

# **The role of phosphonate speciation on the inhibition of barium sulfate precipitation**

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## **Abstract**

The inhibition of barium sulfate precipitation in the presence of phosphonate containing molecules was investigated experimentally and speciation curves were used to elucidate the interactions involved. Inhibition of precipitation was found to be pH dependent and loss of inhibition was observed at both very high and low pHs. Maximum inhibition for all the inhibitor molecules occurred at pH 8. While speciation curves showed that inhibition could be improved by the presence of 2 or more fully de-protonated phosphonate groups (for pure aminophosphonates) on the molecule at  $\text{pH} \leq 8$ , at pH 12 inhibition was insensitive to the number of de-protonated phosphonate groups. It is, therefore, suggested that surface charge repulsion affects inhibition at very high pH. For molecules which are not pure aminophosphonates, stereochemistry as well as functional groups and their ionisation state appear to play a significant role in inhibition at  $3 < \text{pH} \leq 8$ .

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## **Introduction**

The precipitation of sparingly soluble salts in nature, and in industrial processes, has been of much interest to chemists in recent years. In nature, the phase, structural properties, and morphology of biominerals is controlled with remarkable precision [1]. Therefore, many scientists have tried to understand the mechanisms involved with a view to the development of novel, new synthetic routes for the manufacture of advanced materials. In industrial processes the precipitation of sparingly soluble salts as scale is a cause for concern due to down-time required to clean equipment and the cost of possible loss of product purity due to the presence of these unwanted minerals [2]. Phosphonate molecules have been identified as compounds that strongly interact with a host of mineral phases [3-7]. These phosphonates have been used both as templates for the crystallization of unusual morphologies and phases [6,7] as well as inhibitors to prevent scale formation in industrial circuits [4, 5]. To date, the mechanism of phosphonate interaction with the mineral surfaces is assumed to be a combination of stereochemistry (lattice matching) and the presence of two fully deprotonated phosphonate groups [3]. It is the intention of this paper to elucidate the effect of phosphonate ionisation state on the interaction of polyphosphonate molecules with barium sulfate and thereby either confirm or discount this hypothesis for the system studied here.

Phosphonate molecules are multi-protic and their charge depends not only on the pH but also on any interactions with any cations present. Chelation with the cation can alter the speciation for the inhibitor molecules and thus needs to be considered when creating speciation models. In an effort to understand which species interact with barium sulfate surfaces, we present experimental data that have been obtained for various inhibitors with different numbers of phosphonate groups at different pHs. These are correlated to the calculated speciation curves for these inhibitors based, where possible, on literature protonation and complexation constants.

## **Materials**

BaCl<sub>2</sub>, NaOH and Na<sub>2</sub>SO<sub>4</sub> (AR grade, from Ajax or BDH) were dissolved to the required concentrations using MilliQ water. HCl was diluted from 32% (AR grade, Ajax) concentrated solution. Filtered MilliQ water, having a resistance of 18 MΩ, was used throughout.

Organic additives were either AR grade from Aldrich or synthesised in-house. They were:

NDP = nitrilodimethylenephosphonate

HEDP = hydroxyethylenediphosphonate

NTMP = nitrilotrimethylenephosphonate

EDTP = ethylenediaminetetraphosphonate

These are shown schematically in Figure 1.

## Methods

### *Experimental*

Non-seeded, de-supersaturation curves were obtained using a thermostatted cell kept at a temperature of 25 °C as described in detail in [8]. The precipitation of barium sulfate was monitored using a conductivity meter. The initial supersaturation ratio,  $S$ , (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) was  $\sim 21$  for all experiments. At lower pH, the faster de-supersaturation rate resulted in higher errors than at the higher pHs. The graph of conductivity versus time was used to calculate  $k_{\text{obs}}$  by fitting the linear region of the de-supersaturation curve [8]. 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 degree of inhibition at any given pH was determined by taking the ratio of the slope in the linear regime of the conductivity curve ( $k_{\text{obs,inh}}$ ) with the inhibitor present to the  $k_{\text{obs,con}}$  for the control (absence of inhibitor) run at the same pH. A low ratio implies good inhibition. All of the molecules inhibited to different degrees and at different concentrations, a range of concentrations was tested. In an effort to assess the impact of pH on the degree of inhibition, the concentration of organics presented are those which allowed differences in de-supersaturation rate to be observed.

An investigation of the effect of ionic strength was attempted at pH 12 by the addition of 1 mL 100mM NaCl and subsequent analysis by AAS (Atomic Absorption Spectroscopy), however, the presence of such large salt concentrations gave irreproducible results. The effect of ionic strength was, therefore, investigated at pH 8 using the additive NDP. The supersaturation does alter slightly when ionic strength is increased and the addition of 1mM NaCl at pH 8, on an ionic strength basis, is more

comparable to pH 3 and pH 12 than the pH 8 experiment without additional salt. However, the difference in supersaturation is at most 15%. The NDP molecule, without additional NaCl, gave a de-supersaturation rate ~60% of the control. These experiments could be followed by the conductivity meter as per the usual experiments and involved an additional 0.5 and 1 mL of 100mM NaCl being added to the control and additive runs.

Solids were filtered and dried in a desiccator. A small portion of the filter paper was placed onto an SEM (Scanning Electron Microscopy) stub that had carbon tape on it. The stub was then gold sputtered before being viewed in an Philips XL30 SEM.

### *Speciation curves*

Speciation curves were calculated using the Hyss program [9]. Equilibrium constant data, both for protonation and complexation reactions, were obtained from the on-line JESS thermodynamic database [10].

No barium complexation constants were available for NDP and therefore only protonation constants are compared with the growth experiments.

## Results

### *Experimental*

Inhibition, for the purposes of this paper, is defined as a lower de-supersaturation rate than the control. Thus, inhibition could be due to an effect on either nucleation rate, and/or growth rate. Conductivity alone cannot differentiate between these mechanisms and therefore we make no assumptions about which of these possibilities results in the decreased de-supersaturation rate. However, for both nucleation and growth inhibition, the additives must interact with either the surface of the critical nuclei or the surface of the growing crystal and it is this interaction that we are presently investigating. Our previous work [8] showed that the degree of inhibition is sensitive to pH.

Of the diphosphonate molecules investigated, at the natural pH of 5.6, only HEDP showed significant inhibitory action on the precipitation of barium sulfate. In contrast, NDP had no effect on either morphology or inhibition. NTMP (containing 3 phosphonate groups) showed inhibition and EDTP, containing 4 phosphonate groups, showed the greatest inhibitory action at pH 5.6. On a mole basis (for 50% inhibition compared to the control), it was found that the strength of inhibition followed: EDTP>HEDP≈NTMP>NDP. However, given that HEDP only contains two phosphonate groups compared to NTMP which has three, on a phosphonate group basis the trend would be EDTP>HEDP>NTMP>NDP.

The results with changing pH (see Figure 2 and Table 1) clearly show that as pH increases, inhibitory action increases up to pH 8. Interestingly, even the originally ineffective molecule NDP shows some inhibition activity at this pH and the resultant

particles are equivalent to those obtained by Black *et al.*, [3]. In all cases, where inhibition occurred, the crystal morphology was also altered relative to the control. There was no change in morphology on going from pH 8 to 12 and so only the resultant barium sulfate particles at pH 5.6 and pH 8 are shown in Figure 3. For those additives which inhibited at pH 5.6, the morphology altered little on raising the pH to 8. For most additives, the first morphological change on inhibition is to round the ends of the normally rectangular particles.

It is then clearly observed that the inhibitory efficacy for all additives decreases as the pH is increased from pH 8 to 12. Of particular interest is that all of the additives at pH 12 inhibit to a similar degree (all ratios lie between 59-66% of the control, with most additives inhibiting to ~60% of the control).

All of the additive molecules are ineffective as inhibitors at pH 3 (only showing at best 20% inhibition) despite being at least partially ionised (according to speciation curves) and despite the barium sulfate surface being positive at this pH (pzc of barium sulfate ~pH 6 [11]). Therefore, the effect of electrostatic attraction between the surface and the additive molecule at pHs < 5.6 is not as significant as might be expected.

In the range  $3 < \text{pHs} \leq 8$  the effect of all the additives increases with increasing pH. In this regime, both the additives and the barium sulfate surface are becoming more negative. It appears most likely that the inhibitory action is, in this pH regime, able to overcome the electrostatic repulsion between the negative surface groups and the increasingly negative phosphonate groups. However, it also cannot be ruled out that

the interaction is between the negative functional groups of the additive and surface waters (physi- or chemi-sorbed) to the barium sulfate particles.

At pHs > 8 it is possible that the increased negative repulsion between a negative additive species and a more negative surface causes the decreased inhibition. As stated previously (Experimental section), attempts to test this at pH 12 were unsuccessful, therefore, tests were carried out on NDP with additional NaCl to screen the negative charge on the surface at pH 8. Controls under the same conditions were performed in order to allow for the increased solubility of barium sulfate at higher ionic strength [11]. The ratio of de-supersaturation in the presence of inhibitor to the control was taken as described previously. The only factor not taken into consideration is that the increase in solubility of the barium sulfate in the presence of salt will mean that the additive will be acting on a less supersaturated solution. The difference in supersaturation was overestimated (due to the non-linearity of the solubility curve - interpolation of the values given by Gallardo et al., [11]) to change from  $S \sim 21$  to  $S \sim 17$ . This difference (15%) is not insignificant but is, it must be remembered, an overestimation. Interestingly, inhibition by NDP improved substantially (ratio dropped from  $\sim 60\%$  to 15%) with only 0.5 mM increase in NaCl, improving only slightly with a further 0.5 mM increase in ionic strength (see Table 1). Since the results show that the initial substantial drop in precipitation is only slightly improved with further salt addition it is surmised that the improved NDP inhibitory action is largely due to charge screening rather than the decrease in supersaturation. This is consistent with electrostatic repulsion causing the decreased inhibition at higher pH.



### *Speciation curves*

Firstly, for all additive molecules where the data are available, complexation of the additive with barium at the levels investigated experimentally is negligible up to pHs=9, thus using protonation constants alone does not seriously undermine the comparison with experimental results. For all molecules, the maximum concentration investigated was at ratios of roughly 10 Ba:1 additive molecule, therefore, the speciation curves are calculated accordingly. Also, the species which are aminophosphonates are known to form zwitterions [12, 13] and therefore the species have been presented accordingly. Schematics of the inhibitor molecules with their different degrees of protonation are given in the Appendix.

In Figure 4, when NDP is present, we can see that at pH 3 the dominant species is  $N^+H_2(CH_2PO_3H)_2$  while at pH 5.6 the  $N^+H_2(CH_2PO_3H)(CH_2PO_3^{2-})$  dominates. Only by pH 8 does the species with both fully de-protonated phosphonate groups become significant, and this coincidentally matches the inhibition data. On going from pH 8 to pH 12 the NDP molecule is either fully de-protonated or contains two  $PO_3^{2-}$  groups.

For HEDP there is no zwitterion formation, so at pH 3 there are no  $PO_3^{2-}$  groups, the molecule being  $C(CH_3)(OH)(PO_3H)_2$ . However, despite only 5% of the HEDP at pH 5.6 having at least one  $PO_3^{2-}$  group, inhibition is quite strong. The maximum inhibition occurs at pH 8 as for all the other additives and at this pH the additive has predominantly one  $PO_3^{2-}$  group. By pH 12 the HEDP is predominantly fully de-protonated or complexed but inhibition is much compromised. Thus, it could be argued that the complexation of the additive with barium also contributes to a loss in inhibition.

At pH 3 the dominant species of the NTMP molecule is  $MH_4$ , implying no  $PO_3^{2-}$  groups are present at this pH. At pH 5.6, approximately 31% of the NTMP is  $MH_2$  which gives rise to two  $PO_3^{2-}$  groups within the molecule. At pH 8 and all the way to pH 12, the dominant species is the  $MH$  molecule, meaning there are three  $PO_3^{2-}$  groups present. The change in speciation from pH 8 to 12 is similar to HEDP (ie complexation occurs).

EDTP follows the trend of NTMP which improves in inhibitory activity as the number of  $PO_3^{2-}$  groups increases up to pH 8. At pH 3 the EDTP molecule contains at most one  $PO_3^{2-}$  group. On raising the pH to 5.6 the major EDTP species contains two  $PO_3^{2-}$  groups and by pH 8, EDTP has 3 fully de-protonated phosphonate groups. On increasing the pH further we see that complexation of barium to EDTP begins to occur, and, by pH 12 this accounts for most of the EDTP molecules.

## **Discussion**

If we exclude HEDP for the time being, it can be seen that the maximum inhibitory action for the phosphonates at pH 8 corresponds in all cases to the presence of *at least* 2  $PO_3^{2-}$  groups within the molecule. It might be that complexation of the additive to barium results in lowered inhibition efficacy; however, the results at pH 8 with additional salt added (where the degree of complexation would have remained the same) shows that there is also a substantial electrostatic interaction present. Thus, the lowered inhibition on raising the pH further is most probably due to charge repulsion between the negatively charged surface and the negatively charged additive. For all additives this electrostatic repulsion appears to become more and more dominant as

the pH increases. Thus, for all of the additives, increasing the pH to 12 results in at least partial loss of inhibitory activity due to the increased repulsive interaction between additive and surface. This is supported by the similarity of inhibition at pH 12 regardless of structure (~60-65%).

It appears that in fact the presence of 2 fully ionised phosphonates is only part of the answer for optimal inhibitory action, as this occurs for EDTP and NTMP at pH 5.6, yet the maximum inhibition still occurs at pH 8. This may, in part, be due to the stereochemical differences between EDTP and molecules such as NDP and NTMP when two phosphonate groups are fully ionised. It also suggests, however, that while it is necessary for the pure aminophosphonates to have at least 2 phosphonate groups fully ionised for significant inhibition to occur, the surface plays the deciding role in whether that inhibition is at its maximum level. Only at pH values around 8 where the surface has developed a reasonably negative charge but does not repel the ionised phosphonates groups too strongly does maximal inhibition occur.

The question then remains as to why HEDP does not follow this trend. While previous literature [3] has suggested that inhibitors generally contain at least two phosphonate groups and a “three atom chain” (the chain is from the centre of the molecule, normally a nitrogen atom, to the phosphorous atom on the phosphonate group), HEDP is an effective inhibitor and only has a ‘two atom chain’. HEDP contains an -OH group and van der Leeden [14] has suggested that H-bonding plays a significant role in inhibitory action. We can see that at pH 8 the dominant species has at least one  $\text{PO}_3^{2-}$  group present, and perhaps with the additional influence of H-bonding this results in strong inhibitory action. However, it does not explain the

strong inhibition observed at pH 5.6 where only 5% of the HEDP molecules would contain even one  $\text{PO}_3^{2-}$  group. Thus, the presence of the -OH group significantly improves the inhibitory behaviour of this additive. The mechanism of this, however, is yet unclear. It must be noted that HEDP is not only chemically different but stereochemically different and this may also play a part in the enhanced inhibitory action of this molecule.

As stated previously, it is unknown at this point whether the interaction of the additive is a replacement/substitution with the bare barium sulfate surface or whether water molecules physi- or chemi-sorbed on the barium sulfate surface are involved. Recent literature [15] suggests that it is the surface barium ions that are coordinated with water. This tentatively suggests that surface water species may not have an important role in the inhibition activity.

## **Summary and Conclusions**

Speciation has shown that for pure aminophosphonate additives the presence of two completely de-protonated phosphonate groups is required for good inhibition to occur. For all molecules, however, maximal inhibition occurred at the pH where the surface interaction is balanced between chemical interactions with the additive and electrostatic interactions between the surface and additive. As pH increases, the likelihood of two or more fully de-protonated phosphonate groups increases and a point is reached where maximal inhibition occurs. However, beyond this point, as the surface becomes more negative, charge repulsion (and possibly complexation) begins to play a stronger role and inhibition efficacy is lost. This is only valid for pure aminophosphonates.

If the stereochemistry and functional groups are altered this 'rule of thumb' does not hold. HEDP had maximal inhibition at pH 8 like the other additives suggesting that again surface electrostatic behaviour as well as chemical interactions are important, but significant inhibition was also observed at pH 5.6 where none of the phosphonate groups were expected to be fully ionised. Thus, stereochemistry and functionality are also dominant features in determining the strength of inhibition.

The hypothesis that inhibition is determined by a combination of stereochemistry (lattice matching) and the presence of two fully de-protonated phosphonate groups [3] is still to be thoroughly investigated. The presence of two fully de-protonated phosphonate groups occurs at different pHs, yet the maximal inhibition always occurs at pH 8. This suggests that two fully de-protonated phosphonate groups are a pre-requisite but that surface charge is the controlling factor for maximal inhibition. Yet to be elucidated, however, is the significance or otherwise of lattice matching. This will be the focus of future work.

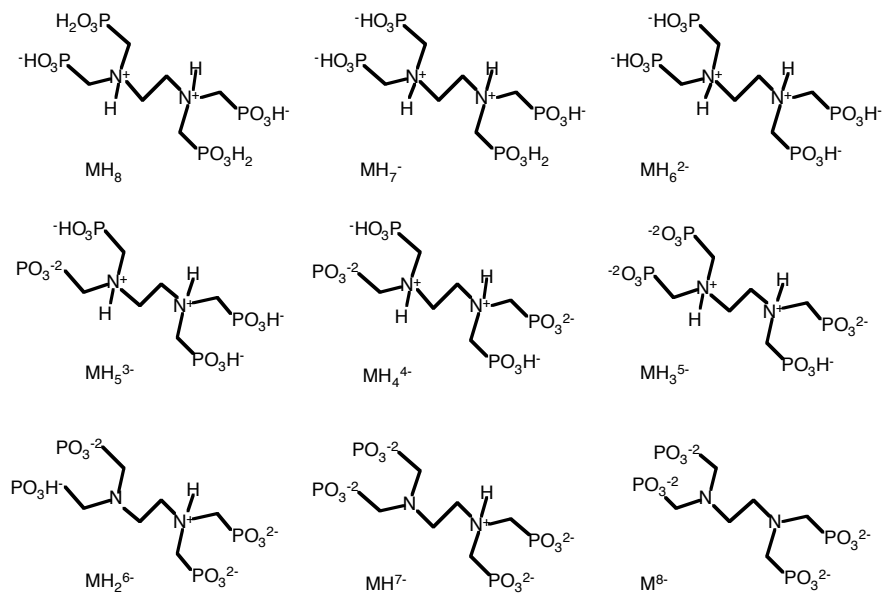
### **Acknowledgements**

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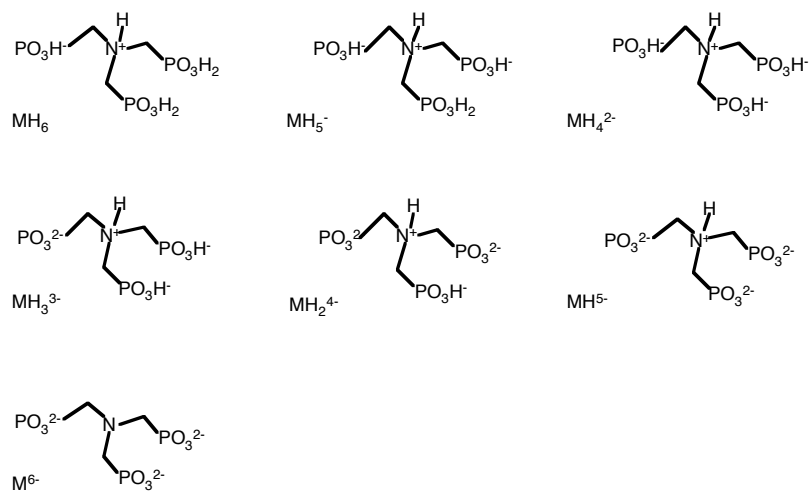
## Appendix

Schematic of the additives investigated at differing degrees of protonation.

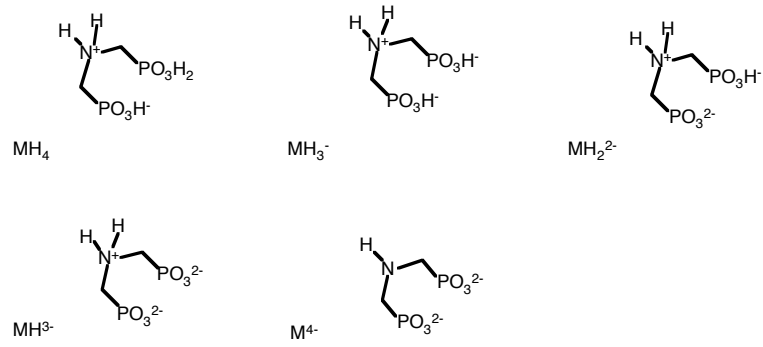
### EDTP



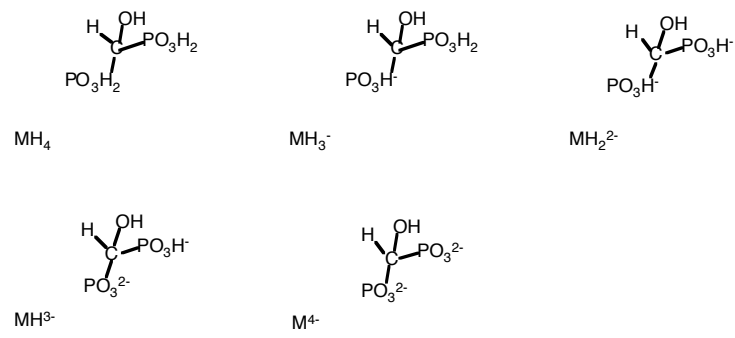
### NTMP



## NDP



## HEDP



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### **Figure Captions**

- Figure 1. Schematic of organic additives investigated in this work
- Figure 2. Ratio of de-supersaturation rate in the presence of inhibitor to the control at changing pH for all the additives investigated. Concentrations of additives used are the same as in Table 1.
- Figure 3. Morphology of barium sulfate particles formed in the presence of the inhibitors at pHs 5.6 and 8. (Porous background on some photos is due to filter paper)
- Figure 4. Speciation curves for the inhibitor molecules investigated.

## Tables

Table 1. The de-supersaturation rate when additive is present compared to the de-supersaturation rate of the control under the same conditions.

Additive	Ratio of additive to control slope					
	pH 3	pH 5.6	pH 8	pH 8, 1 mM NaCl	pH 8, 1.5 mM NaCl	pH 12
HEDP (0.010mM)	1.36	0.19	0	N/A	N/A	0.65
NDP (0.049mM)	0.84	0.88	0.54	0.15	0.12	0.59
NTMP (0.006mM)	1.08	0.64	0.01	N/A	N/A	0.60
EDTP (0.001mM)	0.76	0.31	0	N/A	N/A	0.59

## Figures

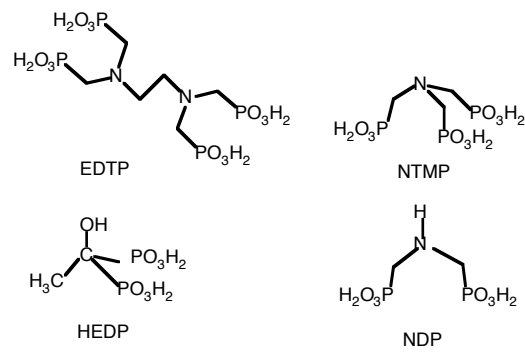


Figure 1

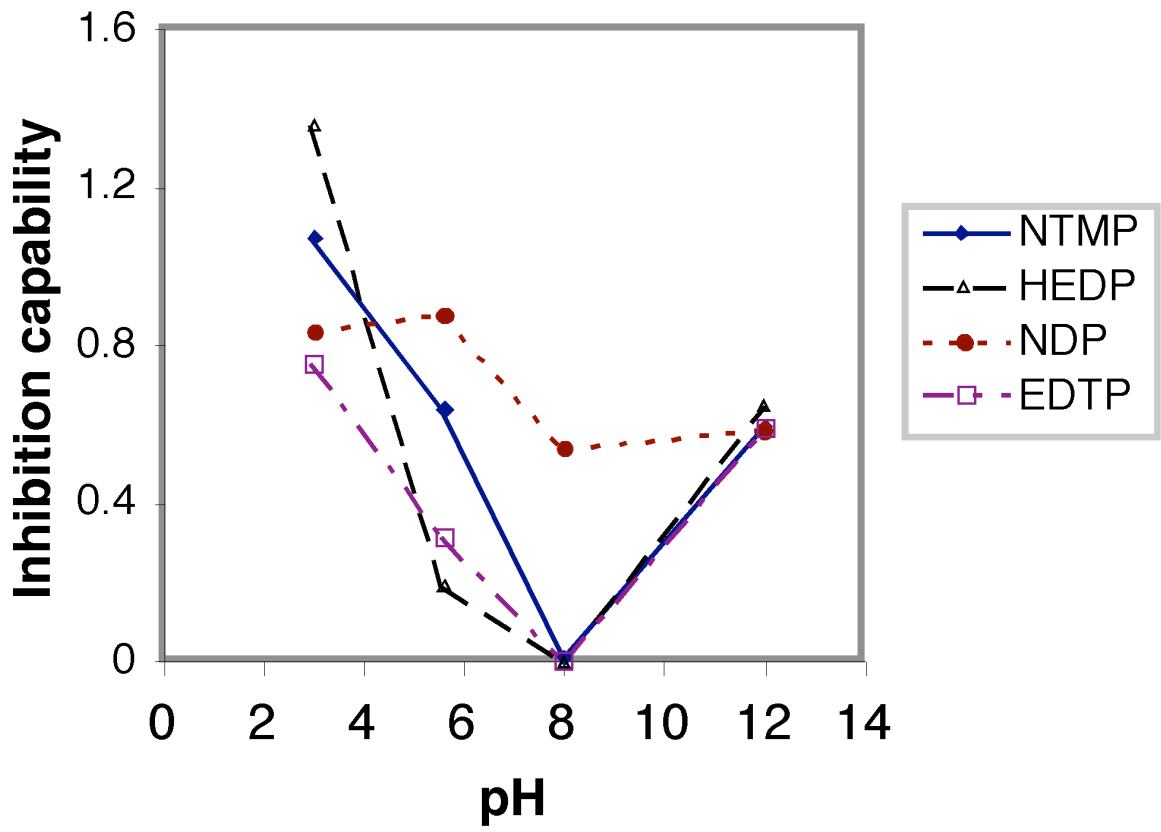


Figure 2.

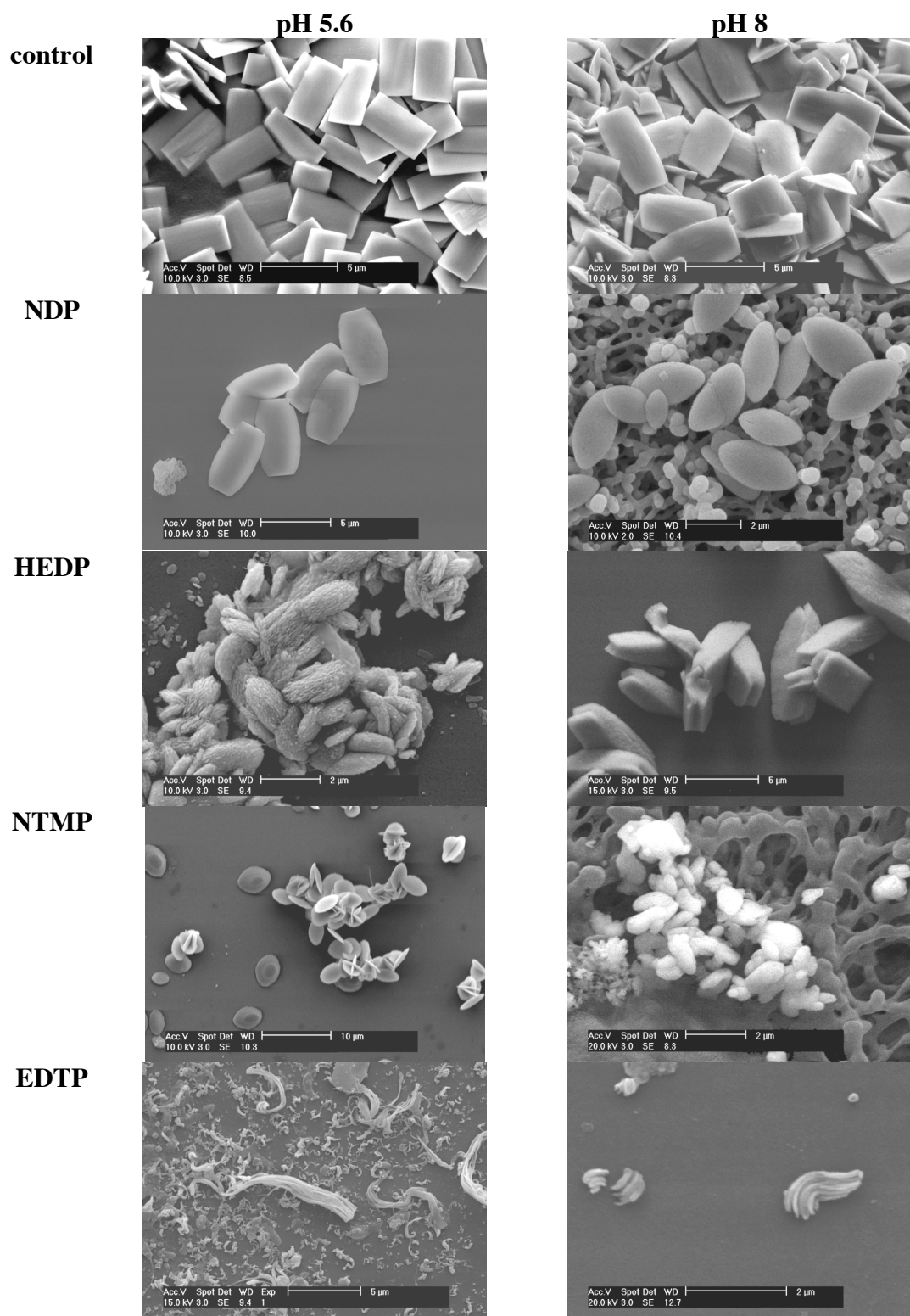


Figure 3.

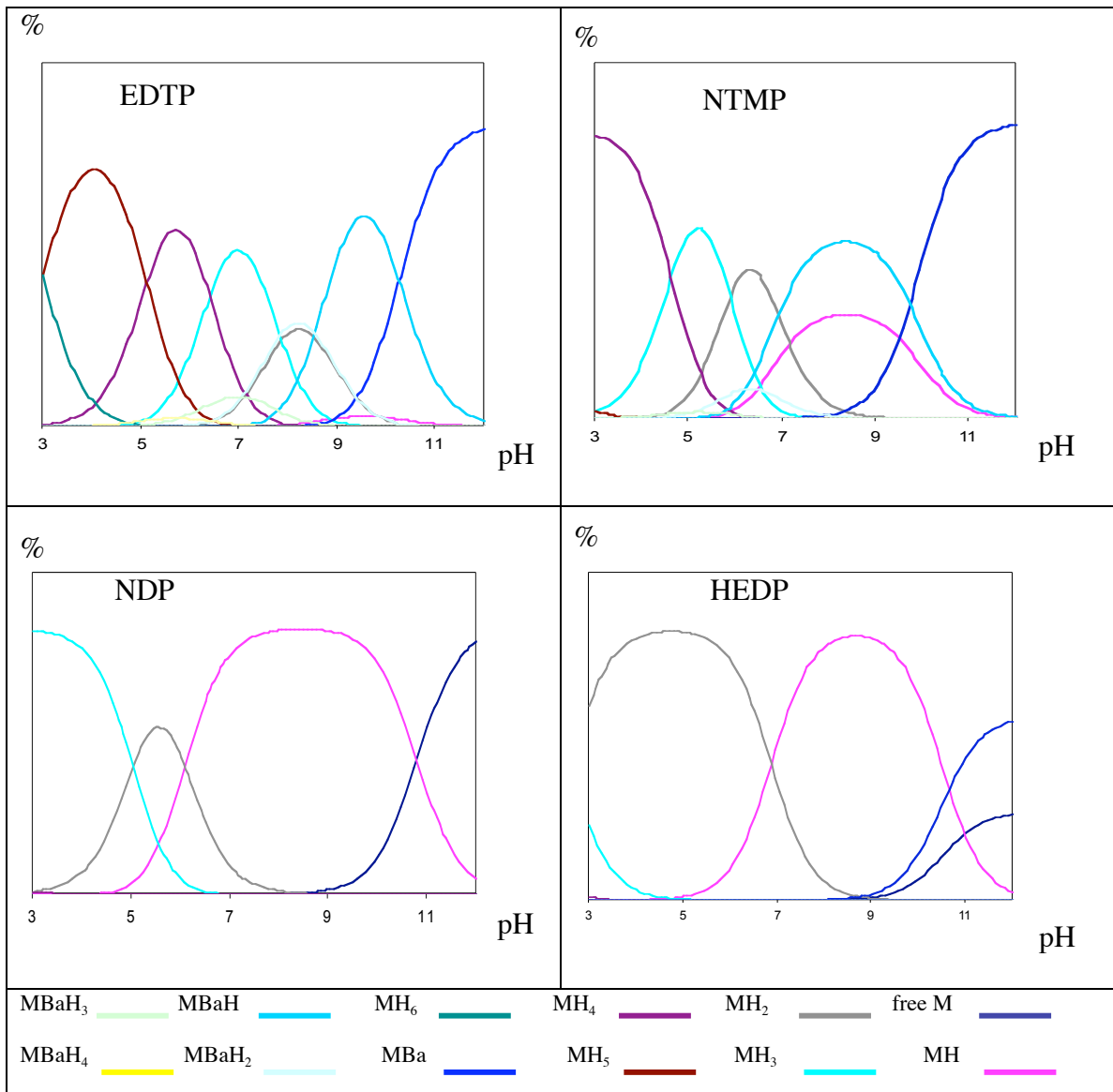


Figure 4.