

Paper

Comparison of the effect inhibitors have on an isostructural pair of salts

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Barium sulfate and potassium perchlorate have the same crystal structure but differ widely in their solubility and in their ionic charge. These systems, therefore, are an interesting means to probe how growth modifiers affect precipitation and what role the charge or stereochemistry of the modifier has on precipitation. It was found that the mode of interaction of the additive is dependant on the solubility of the system. Also, additives have a far greater effect on morphology when the solubility of the salt is low.

Introduction

There is an abundance of literature which suggests that an important feature of crystal growth modifiers and precipitation inhibitors is that of 'lattice matching' where the functional groups on an additive have a distance between them that is close to the spacing of one of the inorganic ions in the lattice.¹⁻³ Molecular modelling has shown that the distances do not have to be perfectly matched for this type of adsorption to occur.⁴ Charge matching, *i.e.* the charge of the functional group on the inhibitor needs to match one of the charges of the precipitating salt, has also been proposed as an important criterion.³ However, this proposition has not been as extensively studied. We began a systematic study probing the effect of additive charge on barium sulfate precipitation by assessing the inhibitory power of a group of molecules containing a decreasing number of phosphonate groups which are progressively replaced by carboxylic acid groups but within a consistent framework.⁵ The structures of these molecules are given in Fig. 1.

The organic molecules studied were: NTMP = nitrilotrimethylphosphonic acid, NTA = nitrilotriacetic acid, NDMPA = nitrilo(acetic acid)di(methylenephosphonic acid), NMPDA = nitrilo(diacetic acid)(methylene phosphonic acid). In this series, the 'backbone' remains constant so all four molecules should have almost the same ability to lattice match. However, it must be stressed that these additives are both chemically (different number of each type of functional group) and stereochemically (phosphonate—tetrahedral, carboxylate—planar) different to each other. In the case of barium sulfate, the molecules containing phosphonates would be predicted to be better inhibitors than those with carboxylates if charge matching is

important. If lattice matching dominated, all molecules should have inhibited similarly though not necessarily exactly the same due to the differences between the phosphonate and carboxylate stereochemistries. Thus, the predicted inhibition efficacy based on charge matching considerations would be:



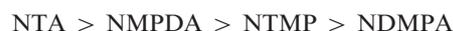
However, we found the following order of inhibition:⁵



The results from this study suggested that charge matching is indeed important (note, for instance, the trend $\text{NTMP} > \text{NDMPA} > \text{NMPDA}$) but the fact that inhibition was observed for NTA at all suggests that the phenomenon is more complex than simple charge matching.

We have decided to further probe the importance of charge matching in the inhibitory performance of organic molecules by retaining this systematic series of modifiers but varying the charge of the moieties at the surface. To this end we chose to study potassium perchlorate which is isostructural to barium sulfate⁶ but with different ionic charges (Ba^{2+} *cf.* K^+ and SO_4^{2-} *cf.* ClO_4^-). If charge matching is an important factor the order of inhibition should be reversed, or at least altered, for potassium perchlorate when compared to barium sulfate. If however, charge matching is less important and lattice matching is the dominant factor, all additives should inhibit relatively similarly (they may not be equivalent due to the stereochemical differences of the two functional groups).

If the perchlorate system showed exactly the same behaviour as the barite system, the expected trend for the perchlorate system would follow



(assuming that the NTMP would then have a slightly greater inhibitory effect than expected as found for NTA in the barium sulfate system).

In this study of potassium perchlorate, both morphology of the resultant particles and the kinetics of crystallization were assessed. For all experiments, the procedure consisted of monitoring crystallization using conductivity and then filtering (and washing) the particles for SEM preparation. A

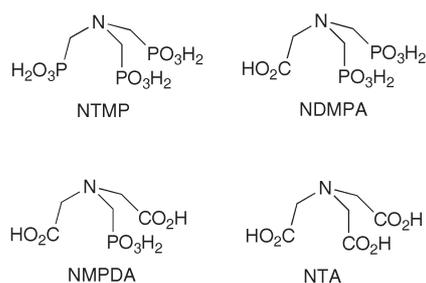


Fig. 1 Molecular structure of the organic molecules investigated in ref. 5 and this study.

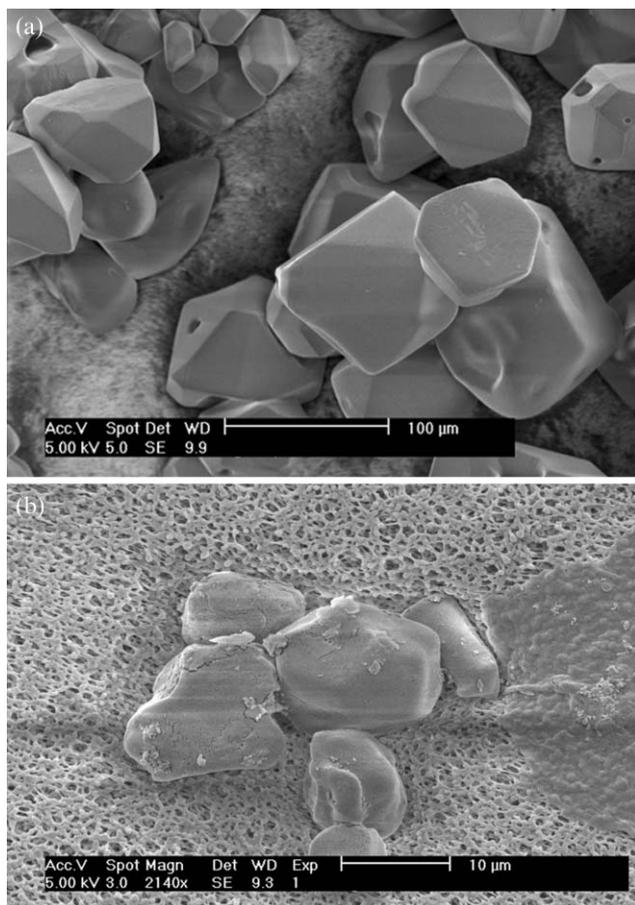
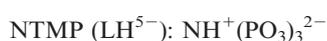


Fig. 2 Potassium perchlorate particles obtained in the presence of (a) control—no additives and (b) 0.018 M NTMP.

stoichiometric amount of potassium chloride was added to the sodium perchlorate solution to give an initial KClO_4 concentration of 0.083 M. Due to the high solubility of KClO_4 at room temperature, the precipitation reaction was conducted at 7 °C,⁷ the pH was 8 for all experiments and the resulting supersaturation ratio was ~ 1.2 (s/s_0). For the barium sulfate system errors of $\pm 10\%$ were found, for the perchlorate system, there appears to be a greater variation despite the method being equivalent ($\pm 20\%$). The standard conditions for the perchlorate system result in rhombohedral-type crystals with a large number of facets (Fig. 2a). One of the first differences noted between the two systems (barium sulfate *versus* potassium perchlorate) was the higher concentration of organic required for inhibition to be observed. The additives were added at concentrations ranging from 0 to 0.026 M to the sodium perchlorate solution prior to the potassium chloride being added to start precipitation. This concentration required the higher pH (compared to a pH of 5.6 for the barium sulfate system)⁵ as NTA is not very soluble in its protonated form.

Theoretical speciation curves derived from literature data⁸ show that at the pH investigated here (pH 8), the additives would all be in the LH state (L being the fully deprotonated ligand) due to zwitterion formation.⁹ This means that the additives would have the following ionisation states:



As such, the functional groups are essentially fully ionised.

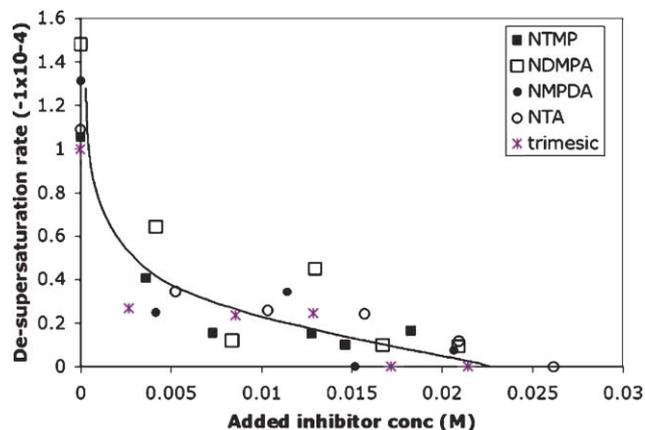


Fig. 3 De-supersaturation rate ($-1 \times 10^{-4} \text{ mS s}^{-1}$) of potassium perchlorate *versus* concentration (M) of additive present. Line drawn to aid reader only.

The morphologies of the potassium perchlorate particles observed in the presence of the various additives were only dependant on the concentration, and not on the additive present. As the concentration of inhibitor increased, fewer particles were observed and these particles were smaller and much more rounded than the control particles. As an example, the case for precipitation in the presence of NTMP is shown in Fig. 2.

As can be seen in Fig. 3, the de-supersaturation rate is also independent of the inhibitor molecule. As concentration increases, the precipitation rate decreases to essentially zero (complete inhibition) when $>0.025 \text{ M}$ additive is present.

Discussion

As previously stated, for barium sulfate, precipitation inhibition *almost* followed the expected trend for charge matching except for NTA. For the perchlorate system NTMP, NDMPA and NMPDA all show an inhibitory effect on potassium perchlorate crystallisation and their inhibition is equivalent to NTA. That is, all four inhibitors were found to have the same effect within experimental error.

The concentrations required to observe changes in the de-supersaturation rate are much greater for the more soluble species (potassium perchlorate) than for the less soluble species (barium sulfate). While the phenomenon of more soluble salts requiring higher additive concentration has been previously stated within the literature, no explanation for this has been given.¹⁰ Note that the difference in solubilities (solubility ratio $[\text{BaSO}_4]/[\text{KClO}_4] = 6831$) means that a greater number of ions are present in solution for the perchlorate system so the ratios of additive to metal atom were calculated (at the highest additive concentrations used), see Table 1. Thus, we can see that the additive to cation ratio is almost equivalent for both experiments. We can conclude, therefore, that at least one factor is that the greater concentration of salt ions (in the potassium perchlorate case) meant greater additive concentrations were required.

Table 1 Additive to metal ratio at the highest additive concentration used for the two systems investigated

Additive	Maximum ratio of additive/ Ba^a	Maximum ratio of additive/K
NTMP	0.13	0.18
NDMPA	0.25	0.23
NMPDA	0.26	0.25
NTA	0.31	0.29

^a Ratios calculated from data presented in the Appendix of ref. 5.

It is also possible that the increased concentration of ions in the more soluble system results in charge screening, thereby making the system behave as if the charge on the inhibitor is unimportant. To test this, we performed barium sulfate precipitation runs at higher ionic strength to determine whether the presence of more ions screened the charges in solution and lead to the additives all behaving similarly. The potassium perchlorate system has an ionic strength of 0.166, while the barium sulfate system had an ionic strength of 0.001. Thus, for the ionic strength to be completely matched a sodium chloride concentration of 0.165 M would be required. However, sodium chloride at 75 mM was chosen since higher concentrations made it impossible to determine the de-supersaturation rate from the conductivity data. This is ~ 2 times less than is required to match the ionic strength of the potassium perchlorate system but since the original background NaCl concentration was 0.5 mM, this is a 150 times increase in the ionic strength.

It can be seen in Fig. 4 that despite the much higher ionic strength, the order of efficacy has only changed slightly for the additives. Notably the NDMPA showed greater inhibitory action at the higher ionic strength while the NTA showed none. Quite clearly, the effect of the increased ionic strength is to magnify the “charge matching” behaviour of the system. This is most noticeable in the slight inhibitory action of the NMPDA at the highest concentration. Thus, at the higher ionic strength the additives perform in the expected order based on charge matching considerations alone. This is quite the opposite behaviour to the perchlorate system.

Since increases in ionic strength result in lower supersaturations,¹¹ the lower supersaturation of barium sulfate improved the performance of NDMPA. For NTA, the increased ionic strength appears to be shielding the charge to the point where it does not interact with the barium sulfate.

The supersaturation of potassium perchlorate in these experiments was ~ 1.2 while that of barium sulfate was ~ 25 in the low ionic strength case. One reasoning is that as the supersaturation increases more additive is required to produce an inhibitory effect.¹² If this were the case between systems as well as within a system we would expect less additive to be required on an additive to cation ratio basis for potassium perchlorate than for barium sulfate.

Apart from the ionic differences between the two salts, the other notable difference between the barite system and the perchlorate system is that of solubility. The solubility for BaSO₄¹³ is 0.0101 mM at 25 °C, while the solubility for KClO₄⁷ at 7 °C is 0.069 M. Thus, there is something different occurring in the more soluble system, which requires equivalent inhibitor concentrations for effects to be observed. One argument is that the more soluble species has the lower surface energy and

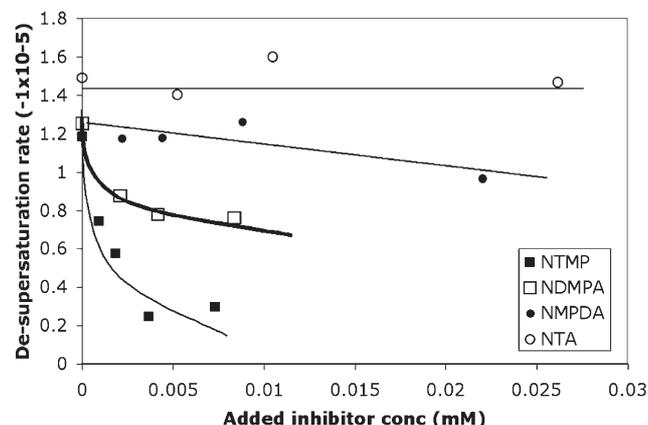


Fig. 4 De-supersaturation rate ($-1 \times 10^{-5} \text{ mS s}^{-1}$) of barium sulfate versus concentration (mM) of additive present with 0.5 mM NaCl background electrolyte. Lines drawn to aid reader only.

Table 2 Values used in the determination of nucleation rate and critical nucleus radius

	BaSO ₄	KClO ₄
MW/kg mol ⁻¹	0.23343	0.1385
Density/kg m ⁻³	4474	2520
Molecular volume/Å ³	8.6638×10^{-29}	9.1263×10^{-29}
Surface tension \times energy ⁻¹ /J m ⁻²	0.136	0.044 ^a
Supersaturation ratio	25	1.2
θ/J	$= 2.6487 \times 10^{-20}$	$= 1.4096 \times 10^{-21}$
Solubility/M	0.0000101	0.069
$D/\text{m}^2 \text{ s}^{-1}$	1×10^{-9}	1×10^{-9}

^a Calculated according to eqn. (2.107) in ref. 13.

results in a greater number of nuclei at a given supersaturation.¹⁴ To test this, data shown in Table 2 were taken and used to calculate the nucleation rate and critical nucleus size.

The critical nucleus radius can be obtained from¹⁴

$$R = (2k_a V \gamma^2) / (3k_b \theta)$$

where k_a is assumed to be equal to 6 and k_v is 1 (shape factors), V is the molecular volume and θ is given by $\theta = \nu k_b T \ln S$. Here S is the supersaturation ratio, ν the number of ionic units the salts dissociate into, k_b is the Boltzmann constant and T temperature (K).

The critical nucleus comes out to be 0.24 and 0.50 nm for BaSO₄ and KClO₄ respectively under these conditions.

The nucleation rate is given by¹⁴

$$J = \Omega \exp\{-\beta \nu^2 \gamma^3\} / \{k_b T \theta^2\}$$

and Ω is approximated by

$$\Omega = 2D/(V^{1/3})^5$$

where D is the diffusion co-efficient. Using these values the nucleation rate of barium sulfate is found to be significantly greater!

$$J = 1.179 \times 10^{38} \exp(-209.34) \text{ —BaSO}_4$$

$$J = 1.081 \times 10^{38} \exp(-2955.7) \text{ —KClO}_4$$

If the argument is that the greater number of nuclei and the smaller size results in a larger surface area of nuclei thereby needing more additive, then on this basis we would conclude that more additive would be required in the case of barium sulfate—this was not observed experimentally. Thus, the surface energy argument does not explain the greater need for higher concentrations of additive for the potassium perchlorate system. Only when the supersaturation ratio, S , is equivalent for both systems does the critical nucleus become smaller for the potassium perchlorate system and the nucleation rate becomes much greater than that for the barium sulfate system.

Finally, the possibility that the inhibitory effect in the potassium perchlorate system is due to a non-specific charge interaction was investigated by using a tricarboxylate molecule with a completely different stereochemistry; trimesic acid (1,3,5-tribenzoic acid). Here we would expect either the same inhibition as observed with the other additives (non-specific interaction would be implied) or a different inhibition (lattice matching is implicated).

When trimesic acid was added to the barium sulfate system at low ionic strength, inhibition was observed to a small extent for concentrations ≥ 0.025 mM. In the potassium perchlorate system the trimesic acid behaves differently. The results are

shown in Fig. 3. Now we can see that the effect of these additives is non-specific in their nature, *i.e.* neither charge nor lattice matching is the significant interaction in their inhibitory action. The interaction of negatively charged inhibitors with potassium perchlorate suggests that the surface is positively charged. No data exists on the surface charge of potassium perchlorate thus the surface is positive either because potassium ions are exposed at the surface or because a layer of counter ions at the surface (Na^+ or K^+) are screening the exposed, negatively charged perchlorate ions. This positive surface appears to interact with the charged additives (which are deprotonated at pH 8) purely on electrostatic grounds. It also suggests that the surface is sufficiently positive to observe little difference between the more negative phosphonates compared to the carboxylates (although this could be a consequence of the greater scatter found for the perchlorate system from the conductivity method). This non-specific interaction would best explain why greater amounts of additive are required as inhibition is then dependant solely on the fraction of surface coverage. It may be that we don't see this for the barium sulfate system because the ionic strength was not high enough for this interaction to dominate.

Even when inhibition is observed, morphology is not altered significantly in the more soluble system, unlike the case for barium sulfate, where the morphology was greatly altered in the presence of several of these additives even at very low concentrations.⁵ Calculations show that this is not due to the magnitude of the inhibition (that is, the % inhibition for both systems was comparable).

Several conclusions can be drawn:

- Lattice matching is not the dominant interaction experienced by crystal surfaces and additives for the high solubility salt. For the low solubility salt, charge matching more appropriately explains the behaviour of the additives especially at elevated ionic strength. This is not to say that lattice matching does not occur or is not significant in the barium sulfate system as lattice matching may contribute to the additive's ability to 'charge match' more efficiently.

- The solubility of the salt influences the amount of additive required to observe an effect on both the precipitation rate and the morphology obtained. This is due to the non-specific interactions which occur for the highly soluble salt.

- The non-specific interaction is essentially due to surface charge screening.

This study started with the aim of understanding the importance of charge matching in crystal growth inhibitors,

but it has raised the idea that the solubility (and, therefore, ionic strength) is a major factor in determining the manner in which additives interact with precipitating systems. At very high solubilities, the ionic strength of the system begins to affect the manner in which additives interact. Not surprisingly, additive charge and structure become less important as behaviour is determined solely by the amount adsorbed and additives adsorb more or less equivalently. Future work in this area includes the determination of the surface properties of potassium perchlorate as well as investigating the precipitation at different temperatures (which will allow us to investigate changes in the ionic strength of the perchlorate system) and with more additives.

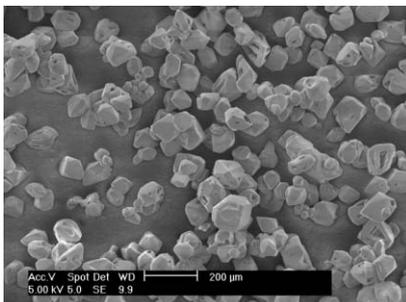
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Solubility (and, therefore, ionic strength) is a major factor in determining the manner in which additives interact with precipitating systems.

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