PAPER

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Amides as anticaking agents for sodium chloride: is a triple branched variant necessary?

Eleanor R. Townsend,[a] Willem J. P. van Enckevort, (iD) *[a]
Jan A. M. Meijer[b] and Elias Vlieg[a]

Amides are well known for their potential as anticaking agents for sodium chloride. We have investigated what is the ideal structure for an amide based anticaking agent and what features lead to effective anticaking. Through a series of experiments, we have found that a triple-branched structure, with the three branches radiating from the same nitrogen centre, is the only effective compound for preventing caking for sodium chloride. We conclude that this is likely due to bonding between the atoms of the amide functional group and the ions of sodium chloride, with an extra bond from the central nitrogen giving a strong attachment to the surface, thus leading to blocking of growth. We have also outlined a list of four categories, of which a compound must obey all of in order to act as an effective anticaking agent.

Introduction

An anticaking agent for a crystalline compound can be identified by its specific properties, in that it is able to bind effectively to the facets of the crystals and prevents the propagation of steps across the surface at a microscopic level, thus blocking growth. The interaction between the species and the surface (of, for example, NaCl) is thus vital to have the desired anticaking effect.

It is well known that amide containing compounds have a strong interaction with the NaCl surface. For example, urea was reported by Romé de l'Isle in 1783 (ref. 1) as having an effect on the growth of NaCl. He demonstrated that using 30% (w/w) urea in a brine solution caused octahedral NaCl crystals to grow from solution. In 2010, Smith[2] suggested a mechanism for this process, that urea is being preferentially excluded from {100} facets, leading to the characteristic octahedral form of the crystals. A habit modification effect has also been reported for crystals grown in the presence of 20% and more (w/w) formamide,[3] of which a mechanism has also been discussed by Radenovic *et al.*[4] Also, as far back as in 1961,[5] it has been reported in the literature about the effectivity of a triple branched, amide containing compound, nitrilotriacetamide (NTAA), as an anticaking agent for sodium chloride. It has been shown that this compound has effects on the surface growth at concentrations as low as 1×10^{-4}% (w/w).[6,7] We have previously shown that NTAA also acts

as a habit modifier for NaCl in high concentrations. The crystals grow instead of in the expected cubic form, as ultrathin needles.[8,9]

However, what we have discovered is that habit modification is no guarantee for a clear anticaking effect. While NTAA shows a strong anticaking effect, neither urea nor formamide have been reported to have an effect on the anticaking of sodium chloride crystals. From this we can deduce that an increasing number of amide groups on a molecule leads to a stronger interaction with the NaCl surface. Conversely, there is some evidence to dispute this theory, in that we have shown that the polymer variant of these compounds, polyacrylamide, which has chain length of up to twenty units, also does not have an anticaking effect.[10] This shows it seems that a happy medium must be struck between the size of a molecule and the amount of amide groups present to have an effective growth blocking effect and thus make a good anticaking agent.

The aim of this paper is to therefore explore in more detail, what makes a good amide-based anticaking agent. We have characterised the effect in crystal growth and nucleation and the anticaking effects of a series of amides, both short and long, and with different levels of branching.

Methods

In addition to the known anticaking agent nitrilotriacetamide (NTAA); urea, 2-[(carbamoylmethyl)amino]acetamide (2-CMAA), two polyacrylamide molecules of differing sizes and two other triple branched molecules, methyl glycine diacetamide (MGDA) and glutamic acid diacetamide (GLDA), were examined. The structures of these molecules are outlined in Fig. 1.

[a] *Radboud University, Institute for Molecules and Materials, Nijmegen, 6500 GL, The Netherlands. E-mail: w.vanenckevort@science.ru.nl; Fax: +31 (0)24 3653067; Tel: +31 (0)24 3653433*
[b] *AkzoNobel Industrial Chemicals, Salt and Crystallization, Deventer, 7418 AJ, The Netherlands*
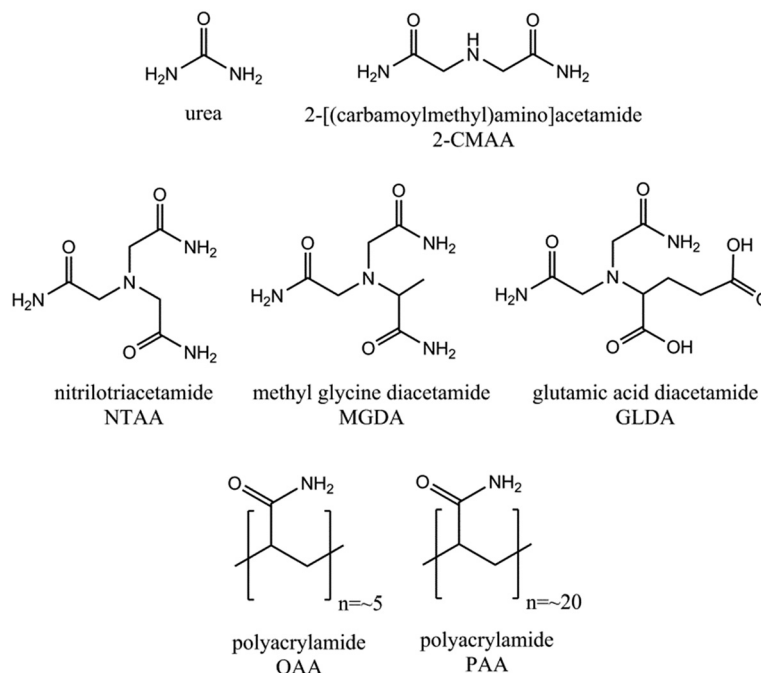
Fig. 1 Chemical structures of chosen amide containing additives.

Urea and PAA were both obtained from Sigma Aldrich. Urea was provided in powder form with a purity of ≥98% and PAA was obtained in a 50% (w/w) aqueous solution. 2-CMAA, NTAA, MGDA, GLDA and OAA were all synthesised and obtained through AkzoNobel as they are not commercially available.

It is also known that the pH of an additive can have a large effect on its anticaking abilities,[11] and so it was monitored closely during our experiments. The "natural" pH values of each additive in brine solution are listed in Table 1.

Creeping tests

In our previous work,[12] we have shown that creeping can be used as a simple initial method to test for potential anticaking effects on sodium chloride crystals. A solution was made using saturated brine and 1% (w/w) of the chosen additive at ambient temperature (20–25 °C). The solution was filtered using a syringe fitted to a 0.45 μm Pall GHP Acrodisc filter, and then dropped onto a glass microscope slide using a micro-pipette. These slides were previously cleaned using EtOH and dried using a dust-free tissue to minimise external

nucleation effects. The amount of solution in each droplet varied from 5–10 μL. The droplets were allowed to evaporate in a temperature and humidity controlled climate chamber at 20 °C and 50% relative humidity. The resulting crystals were imaged using a Leica DMRX optical microscope.

Supersaturation experiments

It is well known that growth blocking additives delay the nucleation of crystals in solution, leading to sudden and extremely fast nucleation at higher supersaturations. Therefore, the determination of the supersaturation at which 3D nucleation commences appears to be a powerful method for detecting the blocking activity of additives and subsequent anticaking activity.

These tests were performed by weighing a siliconised glass slide, which had been pre-cleaned using ethanol to remove any dust which could promote nucleation. In contrast to the creeping experiments, the siliconised glass slide proved necessary in this experiment, as it has less wetting than a normal glass slide and therefore, the droplets had a higher contact angle and did not evaporate so quickly. The contact angle of all droplets were all very similar. The slide was placed on a precision balance and single 20 μL droplet of brine (with or without additive) was dropped on top. The initial weight was recorded and the sample was closely observed until nucleation and subsequent initial crystal growth could just be discerned with the naked eye. At times, the edges of the droplet were observed using a magnifying glass to detect any tiny crystallite growth. The weight at nucleation was recorded and the average supersaturation was calculated through the weight difference at the beginning and the end of the

Table 1 pH values of 1% (w/w) additive in concentrated brine solution

Additive	pH
Urea	6.9
2-CMAA	7.4
NTAA	5.6
OAA	6.4
PAA	6.0
MGDA	5.1
GLDA	3.5

experiment. As nucleation is a stochastic process, the experiments were performed in triplicate to obtain an average value for the approximate supersaturation.

Powder flow analysis (PFA)[12]

Caking tests were performed following a standardized measurement employed by AkzoNobel.[13] The measurements were performed in quadruplicate using a powder flow analyzer rheometer to determine the caking strength of the sodium chloride when treated with additive solutions. 50 g batches of high-purity AkzoNobel Sanal P® salt were placed into separate plastic bags and treated with 2% (w/w) moisture. The moisture consisted of a solution of a chosen concentration of additive in MilliQ water. Using this dilution factor, a 1% (w/w) solution yields an additive concentration of 0.02% (w/w) with respect to the salt. In the cases of varying pH of additive solution, the pH was set before the experiment using either a dilute solution of HCl or NaOH. The treated salt batches were then placed in separate plastic containers of 50 mm diameter and preconditioned by compressing with 1 kg weight and purging with dry air for 2 hours. The strength of the cake of the samples was then measured using the rheometer (type TA-XT21, Stable Micro Systems), which is a screw-like moving blade which enters the salt cake and continuously measures the vertical force imposed by the salt. The measurement unit is CE20, which is the relative caking energy in N·mm required to enter a cake of 20 mm. All results were compared to a standard blank test, without additive. These experiments were carried out at ambient temperature. The error of the measurements was calculated using a standard deviation calculation over the four measurement values. The limit of the machine occurs when a force of 55 N is exceeded.

Results and discussion

Creeping tests

In order to initially determine whether the chosen additives had any effect on the growth of NaCl, creeping tests were performed. These tests were performed at a concentration of 1% (w/w) and at a pH value as determined by the acidity of the compound. Therefore, this varied over the experiments, but was always in the range of pH 3–7. This technique was chosen as it is extremely fast and effective when employed as a qualitative screening method for caking activity.[12] The results are shown in Fig. 2.

From these results, we can conclude that the only additives, at this concentration, which have any effect on the
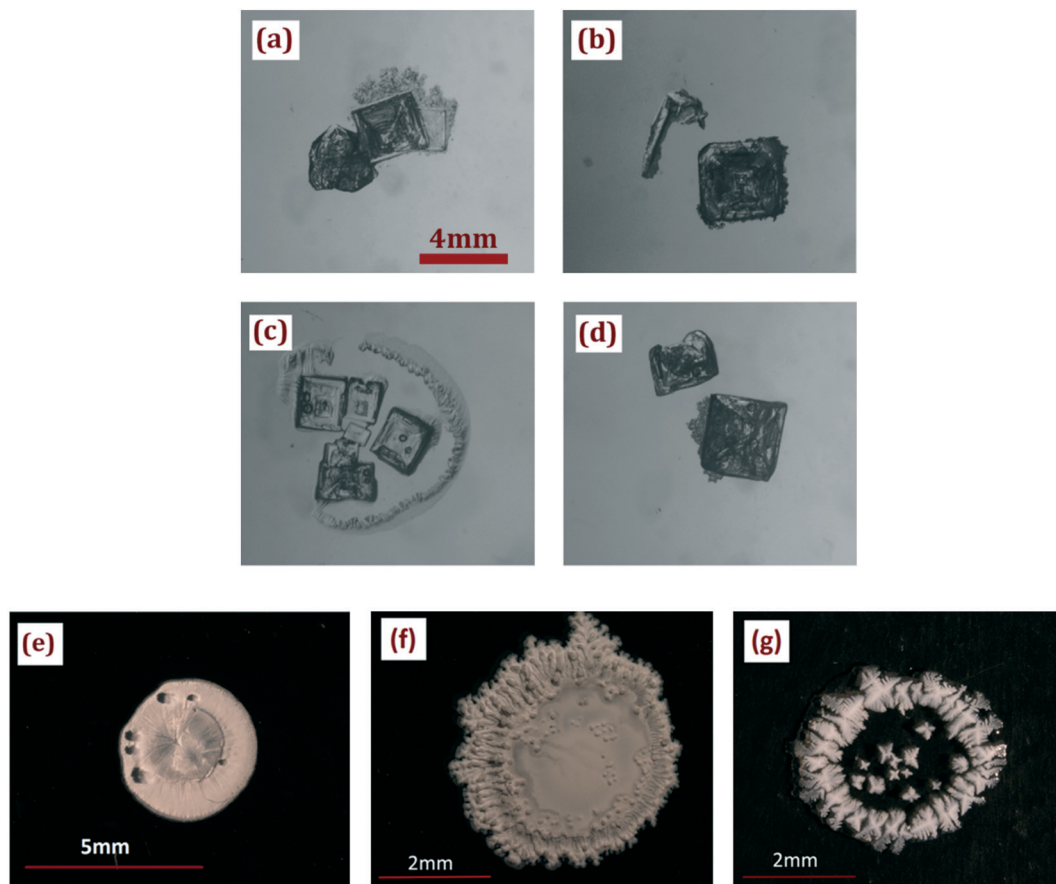

Fig. 2 Crystal growth patterns from saturated brine solution containing: (a) 1% (w/w) urea, (b) 1% (w/w) 2-CMAA, (c) 1% (w/w) OAA, (d) 1% (w/w) PAA, (e) 1% (w/w) NTAA, (f) 1% (w/w) MGDA and (g) 1% (w/w) GLDA.

growth of NaCl are NTAA, MGDA and GLDA. In the cases of urea, 2-CMAA, OAA and PAA as additives in the brine solution, the resulting creeping patterns consisted of crystals only of cubic morphology. This result was expected in the case of urea, as it has been reported that a concentration of >20% (w/w) in solution is required to have any habit modification effect.[1] In the case of PAA, some discernible octahedral type growth was expected as it has been previously reported,[10] however it is likely that the crystals formed extremely quickly due to the small amount of growth solution (5–10 μL) and the {111} facets are reported to only develop at low supersaturations, involving slow growth.[10]

In contrast to Fig. 2(a)–(d), it can be seen in Fig. 2(e) that NTAA causes the formation of an extremely dense opaque crystal pattern, with no apparent cubic crystal growth. Microscopically, this crystal growth pattern consists of numerous crystals in a needle-like morphology.[9] MGDA and GLDA exhibit more traditional branched creeping patterns (Fig. 2(f)–(g)).

Supersaturation experiments

For NaCl-additive systems, the effect that additives have on the nucleation of NaCl crystals in solutions is significant.[14] These experiments were carried out to determine whether an additive which has an effect on the growth also has a significant nucleation hindering effect. The control brine solution containing no additive gave a calculated approximate supersaturation value at nucleation of 6%.[8] On addition of the range of additives to the saturated brine solution, it was clear that in all cases, the approximate supersaturation values at which nucleation occurs is significantly increased. The values are shown in Table 2.

In comparison to the control value of 6%, the measured supersaturations are all approximately three times larger, except for that of PAA, which has a much higher value. From previous research,[10] we know that PAA is a habit modifier, but is not an anticaking agent. This leads us to the conclusion that nucleation inhibition is an important criterion for making a good anticaking agent, but it is not the only one which needs to be fulfilled in order to find an effective additive.

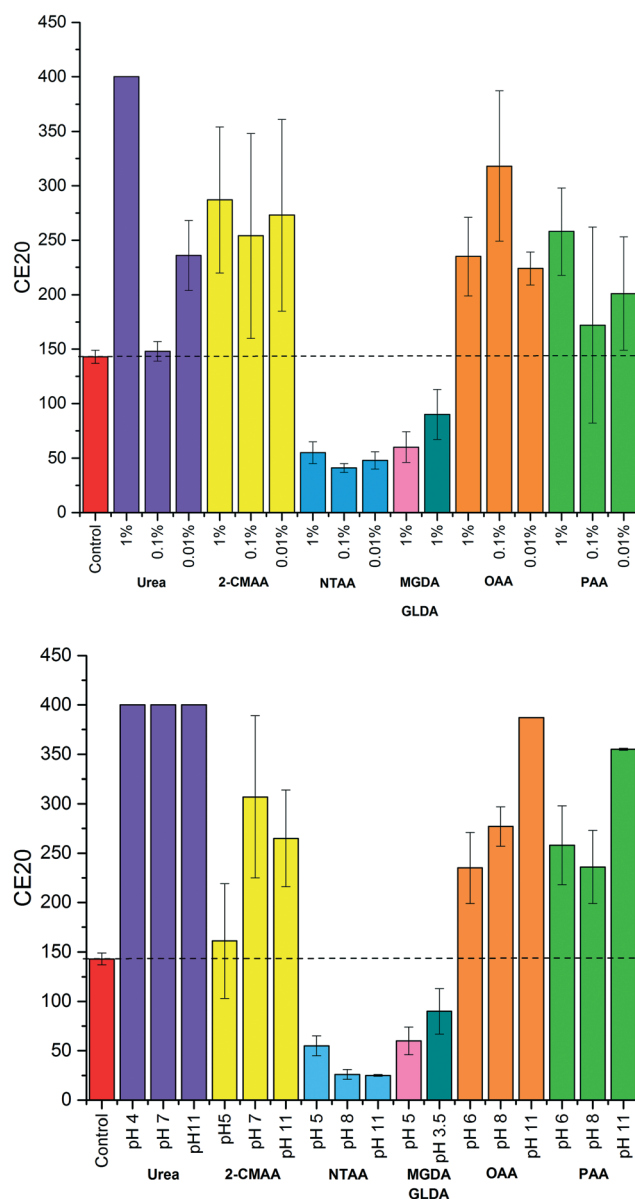### Powder flow analysis – variation of pH and concentration

Creeping tests and supersaturation tests are extremely useful initial techniques, but it is important to quantify our findings

to be able to properly conclude the extent of anticaking effects. In order to do this, the caking energy exhibited by sodium chloride treated with various amide based additives was measured using the technique of powder flow analysis. The results are shown in Fig. 3 for different pH values and different additive concentrations. The level at which normal salt cakes, *i.e.* treatment with water containing no additive is indicated on the graph with a dotted line. Any value above this line indicates that an additive acts as a pro-caking agent.

From these results, the overall finding is that the additives which have an anticaking effect on sodium chloride are NTAA, MGDA and GLDA. The other four additives; urea, 2-CMAA, OAA and PAA all give average caking energies which

Table 2 Approximate supersaturation values at the point of nucleation for additives at 1% (w/w) concentration in a saturated brine solution

Additive	Approximate $\Delta\mu/kT$ (%)
None (pure brine)[8]	6 (±0.4)
Urea	16.5 (±4)
2-CMAA	15.5 (±3)
NTAA[9]	17 (±1)
OAA	21.5 (±5)
PAA	48 (±6)
MGDA	22 (±3)
GLDA	13 (±2)

Fig. 3 Powder flow experiments comparing amides of different sizes. Above: As a function of additive concentration at "natural" pH value; Below: as a function of pH, with the concentration remaining at 0.02% (w/w) w.r.t salt.

surpass that found for the control measurement of 143 ± 6 CE20. These overall findings mirror what we have found in the Creeping experiments section.

It is evident from the results that pH does not have a large effect on the effectivity of each anticaking agent. However, it seems that there is a slight tendency towards the lower pH values for the majority of additives except NTAA. As regards to the variation in concentration, there is also not a clear correlation between the amount of anticaking and the level of additive down to a minimum concentration of 0.01% (w/w) w.r.t the solution, which equates to fifty times less, w.r.t salt. Due to the similarities between NTAA and MGDA/GLDA and the time-consuming nature of PFA experiments, only one experiment was performed for MGDA and GLDA, at a concentration of 1% (w/w) w.r.t solution and at the natural pH. It is also noticeable from the results that the CE20 value for GLDA is higher than those of NTAA and MGDA; this is likely to be attributed to the fewer amide groups on this molecule, which have been replaced by acid groups.

For NTAA, it was found that extreme pH differences in the additive solution did not have a large effect on the anticaking properties. This is likely due to the stability of amides in solution, in that they are not particularly acidic or basic (the conjugate acid of an amide has a pK_a value of 9.5). As PFA experiments are time-consuming, only three pH values were measured, but all showed values far below that of the control and in the same order of magnitude as each other. This indicates that the NTAA complex and its interaction with the NaCl surface is stable at a wide range of pH values.

Especially for the case of urea as an additive, it was shown that all measured pH values and concentrations showed only values higher than the control and thus showed a pro-caking effect, *i.e.* "glued" the crystals together. Urea is a known habit modifier for NaCl, but does not show a growth blocking effect. The reason for the enhanced caking effect is not clear, a possible explanation is the formation of a thin layer of urea connecting adjacent crystallites. The thickness of the urea layer between adjacent crystals in the cake is estimated to be between 0.3 and 30 nm for the 0.1% and 1% solutions. Urea is a widely used industrial product in the fertiliser industry and many studies have been undertaken to attempt to lessen the amount of caking between urea crystals.[15,16] Therefore it is likely that the urea actually contributes to the caking of NaCl.

At 0.1% (w/w) additive concentration, urea gave a CE20 value very similar to that of the control. The difference between this and those at the higher and lower concentrations can possibly be attributed to the salt samples being slightly wet, which aids in breaking the cake. In this, it should be realised that the solubility of urea in water is extremely high (119 g/100 g H_2O).

What makes a good anticaking agent?

We can conclude that there are a set of criteria which must be fulfilled for an additive to be deemed an effective anticaking agent. These criteria are outlined in Fig. 4 and made explicit in Table 3. It should be realised that only creeping is not sufficient, as some pure compounds show creeping as well.[17]

From this table it is clear that the only additives which fulfill all necessary criteria to act as anticaking agents for NaCl are NTAA, MGDA and GLDA. This agrees with our experiments, and it points to a specific feature of three branched amide molecules that induces an anticaking effect which is impossible for those compounds with a differing structure.

It seems that some type of "happy medium" exists between the amount of amide groups on the molecule and its size. Habit modification of the NaCl by the additives from {100} to {111} and a delayed nucleation are not enough to have an anticaking effect. Although the additive binds some extent to the surface, it does not block the surface strongly enough to produce the "weaker" crystals with needle like or dendritic habits needed to have the desired creeping effect, which is indicative for a roughened and blocked surface during anticaking treatment.[13,18] Insufficient bonding was observed for both the smallest compound, urea, and the largest polymer, PAA. This also shows that there is no correlation between the anticaking effectivity of a molecule and its chain length and subsequent amount of amide groups. This points to the idea that the unique structure of the triple branched amides is vital to the explanation for their effectivities.

We hypothesise that there are two possible mechanisms with which the triple branched amides can bond to the NaCl. The first is inspired by the Sarig model[7] for the binding of NTAA onto NaCl {100}. This model suggests that the partially negatively charged oxygens of the amide groups are bonded to the sodium ions of the substrate, assisted by a weaker bonding of the amine to the chlorine ion. The compound therefore anchors itself to the substrate with three contact points at the ends of each branch radiating from the central nitrogen and a final contact point from the central nitrogen. The second model is inspired by the model from Bode *et al.*[18] in which the additive anchors itself *into* the surface at one point, by replacing some of the surface atoms of the substrate.

From an estimation of bond lengths, the Bode mechanism is unlikely, as the length of the amide branch (approximately 4.5 Å) is much larger than the distance between the surface Na and the Cl below (2.81 Å) if they are removed. It is thus unlikely that an amide functional group would be incorporated into the crystal lattice as observed for ferrocyanide and $PbCl_2$.[19]
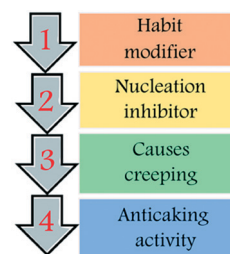
Fig. 4 A flow chart depicting the necessary criteria for an effective anticaking agent.

Table 3 Relating the properties of the tested additives to the anticaking agent criteria

	Habit modifier?	Nucleation inhibitor?	Causes creeping?	Anticaking activity?
Urea	✓[1]	✓	✗	✗
2-CMAA	✗	✓	✗	✗
NTAA	✓	✓	✓	✓
MGDA	✓	✓	✓	✓
GLDA	✓	✓	✓	✓
OAA	✗	✓	✗	✗
PAA	✓[10]	✓	✗	✗

Thus, the most likely model seems to centre on the idea that the triple-branched amide lays on the surface of the NaCl, bonded by three amide group branches and a central nitrogen atom, as described by Sarig. However, it can be said that it is likely not the matching of the three-fold symmetry of the amide molecules with the threefold symmetry of NaCl {111}, as only {100} growth is involved in anticaking experiments. Density functional theory (DFT) was employed to calculate the charge distribution over the NTAA molecule and its 2-branched counterpart 2-CMAA to determine if there are any large differences over the molecules which can explain the tendency of one to bind over the other. However, this did not give any meaningful results, it was found that the charge distribution over both molecules was very similar. So it is the addition of an extra amide group (or the acid groups in GLDA) reinforcing bonding to the NaCl surface, which is decisive. Inspired by the work of Pastero *et al.*,[3] it is possible that the additives are ordered in layers. The three-fold branching of the triamide allows the formation of highly distorted 2D connected network patterns interlinked by C=O⋯H₂N hydrogen bonds. This grouping leads to strong bonding, both vertically to Na⁺ and Cl⁻ and horizontally by hydrogen bonds. However, a more in-depth molecular modelling study is necessary to confirm this suggestion or to find an alternative as to why the triple branched amides are so effective for blocking the growth of NaCl, in contrast to the other amide compounds.

Conclusions

The overall conclusion that we can draw from this investigation, is that the three branched amide compounds nitrilotriacetamide, methyl glycine diacetamide and glutamic acid diacetamide all act as anticaking agents for NaCl, whereas single and double branched and polymer analogues do not have the same effect. This indicates that there is a clear correlation between the amount of amide branches radiating from one centre and the anticaking ability of a compound.

In contrast to the growth blocking tri-amides, the other non-blocking compounds show an enhanced caking effect on NaCl. A possible explanation is the formation of a thin layer of additive between adjacent NaCl crystallites, acting as an adhesive.

We have also determined that an effective anticaking agent must obey all of the criteria in a four-step process:

habit modification, nucleation inhibition, ability to induce creeping, leading to anticaking activity. If it fails in any of these categories, then it is ineffective as a growth blocker.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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