going from pH 3 to 8 there is a benefit in the inhibitor molecule becoming more ionized. This happens even though the surface of the barium sulfate is more negative at the higher pHs (point of zero charge of the barium sulfate surface is between pH 5-6 [8]). One possibility is that inhibition becomes significant when the organic additive is ionized such that a PO_3^{2-} species is present. However, this hypothesis is not supported by the speciation curves of the active HEDP which suggest that the dominant species is most likely that with two PO_3H^- groups. It must be remembered though that the speciation curves may not actually determine what species are present in our system as the effects of complexation of barium with the inhibitor molecules and the effect of surfaces on speciation are not included.

On increasing pH further, it can be seen that the degree of inhibition is reduced. This is well known for polymer inhibitors and is considered to be due to an increase in charge density on the polymer [9]. Using our preliminary speciation curves it was found

that the dominant NTMP species at pH 8 was unchanged at pH 12 (the 5^- species) and hence it is unlikely that the change in the efficacy is related to the protonation state of the additive. However, two other possibilities exist:

- i) The surface becomes increasingly negative and thus electrostatically repels the ionized inhibitor molecules.
- ii) The surface becomes increasingly negative, losing surface protons (from hydration water) and loses its hydrogen bonding capability with the inhibitor molecule.

No effort was made to match the ionic strength as pH was changed. Therefore, an increase in pH may also be associated with an increase in ionic strength. As such, electrostatic repulsion may be screened by the several fold increase in ions. This is currently being further investigated. It appears, however, that the surface properties of barium sulfate particles are the dominant factor determining the change in the inhibition activity with pHs above 8.

4. Summary

A general indicator into the inhibition strength of additives on the precipitation of barium sulfate is the number of phosphonate groups within the molecule. However, this should be used with care as other factors also determine the degree of inhibition as shown by the strong inhibition observed in the presence of HEDP and the non-inhibition of barium sulfate precipitation when DOTP was present. These 'other' factors include structural matching with the crystal lattice, ease of removal of the hydration layer, degree of dissociation, complexation with ions in solution and the ability to hydrogen bond.

Changes in pH show that the greater the degree of dissociation of the inhibitor molecule, the better is the inhibition (up to pH 8). However, on further increasing the pH

to 12, a decrease is observed which is associated either with the surface charge and/or the surface hydration configuration of the barium sulfate particles formed.

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Figure Captions

- Fig. 1. Schematic of the phosphonate inhibitors used in this study and the acronyms assigned to them.
- Fig. 2. De-supersaturation curves in the presence of the phosphonate inhibitor molecules. (a) 10 ppm NDP and 10 ppm MNDP, (b) 10 ppm NTMP and 10 ppm DOTP, (c) 2 ppm HEDP and 0.5 ppm EDTP. A control curve is shown in each figure for comparison.
- Fig. 3. SEM pictures of barium sulfate formed in the presence of the phosphonate molecules at pH 5.6: (a) Control, (b) 10 ppm NDP, (c) 10 ppm DOTP, (d) 10 ppm NTMP, (e) 0.5 ppm EDTP and (f) 2 ppm HEDP.
- Fig. 4. Dependence of inhibition capability of different additives (measured as ratio of growth rate in presence of additives to growth rate of blank) on pH. Concentrations used were: 10 ppm NDP, 2 ppm HEDP, 0.2 ppm EDTP and 2 ppm NTMP.

Fig 1

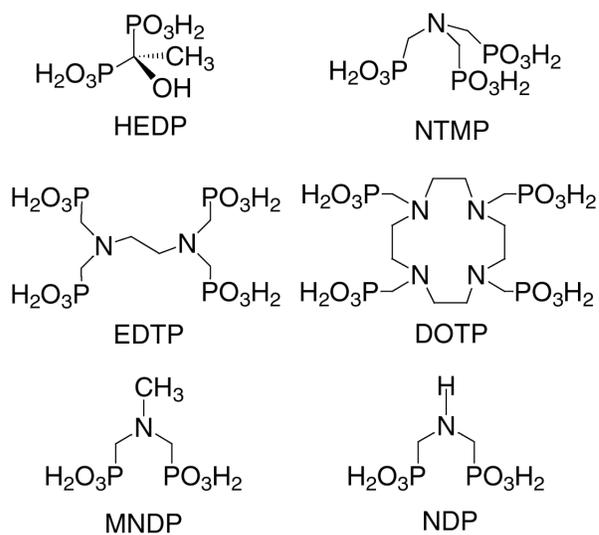


Fig 2(a)

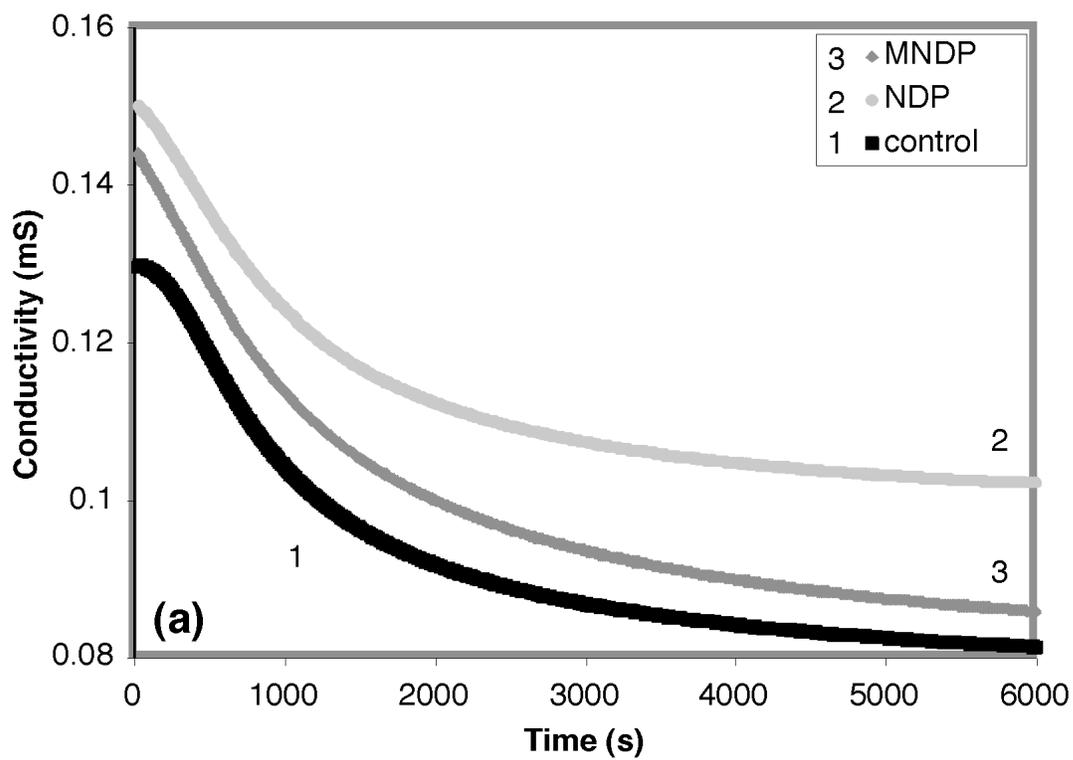


Fig 2(b)

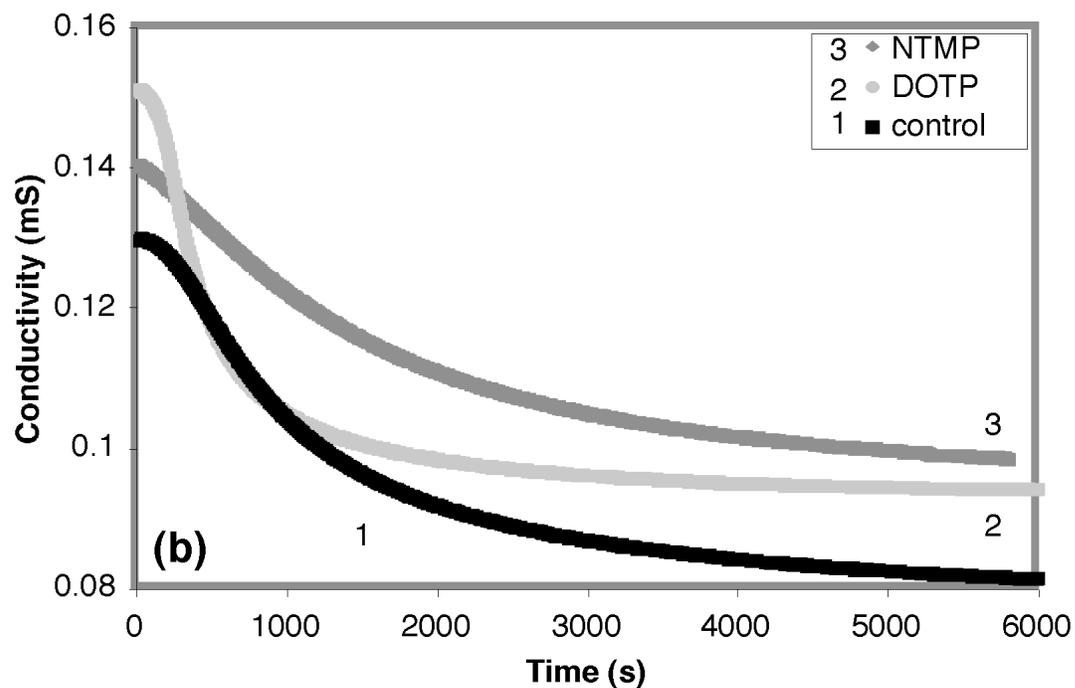


Figure 2(c)

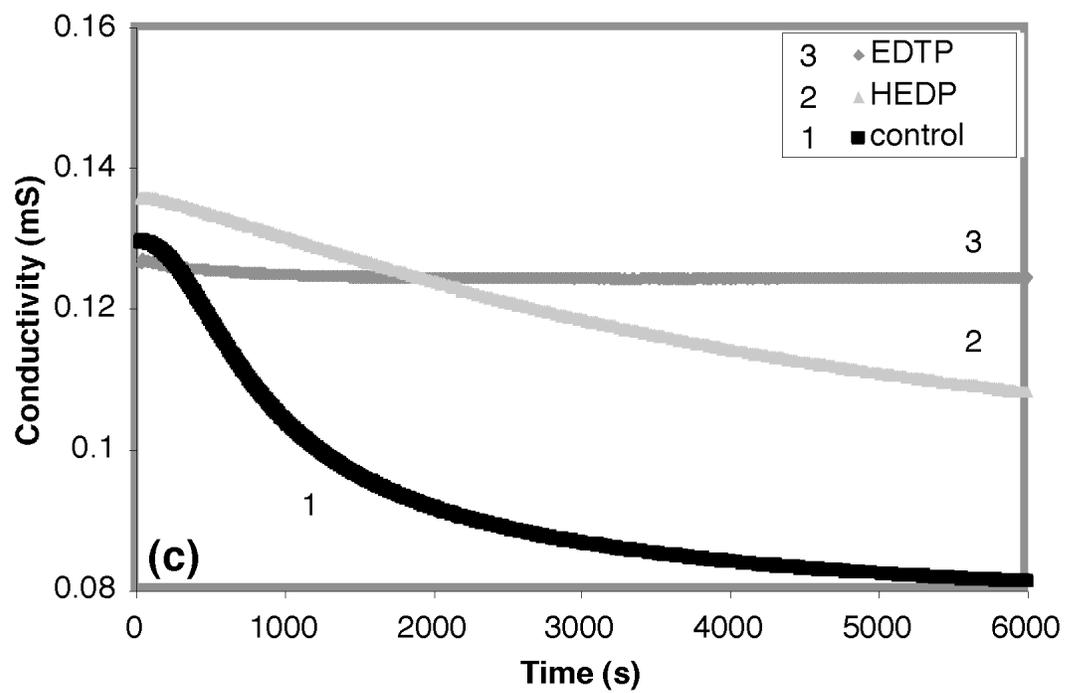


Figure 3

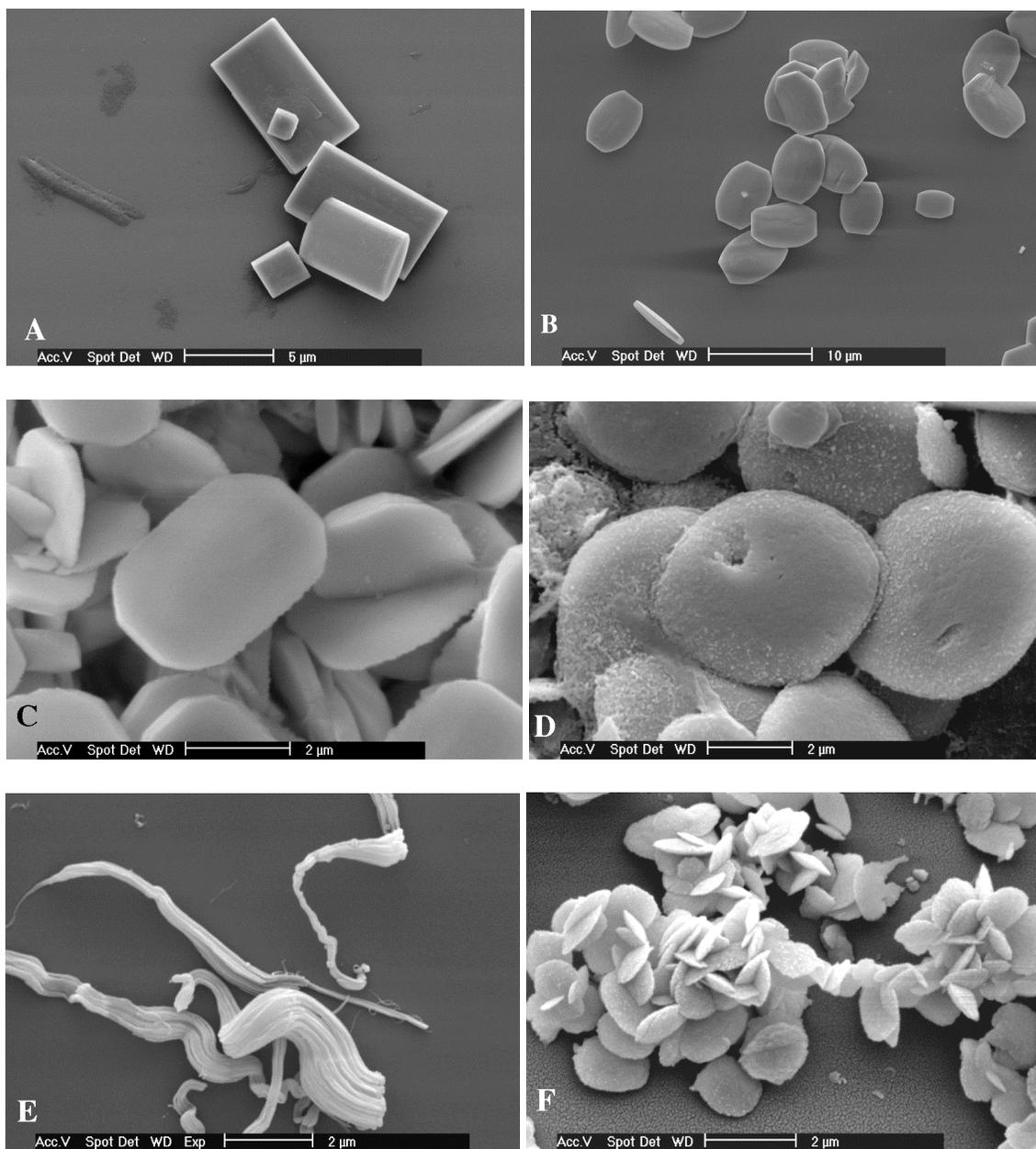


Figure 4

