Stellingen

behorende bij het proefschrift:

"Calcium carbonate precipitation in relation to detergent performance"

1. Bij de analyse van gemeten induktietijden wordt vaak ten onrechte gebruik gemaakt van het mono nucleaire model voor kiemvorming. 

2. Het gebrek aan inzicht op de invloed van additieven op de nucleatie wordt vooral veroorzaakt door het ontbreken van geschikte meettechnieken voor deeltjes in het sub-micron gebied.

3. De neiging van een systeem om uit te kristalliseren wordt vaak weergegeven door de oververzadiging. De stoichiometrie van de verschillende reactanten speelt echter ook een grote rol.

4. De toepassing van additieven in kristallisatie processen blijft vaak in het "trial and error" stadium hangen doordat hun invloed op processen als nucleatie, groei en agglomeratie moeilijk apart te bepalen is.

5. Hoewel berekeningen laten zien dat de aanwezigheid van vacatures in kristalstructuren energetisch ongunstig is, komen dergelijke structuren in de praktijk wel degelijk voor. 

6. De onbenulligheid van de TV-reclames voor wasmiddelen doet ten onrechte vermoeden dat er weinig onderzoek voor nodig is om deze produkten te ontwikkelen.

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Dirk Verdoes
9 december 1991
CALCIUM CARBONATE PRECIPITATION
IN RELATION TO
DETERGENT PERFORMANCE
CALCIUM CARBONATE PRECIPITATION
IN RELATION TO
DETERGENT PERFORMANCE

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de
Technische Universiteit Delft, op gezag van de
Rector Magnificus, Prof. Drs. P.A. Schenck,
in het openbaar te verdedigen ten overstaan van
een commissie aangewezen door het College van Dekanen,
op maandag 9 december 1991 te 14.00 uur

door

DIRK VERDOES

geboren te Katwijk
doctorandus in de chemie

Delft University Press, 1991
Thesis Technische Universiteit Delft. - With ref. - With summary in Dutch.
ISBN 90-6275-741-3
NUGI 813
Subject heading: calcium carbonate precipitation ; detergents.

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Aan mijn ouders,
en voor
Krijna en Daniëlle
CALCIUM CARBONATE PRECIPITATION
IN RELATION TO
DETERGENT PERFORMANCE

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CHAPTER 1

INTRODUCTION AND SCOPE OF THE THESIS

1.1 Keywords of the investigation

The main keywords of the investigation described in this thesis are: detergents, calcium carbonate and additives. In this general introduction of the thesis the relation between these subjects will be demonstrated and some background information on these subjects will be given. This chapter will be concluded with the general aim and the scope of the thesis.

1.2 Background information on detergents

The washing process in the ancient times was very simple: laundry of every kind was subjected to purely mechanical treatment consisting of beating, treading, rubbing and similar procedures. It was already known that the washing power could be increased in various ways. Rainwater was e.g. more suitable for cleaning than well water and the washing power increased at higher water temperatures. The use of sodium carbonate, trivially called soda, as wash additive was already discovered by the ancient Egyptians [1]. At the end of the nineteenth century the main ingredients of a detergent were soda, sodium silicate and soap [1]. The first two ingredients ensured the softening of water by the precipitation of calcium and magnesium ions. Detergent components which are added to control the water hardness are called builders. The formulation of multicomponent systems for the routine washing of textiles started at the beginning of the twentieth century.

Another important development was the transition of labour-intensive manual washing to machine washing. This change led to a need for different
formulations of the washing agents [1]. An example of such a change was the replacement of soap by the synthetic surfactants.

The next step in the development of detergents was the substitution of builders like sodium carbonate by complexing agents. The use of sodium triphosphate in detergents started after World War II. This period was also important for the introduction of other ingredients which are still used in modern detergents. Examples of such ingredients for improving detergency performance are e.g. soil antiredeposition agents, enzymes and bleaching activators [1].

The use of phosphates in detergents lead to a satisfactory cleaning performance, but its application was gradually reduced after the discovery of the environmentally unacceptable effect of stimulating the growth of algae. From that time on, the use of three different classes of builders can be distinguished [1]. The first group are the complexing agents and the main examples of such compounds are ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). The second class are the inorganic ion exchangers such as zeolites. The last type of builders are those which cause precipitation, with soda and sodium silicate as the main representatives.

Modern detergents for household use are very complex formulations containing many other ingredients next to the above mentioned builders. These other ingredients can be categorized into the following major groups: surfactants, bleaching agents and auxiliary agents [1]. It would go too far to discuss these groups into detail, but the main functions of the different components will be discussed below.

The main task of surfactants is to dislodge oily and pigmented soils from textile substrates or solid surfaces. The physical removal of soil occurs as a result of nonspecific adsorption of surfactants on the various interfaces present [2] and through specific adsorption of chelating agents on certain
polar soil components [3]. In addition, the freeing of calcium ions from soil deposits and fibres leads to a loosening of any remaining residue [4]. Another important feature is the compression of the electrical double layer at boundary surfaces [2]. A general feature of the surfactants is that they are comprised of a hydrophobic portion (usually a long alkyl chain) attached to hydrophillic or solubility-enhancing functional groups. Surfactants are subdivided into four classes depending on the charge of the molecule after dissociation in aqueous solutions. These four classes, which can all be present in modern detergent formulations, are: anionic, nonionic, cationic and amphoteric surfactants.

In general, bleaching effects can occur through mechanical, physical, and/or chemical means, specifically through change or removal of dyes and soil adhering to the bleached object. In the washing process all these processes occur in parallel but to varying extents [1]. Mechanical and physical mechanisms are primarily effective for the removal of pigmented and greasy soil. Chemical bleaching is employed for the removal of nonwashable soils adhering to the fibres and it is accomplished by the oxidative or reductive decomposition of chromophoric systems. In detergents only oxidative bleaches are used to a great extent and the most frequently employed bleaches are sodium perborate and sodium percarbonate [1]. Sometimes bleach activators [5] and bleaching catalysts [6] are utilized to enhance the bleaching performance at lower temperatures.

The auxiliary agents are only added in small amounts in detergents in contrast with the builders, surfactants and bleaches which are the major components of a modern detergent. Each auxiliary agent has its own specific purpose. The list of examples of these compounds given below is far from complete but it illustrates that it is difficult to formulate modern detergents without auxiliary agents. The first representatives of this group are the
enzymes, which are in particular important for the elimination of stains originating from sources as milk, blood and grass. The main types of enzymes used in detergents are the proteases and the amylases. The second type of auxiliary agents are the soil antiredeposition agents. Their task is to prevent the return of the removed and finely dispersed soil to the fibres. This process causes the so-called greying of the laundry after repeated washing. Antiredeposition agents exercise their effect by becoming adsorbed irreversibly by both soil particles and textile fibres, thus hindering the approach of the soil to fibres [7]. Compounds which are known for their antiredeposition action are e.g. carboxymethyl cellulose and carboxymethyl starch derivatives. The last type of auxiliary agent which will be mentioned here are the so-called fillers, which are inorganic salts and especially sodium sulfate. Their task is for instance to improve the flowability and to reduce the caking of detergents [1].

It is evident that the replacement of soda as builder by phosphates during the fifties was accompanied by an improvement of the overall effectiveness of the detergents. It may therefore be surprising that soda is still one of the possibilities to substitute phosphates despite of the progress in developing high-quality laundry detergents during the last decades. The use of soda offers, however, advantages which can not always be found for the other phosphate alternatives. These advantages are: soda is relatively cheap, its water softening capacity is sufficient for a good detergency, it gives the washing liquor a mild alkalinity which favours detergency because both soil and textile become negatively charged (repulsion) and last but not least soda is an environmentally harmless compound. The major disadvantage of soda-based detergents is and was that part of the precipitated calcium carbonate is deposited on or adhered to the textile surface. This process is often called incrustation. There are some reasons for choosing soda as the
CHAPTER 1

substitute for phosphates in detergents. The first is that the degree of incrustation is dependent on the type of textile in the laundry. High incrustation levels are e.g. in particular observed for cotton, while the incrustation on synthetic types of textile is in general lower. For this reason, it can be expected that the negative effects of incrustation are less pronounced nowadays because the portion of cotton in clothes has decreased during the last decades. Secondly, it is known that polymeric additives are able to diminish the incrustation. The chance that the incrustation can be reduced to an acceptable level is certainly higher than a few decades ago, especially because modern technology provides the possibility to develop tailor-made polyelectrolytes e.g. by changing the functional groups of the polyelectrolyte [8].

1.3 Background information on calcium carbonate

The link between calcium carbonate and detergents is that the reduction of the free calcium ion concentration in the washing liquor in soda-based detergents is the consequence of the precipitation of the slightly soluble calcium carbonate (CaCO$_3$). The uses and problems of CaCO$_3$ in nature are very abundant as is illustrated by the following quotation [9]: "Calcium carbonate seems to be present everywhere: we are in awe of its beauty (pearl); we build our world with it (cement); it shapes our education (chalk); we tap its wealth (oil); we live with its pains (gall stones); we curse its presence (scale); and eventually we use it to build a final monument to ourselves (gravestone)." It is evident that the mentioned formation of calcium carbonate as a crystalline scale is an unwanted process, which occurs e.g. in heat exchangers or cooling towers or during geothermal energy production, desalination, or oil and gas recovery [10]. On the other hand CaCO$_3$ is a
INTRODUCTION AND SCOPE OF THE THESIS

useful mineral which can be applied as filler material in paints, paper and rubber [11]. Also, from a biological point of view calcium carbonate is an important substance which is present in e.g. mollusc and egg shells [12].

Calcium carbonate can be found in different polymorphs which in order of increasing solubility are calcite, aragonite, vaterite, an amorphous hydrated calcium carbonate containing less than one molecule of water, calcium carbonate monohydrate and calcium carbonate hexahydrate [13]. Hydrated phases are often formed as metastable precursor phases during the precipitation from highly supersaturated solutions. The underlying cause is that the nucleation and growth rates are then so high that water molecules get occluded in the crystal structure. In this thesis no indications were found for the precipitation of any hydrated calcium carbonate phase. The background information given below will therefore be confined to the calcite, aragonite and vaterite modifications.

The crystal structure data of these phases were summarized in ref.[14], where it was described that calcite possesses a rhombohedral symmetry with a bimolecular unit cell having the following constants: \( a = 6.3748 \, \text{Å} \) and \( \alpha = 46.08^\circ \) [15]. Aragonite is orthorhombic and the parameters for the unit cell, which contains four formula units, are reported to be: \( a = 7.6971 \, \text{Å} \), \( b = 5.7404 \, \text{Å} \) and \( c = 4.9614 \, \text{Å} \) [16]. For vaterite, a structure with a hexagonal symmetry (\( a = 7.15 \, \text{Å} \), \( c = 16.94 \, \text{Å} \) and \( \gamma = 120^\circ \)) and a unit cell containing twelve molecules has been reported [14].

An extensive study on the solubilities of calcite, aragonite and vaterite was presented in ref.[17]. The logarithm of the solubility products of the three phases are plotted in fig.1.1 as a function of the temperature. This figure shows that calcite is the least soluble modification between 0 and 90°C, which implies that calcite is the thermodynamically stable calcium carbonate polymorph. In the same temperature range aragonite and vaterite are metastable phases of which the latter has the highest solubility.
Figure 1.1 The logarithm of the solubility products of calcite, aragonite and vaterite as a function of temperature.

The figure shows that the solubility decreases with increasing temperature for all three modifications. This contributes to higher incrustation values at elevated washing temperatures.

The precipitation of metastable calcium carbonate phases has been reported in many cases (see e.g.[9,18]) and the transformation of the metastable polymorphs into calcite has also been the subject of several publications (see e.g.[19,20]). In section 2.2 the formation of metastable phases will be discussed in more detail.

The precipitation of calcium carbonate involves both nucleation and growth, and the kinetics of both steps have been thoroughly studied. The references given below are just examples of the many publications on these subjects. The kinetics of nucleation was e.g. investigated for the precipitation
INTRODUCTION AND SCOPE OF THE THESIS

of calcite in refs.[21,22], for a mixture of vaterite and calcite in ref.[23] and for pure vaterite in refs.[18,24]. Experiments in which the kinetics of growth were studied show that calcite [25-28], aragonite [28] and vaterite [18] all grow via the spiral growth mechanism, also known as the BCF mechanism.

It is a generally established fact that additives or impurities can have a great influence on processes as nucleation, growth and agglomeration of crystals. A brief survey of literature data concerning the effect of additives on the precipitation of calcium carbonate will be given in the following section together with some examples of the use of additives in laundry detergents.

1.4 Background information on additives

It is a well-known phenomenon that additives are able to alter the surface properties of the crystals leading to changes in nucleation, and growth kinetics, and thereby to changes in the shape of crystals as well as in their agglomeration and dispersion behaviour. A general review on the use of additives in crystallization processes is given in refs.[29-32].

The effects of additives on processes as nucleation, growth and agglomeration is in most cases directly or indirectly related to the adsorption of the additive on the crystal or nucleus surface.

The influence of metal ions [21,23], organic [21] and polymeric additives [33] on the nucleation of calcium carbonate has been reported in literature. In all these cases the nucleation of calcium carbonate was retarded by the additive. There are, however, also examples where an additive stimulates the nucleation of calcium carbonate (see e.g.[34]).

A good spacial interatomic matching between the functional groups of the additive and the crystal growth centres has been mentioned as an important
CHAPTER 1

parameter which among other things determines the effectiveness of the additive as inhibitor (see e.g.[35]). The influence of all kind of additives on the growth of calcium carbonate is described in many publications (see e.g.[21,28,29,36]). In some cases the supposed relation between inhibiting performance and additive adsorption has been supported by measurements of the adsorption isotherms of the additive [37], sometimes combined with the determination of the effect of the additive on the electrokinetic properties of the substrate (see e.g.[30] for gypsum and [38] for CaCO₃).

The effect of additives on the electrokinetic properties can affect the agglomeration or dispersion of crystals. The idea is that adsorption of the additive changes the surface charge of the crystals, and thereby the degree of electrostatic repulsion or attraction between crystals or crystals and another substrate. The extent of agglomeration can also be influenced when the adsorption of the additive leads to sterical hindrance for a close approach of the crystals to each other or to another surface. The effect of additives on electrostatic repulsion or sterical hindrance is related to colloid chemistry. These effects are also often mentioned as one of the potential causes for the impact of polymeric co-builders in soda-based detergents on the incrustation.

The use of co-builders is not only restricted to the soda-based detergents but is also known for detergents with ion exchangers as builder [39,40]. The most frequently applied co-builders in the soda-based detergents belong to the class of the polyelectrolytes, and especially the polycarboxylates. The publications concerning the application of polymeric co-builders do not give one specific cause for the effect of the co-builders on the incrustation. Potential mechanisms mentioned in literature are: adsorption on solid surfaces, increasing the electrostatic repulsion between CaCO₃ and textile, nucleation inhibition, sequestration of Ca²⁺-ions, growth inhibition and a dispersing action for CaCO₃ and soil [8,41-43]. The lack of a uniform and
INTRODUCTION AND SCOPE OF THE THESIS

unique explanation for the effect of polymeric co-builders on the incrustation in soda-based detergents was the direct motivation for the investigation described in this thesis.

1.5 General aim of the thesis

The general aim of this thesis is to get a better insight into the effects of additives on the precipitation of calcium carbonate in relation to the deposition behaviour of calcium carbonate on textile. The formation of such a deposition is the major disadvantage of soda-based laundry detergents and is often called "incrustation". Polymeric additives are frequently applied as co-builder in soda-based detergents with the task to reduce the degree of incrustation. In the various publications concerning this subject only little attention was paid to the cause of the incrustation and they did not provide a unique and satisfactory answer on the question how additives can affect the degree of incrustation. A better knowledge on these two subjects is needed in order to facilitate the formulation of good soda-based laundry detergents.

1.6 Scope of the thesis

In Chapter 2 the influence of several polyelectrolytes on the extent of calcium carbonate incrustation on cotton in a simple soda-based detergent formulation is investigated. This formulation consisted of a mixed Na₂CO₃-NaHCO₃ builder system and, except for the blank experiment, a polymeric additive as co-builder. Several types of incrustation experiments were developed in order to identify the mechanisms by which the investigated polyelectrolytes affect the incrustation.
CHAPTER 1

In Chapter 3 the simple detergent formulation used in Chapter 2 has been systematically extended with two other frequently used detergent components. These components are an anionic surfactant and a filler material. The aim is to investigate whether the trends observed for the effect of the polyelectrolytes on the incrustation in the simple system are also present in the extended formulations. Secondly, the experiments should give a better insight into the general effects of the surfactant and the filler material on the incrustation.

In Chapter 4 the influence of polyelectrolytes on the development of the particle size distribution of calcium carbonate in batch precipitation experiments is followed in time. The results are used for a qualitative evaluation of the effects of the polyelectrolytes on precipitation related processes as nucleation, growth and agglomeration of calcium carbonate. Knowledge of these effects provides a better insight into the mechanisms by which the polyelectrolytes affect the incrustation.

In Chapter 5 the adsorption of the investigated polyelectrolytes on both calcium carbonate crystals and cotton has been measured quantitatively. Next to this, the effect of the polyelectrolytes on the zeta potential of both substrates has been determined. The aim was to find out whether sterical hindrance and/or electrostatic repulsion between the calcium carbonate crystals and cotton play(s) a major role in determining the incrustation.

The general conclusion from Chapters 2-5 is that the effect of the polyelectrolytes on the incrustation seems to be mainly governed by their specific effect on the nucleation of calcium carbonate in solution or on their impact on the growth rate of the crystals, while colloid chemical aspects like sterical hindrance and/or electrostatic repulsion seem to be of minor importance. Many methods are available to study the influence of additives on growth, but it is more difficult to determine their separate effect on
INTRODUCTION AND SCOPE OF THE THESIS

nucleation. A frequently applied method for this purpose is measurement of the induction time, which is the time elapsing between the creation of the supersaturation and the first moment that the onset of precipitation can be detected. Two limiting cases are known for the interpretation of measured induction times. The first one is applicable when metastability is lost by the appearance of the very first nucleus. The other limiting case belongs to the situation when metastability is lost by the nucleation and growth of statistically many nuclei. In Chapter 6 a general expression was sought for the induction time which was also applicable in the intermediate region, where neither one nor statistically many nuclei lead to the breakdown of the metastability. Such an expression is more generally useful to evaluate the critical supersaturation below which a supersaturated system will stay in metastable equilibrium for an arbitrary chosen time interval.

In precipitation metastability is almost always lost by the nucleation and growth of statistically many nuclei. Consequently the resulting induction time contains mixed terms of both the nucleation and growth rate of the compound. This also explains why it is so difficult to determine separately the effect of additives on nucleation. In Chapter 7 it is proposed to combine the measurements of induction times in seeded and unseeded precipitation to obtain full and separate information about the influence of additives on both nucleation and growth. Theoretical expressions for the induction times in both types of precipitation are derived, for systems growing according to the most frequently encountered growth mechanisms.

In Chapter 8 the theoretical expressions derived in chapter 7 are applied to study the influence of two polymeric additives on the nucleation and growth rates of CaCO₃. These additives were also investigated in chapters 2-5. The applied method indeed revealed the separate effects of the additives on the nucleation and growth rates of CaCO₃. The results are compared with
values reported in literature and the measured effects are checked on consistency with the potential mechanisms which were proposed for the influences of the investigated additives on the incrustation.

In Chapter 9 the effects of CaCO$_3$ and bentonite as seed material on the incrustation were determined. The idea behind these experiments is that the influence of the most effective additives on the incrustation can also be reached by the addition of seeds. The influence of seeds and the seed material on the incrustation is determined and compared to the previously measured effects of the polyelectrolytes.

References

INTRODUCTION AND SCOPE OF THE THESIS


CHAPTER 2

PRECIPITATION IN DETERGENT PERFORMANCE.
PART I: INFLUENCE OF SEVERAL POLYELECTROLYTES

Abstract

Sodium carbonate, trivially called soda, is an environmentally acceptable alternative for phosphates in laundry detergents. The main function of these detergent components is to reduce the free Ca$^{2+}$ concentration originating from the tap water. In case of soda such an effect is reached by the precipitation of the slightly soluble calcium carbonate. A major disadvantage of soda-based detergents is, however, that part of the precipitated calcium carbonate adheres to or is directly deposited on the textile surface. This phenomenon is known as incrustation.

The aim of this chapter is to find the main cause of the incrustation, which can either be heterogeneous nucleation of calcium carbonate on the textile surface or entrapment by the textile fibres of calcium carbonate crystals formed in solution. It will be shown that a combination of soda with a low concentration of various polyelectrolytes can lead to both a higher or a lower degree of incrustation. The mechanisms causing these effects will be identified. The influence of the polyelectrolytes on processes as nucleation and growth as well as on processes which are associated with the adsorption of the polyelectrolytes on calcium carbonate and textile will be considered.

2.1. Introduction

Detergents often contain water hardness controlling agents, generally called builders. One of the main objectives of a builder in detergents is to reduce the free calcium ion concentration in the washing liquor \([1]\). The use of phosphates as builders in laundry detergents had to be reduced for environmental reasons \([2-4]\).

Phosphates form soluble complexes with \(\text{Ca}^{2+}\) ions originating from the tap water. An option to replace phosphates in detergents is sodium carbonate \((\text{Na}_2\text{CO}_3)\). The trivial name for sodium carbonate is soda. Soda causes the precipitation of calcium carbonate \((\text{CaCO}_3)\), which ensures an appropriate reduction of the \(\text{Ca}^{2+}\) concentration. Besides, soda provides a mild alkalinity which is necessary for a good detergency \([5]\). The formation of \(\text{CaCO}_3\) involves both primary nucleation and growth and is thus a precipitation process, but crystallization will sometimes be used as a synonym.

A disadvantage of soda-based detergents is that part of the precipitated calcium carbonate crystals adheres to or deposits on the textile surface. This phenomenon, called incrustation, has a negative effect on detergency \([6]\). Especially at high washing temperatures more incrustation can be expected due to the inverse solubility of calcium carbonate. High incrustation levels are in particular observed for cotton, a cellulose derivate, and therefore this material was selected for our model incrustation experiments.

Two potential causes for the occurrence of incrustation in soda-based detergents can be distinguished. The first is related to heterogeneous nucleation of \(\text{CaCO}_3\) on the textile, followed by growth of these nuclei. Heterogeneous nucleation is likely to occur on the rough surface of cotton, most probably promoted by the hydroxylic and carboxylate groups of the fibres. Secondly, incrustation can follow from entrapment of calcium
carbonate crystals by the textile fibres. Such crystals are previously formed in solution and remain stuck to the cotton either because cotton is a suitable substrate for epitaxial growth of calcium carbonate, or because Ca\(^{2+}\) ions form bridges by charge compensation between the calcium carbonate crystals and the cotton surface, which are both negatively charged.

Small amounts of polyelectrolytes, mainly polyacrylates, are frequently added in soda-based detergent formulations. Polyacrylates are claimed to diminish the incrustation by various mechanisms [7-9]. Like phosphates, they can sequester calcium ions, but the usually applied polyacrylate concentrations are too low to sequester the numbers of Ca\(^{2+}\) ions in the washing liquor sufficiently to reduce the driving force for nucleation and growth of CaCO\(_3\). Furthermore, polyacrylates may inhibit the nucleation and/or growth of CaCO\(_3\) by adsorption at active growth sites through ionic bonding with calcium ions or hydrogen bridges with carbonate ions at the crystal surface. Inhibition will lead to a higher free Ca\(^{2+}\) concentration in the washing liquor, thus partially counteracting the builder action of soda. Polyelectrolytes can not only adsorb on the calcium carbonate crystals but also on the cotton fibres, by means of hydrogen bridges with hydroxylic and carboxylate groups at the cotton surface. Such an adsorption can reduce the entrapment of CaCO\(_3\) crystals by the cotton fibres, when it causes more sterical hindrance for a close approach of CaCO\(_3\) particles towards the cotton surface or leads to a higher electrostatic repulsion between the CaCO\(_3\) particles and the cotton surface. This mechanism will further be referred to as a dispersing action of the polyelectrolytes.

In the first instance, five polyelectrolytes were selected which were expected to act according to one of the above mechanisms. Not only polyacrylates but also (co)polymers with carboxylic and (styrene) sulfonic acid as main functional groups and one with carboxylic and acrylamido methyl
precipitation in detergent performance: part I

Propane sulfonic acid were tested in four types of incrustation experiments. These experiments revealed, as will be demonstrated in section 2.4.3, that especially the polyelectrolytes with styrene sulfonic acid were effective in decreasing the incrustation. Preliminary experiments also showed that vinyl sulfonic acid groups were equally effective. Because of this result, an available series of (co)polymers with a varying content of polyacrylic and polyvinyl sulfonic acid was tested in only that type of experiments that showed the most direct effect of the polymers on the incrustation. The objectives of this last series of experiments was to study whether the effect on the incrustation could be correlated with the sulfonic acid content of the (co)polymer.

The general aim of this chapter is: (i) to quantify the effects of various polyelectrolytes on the degree of calcium carbonate incrustation of cotton, and (ii) to identify the mechanisms causing these effects.

2.2. The effects of additives on the precipitation of calcium carbonate

Calcium carbonate can precipitate from aqueous solutions in several polymorphs. Table 2.1 gives the thermodynamic solubility products of some of the calcium carbonate polymorphs at 50°C, which is the working temperature for the incrustation experiments in this chapter. The amorphous phase in the table contained less than one molecule of water per molecule of CaCO₃ [10]. Other hydrated phases which have been reported in literature are hexahydrate [11,12] and monohydrate [12]. Solubility data of these phases are, however, not available. It can be seen from the solubility products that calcite is the thermodynamically stable CaCO₃ polymorph.
Formation of metastable phases during spontaneous precipitation from a highly supersaturated solution is a quite common phenomenon (see e.g. [14]). The generally accepted explanation for this observation relies on the precipitation kinetics of the salt. The metastable phases have relatively higher rates of nucleation and growth than the thermodynamically stable polymorph. Hydrates are frequently formed as metastable phase because water gets occluded in the crystal structure during precipitation at a relatively high supersaturation. The formation of a metastable phase is often followed by a transformation into the stable polymorph. Examples of systems in which the formation of a metastable polymorph was observed were e.g. the precipitation of hydrates of sodium sulfate [14] and calcium oxalate [15].

The presence of additives or impurities can have important consequences for the formation and transformation behaviour of metastable phases. It has e.g. been reported that nucleation of CaCO₃ induced by the carboxylic headgroups of a monolayer of stearic acid at the air-solution interface resulted in the preferential formation of vaterite [16]. These headgroups form a structure of negatively charged groups at regular distances. A layer of Ca counterions and an associated, more diffuse, layer of carbonate ions is supposed to be formed rapidly at the monolayer surface. This increases the nucleation rate because ion binding lowers the interfacial energy of the incipient crystal surface. It was shown that geometric matching between the
monolayer and the different CaCO₃ polymorphs provides no explanation for the formation of vaterite. Stereochemical recognition between the carbonate groups of the CaCO₃ polymorphs and the carboxylate groups of stearic acid could play a role in the formation of vaterite, but it seems to be more logical that the formation of the metastable phase is just a consequence of the increased nucleation rate.

It has been reported that the transformation of vaterite and aragonite into calcite proceeds via the dissolution of the former polymorphs and the growth of calcite, which is thought to be rate determining [17]. It was found that earth alkali metal ions like Mg²⁺ [17] and Li⁺ [18] retard the transformation of vaterite into calcite. The incorporation of these ions in calcite causes strain in the structure due to their deviating ionic radii, resulting in a retardation of the growth of calcite and consequently a lower transformation rate of vaterite to calcite.

Summarizing the effects of additives it can be concluded that the formation of a metastable phase is promoted either by a stimulation of the nucleation and/or growth of this phase or by a retardation of the same processes of the thermodynamically stable polymorph.

2.3. Experimental

AR grade chemicals, doubly distilled water and standard cotton from TNO Delft for incrustation tests were used in all experiments. Fig.2.1 displays the experimental equipment. Four types of incrustation experiments were all done in duplicate. Table 2.2 gives the procedure followed in these experiments.
Figure 2.1
*Equipment for quantitative determination of the incrustation:*
(1) thermostated vessel (50°C);
(2) sample holder for cotton;
(3) cotton sheet, 5 x 9 cm;
(4) outlet;
(5) baffle;
(6) reaction liquid.

<table>
<thead>
<tr>
<th>Type</th>
<th>Sequence of procedures</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C/CA-R-C/CA-R-C/CA-R</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>P-R-CA-R-CA-R-CA-R</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>P-R-C-R-C-R-C-R</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>PC/PCA-R-PC/PCA-R-PC/PCA-R</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 2.2 shows that each incrustation experiment consisted of several subsequent procedures. The condition in the vessel at the start of a procedure was for the

**Crystallization procedure (C/CA):** 0.5 dm³ 1.07x10⁻² M CaCl₂ and 0.5 dm³ of a mixed solution of 2.27x10⁻² M Na₂CO₃ and 3.39x10⁻² M NaHCO₃, with 100 mg polyelectrolyte (CA) or without polyelectrolyte (C). Time: 30 minutes, cotton sheet present, pH=10.0,

**Rinsing procedure (R):** 1 dm³ water. Time: 30 minutes, cotton sheet present,

**Pretreatment procedure (P):** 1 dm³ mixed solution of 5.35x10⁻³ M Na₂SO₄, 1.135x10⁻² M Na₂CO₃, 1.695x10⁻² M NaHCO₃ and 50 mg polyelectrolyte.
PRECIPITATION IN DETERGENT PERFORMANCE: PART I

Time: 30 minutes, cotton sheet present, pH = 10.0,

Precrystallization procedure (PC/PCA): Similar to the solutions used in a C/CA-procedure. Time: first 5 minutes without and then 30 minutes with cotton sheet present in the vessel, pH = 10.0.

In a pretreatment procedure adsorption of polyelectrolyte on cotton is allowed to occur prior to a crystallization procedure. The objective of the first rinsing procedure applied in the type 2 and 3 experiments directly after the pretreatment of the cotton is to investigate the strength of the adsorption of the polyelectrolytes on cotton. In a precrystallization procedure crystallization of CaCO₃ is allowed to start in the absence of the cotton sheet. The rinsing after a crystallization or precrystallization procedure is meant to remove those CaCO₃ crystals which are not tightly adhered to the cotton surface and to detach weakly adsorbed polyelectrolyte molecules.

In table 2.3 the polyelectrolytes, their abbreviations and their mean molecular weights (MW) are given.

<table>
<thead>
<tr>
<th>Name of (co)polymer</th>
<th>Abbreviation</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>polymaleic acid - polycrylamido methyl propane sulfonic acid</td>
<td>PMA-PAMPS</td>
<td>7500</td>
</tr>
<tr>
<td>polymaleic acid - polystyrene sulfonic acid</td>
<td>PMA-PSS</td>
<td>13000</td>
</tr>
<tr>
<td>polymethacrylic acid - polystyrene sulfonic acid</td>
<td>PMAA-PSS</td>
<td>4310</td>
</tr>
<tr>
<td>polystyrene sulfonic acid</td>
<td>PSS</td>
<td>70000</td>
</tr>
<tr>
<td>polyacrylic acid</td>
<td>PAA</td>
<td>5000</td>
</tr>
<tr>
<td>polyacrylic acid - polyvinyl sulfonic acid 1</td>
<td>PAA-PVS 1</td>
<td>7100</td>
</tr>
<tr>
<td>polyacrylic acid - polyvinyl sulfonic acid 2</td>
<td>PAA-PVS 2</td>
<td>4500</td>
</tr>
<tr>
<td>polyacrylic acid - polyvinyl sulfonic acid 3</td>
<td>PAA-PVS 3</td>
<td>3300</td>
</tr>
<tr>
<td>polyacrylic acid - polyvinyl sulfonic acid 4</td>
<td>PAA-PVS 4</td>
<td>1400</td>
</tr>
<tr>
<td>polyvinyl sulfonic acid</td>
<td>PVS</td>
<td>4100</td>
</tr>
</tbody>
</table>
Table 2.4 shows the generic formulae of the five primarily selected polyelectrolytes which were investigated in all four types of experiments given in table 2.2.

<table>
<thead>
<tr>
<th>Polyelectrolyte</th>
<th>Generic Formula</th>
</tr>
</thead>
</table>
| PAA             | \[
\begin{array}{c}
\text{CH}_2 \text{CH} \\
\text{COOH}
\end{array}
\]
| PMA-PAMPS       | \[
\begin{array}{c}
\text{CH}_2 \text{CH} \\
\text{C=O}
\end{array}
\]
|                 | \[
\begin{array}{c}
\text{CH}_3 \\
\text{C-CH}_3 \\
\text{SO}_3\text{H}
\end{array}
\]
| PMA-PSS         | \[
\begin{array}{c}
\text{CH}_2 \text{CH} \\
\text{COOH}
\end{array}
\]
|                 | \[
\begin{array}{c}
\text{CH}_2 \text{CH} \\
\text{SO}_3\text{H}
\end{array}
\]
| PMAA-PSS        | \[
\begin{array}{c}
\text{CH}_2 \text{CH} \\
\text{COOH}
\end{array}
\]
|                 | \[
\begin{array}{c}
\text{CH}_2 \text{CH} \\
\text{SO}_3\text{H}
\end{array}
\]
| PSS             | \[
\begin{array}{c}
\text{CH}_2 \text{CH} \\
\text{SO}_3\text{H}
\end{array}
\]
PRECIPITATION IN DETERGENT PERFORMANCE: PART I

The five polyelectrolytes from table 2.4 were also added in a relatively simple incrustation experiment which consisted of only one crystallization and rinsing procedure. At the end both the cotton sheet and the crystals formed in solution were collected and dried in air at 50°C. The morphology of the crystals collected from solution and of those deposited on the cotton was examined with a JEOL 35 scanning electron microscope (SEM).

The generic formulae and the ratio of the monomers of the polyacrylic acid-polyvinyl sulfonyl acid (PAA-PVS) (co)polymers are shown in table 2.5.

**Table 2.5**  
*Generic formulae of the PAA-PVS (co)polymers from table 2.3, which are used in type 1 incrustation experiments (see table 2.2).*

<table>
<thead>
<tr>
<th><strong>Formula</strong></th>
<th><strong>PAA</strong></th>
<th><strong>PAA - PVS 1</strong></th>
<th><strong>PAA - PVS 2</strong></th>
<th><strong>PAA - PVS 3</strong></th>
<th><strong>PAA - PVS 4</strong></th>
<th><strong>PVS</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Formula" /></td>
<td><img src="image" alt="Formula" /></td>
<td><img src="image" alt="Formula" /></td>
<td><img src="image" alt="Formula" /></td>
<td><img src="image" alt="Formula" /></td>
<td><img src="image" alt="Formula" /></td>
<td><img src="image" alt="Formula" /></td>
</tr>
</tbody>
</table>
CHAPTER 2

Contrary to the other polyelectrolytes the PAA-PVS (co)polymers were only tested in type 1 experiments (see table 2.2).

At the end of each crystallization and precrystallization procedure the suspension was withdrawn from the vessel and filtered. The residual Ca\(^{2+}\) concentration in the filtrate was determined by an inductively coupled plasma technique (Perkin Elmer Plasma 2 Emission Spectrometer).

The modification of the precipitated calcium carbonate was determined by means of X-ray diffraction using Cu-K\(\alpha\) radiation and a Guinier-de Wolff camera.

At the end of each experiment the cotton was dried and weighed. The deposited calcium carbonate was dissolved by immersing the cotton sheet in a 6% HCl solution and the Ca\(^{2+}\) concentration in the resulting solution was measured by an inductively coupled plasma technique. From this concentration the incrustation was calculated expressed as mg CaCO\(_3\) deposited per g cotton.

2.4. Results and discussion

2.4.1. General remarks

The trends observed in the experiments were reproducible. In some experiments small differences were observed between duplicate values, especially for the residual Ca\(^{2+}\) concentration. The character of the experiments, which are in fact batch nucleation and growth experiments in the presence of cotton, explains the spread in the obtained data.

The change in morphology of the crystals in the presence of the polyelectrolytes (see fig.2.2) and their effect on the modification of CaCO\(_3\) (see tables 2.7 and 2.8) both point at an influence of the additives on the
precipitation process.

The precipitation of calcium carbonate in the crystallization procedures started immediately after mixing of the CaCl₂ and Na₂CO₃ solutions. In solution both homogeneous nucleation due to the high supersaturation and heterogeneous nucleation (e.g. on dust particles) will take place. This supersaturation S is defined as \( [(Ca^{2+})(CO_3^{2-})/K_{sol}]^{1/2} \), where \( (Ca^{2+}) \) and \( (CO_3^{2-}) \) are the activities of the free ions and \( K_{sol} \) is the thermodynamic solubility product. The complexes formed in solution and the supersaturation S were calculated from mass-balance and charge-balance equations by successive approximations of the ionic strength [19]. The equilibria in solution and the values of the thermodynamic constants were obtained from ref.[13]. The supersaturation S at the start of a crystallization procedure was calculated using the solubility products from table 2.1. S was computed to be 14.4 and 25.8 for the precipitation of the metastable vaterite and of the stable polymorph calcite, respectively.

The SEM micrographs of crystals collected from solution and of crystals deposited on the cotton during the same single crystallization procedure will be discussed in section 2.4.2. Comparison of the morphologies gives an indication about the cause of the incrustation (entrapment of crystals from solution or heterogeneous nucleation of crystals upon the fibres), without quantifying the effects of the polyelectrolytes on the incrustation.

The polyelectrolytes will be divided into two groups on the basis of the experiments in which they were tested, as was already mentioned in sections 2.1 and 2.3. The five polyelectrolytes in table 2.4 were added in all four types of incrustation experiments given in table 2.2. The corresponding results will be discussed in section 2.4.3.

The series of PAA-PVS (co)polymers (shown in table 2.5) selected for the investigation of the role of the sulfonic acid content in the polymer was only
added in type 1 experiments, which are closest related to machine washing with soda-based detergents. Type 1 experiments show directly the effect of the polyelectrolyte on the incrustation without pretreatment of the cotton or precrystallization of CaCO₃. The results for the PAA-PVS (co)polymers will be discussed in section 2.4.4.

The potential mechanisms by which the polyelectrolytes affect the incrustation will be given in section 2.5.

2.4.2. The cause of incrustation

Fig.2.2 gives the SEM micrographs of cotton fibres before use and of "free" calcium carbonate particles collected from solution as well as deposited on or adhered to the cotton during the same crystallization procedure in the absence or presence of a polyelectrolyte.

The used cotton is a fabric, which consists of individual fibres, as shown in fig. 2.2 A. The habits of the calcium carbonate crystals which were collected from solution and of the crystals which were deposited on or adhered to the cotton after one crystallization and rinsing procedure are shown in figs. 2.2 B to M next to each other.

The left hand series of SEM views in fig.2.2 shows that the habit of the CaCO₃ crystals taken from solution changes in the presence of the polyelectrolytes. For the blank (B) and in the experiment with PSS (L) blocks and aggregates were the dominant morphologies. In the presence of the other additives dumbbell-like (for PAA (D) and PMA-PAMPS (F)), spherical (for PMA-PAMPS (F) and PMAA-PSS (J)) and cauliflower-shaped particles (for PMA-PSS (H)) are observed. The right hand series of SEM views in fig.2.2 shows the morphology of the crystals which are either deposited on or adhered to the cotton surface. The predominant habits of these crystals are blocks or distorted blocks.
Figure 2.2
Morphology of cotton fibres, and of CaCO$_3$ crystals in solution as well as deposited on cotton after one crystallization procedure.

A: Cotton fabric

Figure 2.2: B and C: Blank experiment,
Figure 2.2: D and E: Influence of PAA, F and G: Influence of PMA-PAMPS.
Figure 2.2: H and I: Influence of PMA-PSS, J and K: Influence of PMAA-PSS.
As said, both the cotton and the crystals from solution were collected after the same crystallization procedure. If incrustation were mainly caused by the entrapment or adherence of crystals, previously formed in solution, a strong resemblance in morphology between the crystals collected from the solution and those deposited on the cotton could be expected. For PMAA-PSS (Figs.2.2 J and K) there is a clear difference in morphology between the spherical crystals in solution and the distorted blocks on the fibres. This indicates that the contribution of entrapment or adherence of crystals to the incrustation is of minor importance. The crystals formed in solution sometimes have two different shapes, see e.g. fig.2.2 L with particles formed in the presence of PSS. With this additive both agglomerates and blocks are formed. On the fibre, however, almost all crystals have a block-like morphology (fig.2.2 M). So the number ratio between the two morphologies
in solution is different from that on the fibre. Differences in morphology or number ratio between the crystals in solution and on the cotton are also observed in the presence of the other additives, although less clear than for the above given examples.

In general the observations indicate that it is more likely that the incrustation is caused by heterogeneous nucleation of CaCO₃ on cotton than by entrapment of crystals previously formed in solution. The fact that the deposited crystals are situated on rather than between the fibres also seems to point at heterogeneous nucleation.

The quantitative effect of the polyelectrolytes on the incrustation was not determined from SEM micrographs, but was measured by dissolving the deposited CaCO₃ and by analyzing the Ca²⁺ concentration in the resulting solution. The results for the five polyelectrolytes from table 2.4 will be discussed in the following section.

2.4.3. Experiments with the five polyelectrolytes from table 2.4.

Fig.2.3 shows the influence of the five polyelectrolytes from table 2.4 on the incrustation of cotton at the end of each type of experiment, expressed as mg CaCO₃ deposited per g cotton.

Fig.2.4 presents the effect of the polyelectrolytes on the residual Ca²⁺ concentration in the filtrate of the crystallization and the precrystallization procedures. The given concentration is the mean value of all measured data from the duplicate incrustation experiments.

Table 2.6 gives the influence of the polyelectrolytes on the percentage of the total precipitated calcium carbonate mass that is deposited on the cotton for the four types of experiments.
Figure 2.3  Influence of the five polyelectrolytes from table 2.4 on the incrustation of cotton.

Figure 2.4  Influence of the five polyelectrolytes from table 2.4 on the residual Ca$_{2}^{+}$ concentration in the filtrate.
### Table 2.6 Percentages CaCO$_3$ deposited on cotton for the different types of experiments given in table 2.2. Polyelectrolytes from table 2.4.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 3</th>
<th>Type 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>33 %</td>
<td>----</td>
<td>----</td>
<td>4 %</td>
</tr>
<tr>
<td>PAA</td>
<td>54 %</td>
<td>34 %</td>
<td>31 %</td>
<td>26 %</td>
</tr>
<tr>
<td>PMA-PAMPS</td>
<td>29 %</td>
<td>22 %</td>
<td>30 %</td>
<td>17 %</td>
</tr>
<tr>
<td>PMA-PSS</td>
<td>19 %</td>
<td>11 %</td>
<td>33 %</td>
<td>7 %</td>
</tr>
<tr>
<td>PMAA-PSS</td>
<td>18 %</td>
<td>12 %</td>
<td>31 %</td>
<td>5 %</td>
</tr>
<tr>
<td>PSS</td>
<td>14 %</td>
<td>14 %</td>
<td>30 %</td>
<td>6 %</td>
</tr>
</tbody>
</table>

**Type 1 experiments**

In these experiments the cotton was not pretreated and the additive was only present during the crystallization cycles except for the blank.

Fig.2.3 shows that addition of PAA resulted in an increased incrustation compared to the blank experiment. An increase of the incrustation in the presence of PAA was also reported by Hudson et al.[6]. PMA-PAMPS hardly affects the incrustation. The other three all PSS containing polyelectrolytes diminished the incrustation with about 50% compared to the blank.

The high percentages of CaCO$_3$ deposited on the cotton varying from 54% for PAA to 14% for PSS, as shown in table 2.6, indicate that cotton is indeed a suitable substrate for heterogeneous nucleation or for entrapment of CaCO$_3$ and show that incrustation is a severe problem in soda-based detergents.

The significantly higher residual Ca$^{2+}$-concentrations for PAA and PMA-PAMPS, shown in fig.2.4, point at growth inhibition. For the three polystyrene sulfonic acid containing polyelectrolytes no indications for growth inhibition were observed. Polyvinyl sulfonic acid (MW 17000) was earlier reported to have no retarding effect on the precipitation of CaCO$_3$ [20].
Table 2.7  X-Ray diffraction determination of the modifications of CaCO₃ in incrustation experiments with polyelectrolytes from table 2.4.

<table>
<thead>
<tr>
<th>Additive</th>
<th>% aragonite</th>
<th>% calcite</th>
<th>% vaterite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1 - 5</td>
<td>15 - 90</td>
<td>5 - 85</td>
</tr>
<tr>
<td>PAA</td>
<td>0</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>PMA-PAMPS</td>
<td>0</td>
<td>15 - 95</td>
<td>5 - 85</td>
</tr>
<tr>
<td>PMA-PSS</td>
<td>0</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>PMAA-PSS</td>
<td>0</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>PSS</td>
<td>0</td>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 2.7 gives the modifications of the dried CaCO₃ crystals grown from solution in the different experiments. For the blank the crystals consisted of a combination of vaterite and calcite, always with a small amount of aragonite. In the presence of PAA the CaCO₃ phase was always calcite. With PMA-PAMPS either calcite or vaterite was developed as the most dominant modification, just as for the blank. The PSS containing polyelectrolytes promote the formation of vaterite with minor amounts of calcite.

It is remarkable that the amount of vaterite in solution is higher in the presence of those polyelectrolytes which diminish the incrustation. For the blank and in the experiments with PAA and PMA-PAMPS more calcite is formed. This indicates the existence of at least an indirect correlation between the modification of the precipitate and the incrustation.

*Type 2 experiments:*

In this case the cotton is pretreated with an additive containing solution followed by rinsing, and the additive is also present during the crystallization procedures of the experiment.

Pretreatment of cotton was done in order to check whether the polyelectrolytes affect the incrustation more effectively when adsorption on cotton
INDUCTION TIME IN SEEDED AND UNSEEDED PRECIPITATION

could proceed without the competition of CaCO$_3$ nucleating on or adhering
to this cotton. Adsorbed polyelectrolytes might be able to protect the cotton
against adherence of CaCO$_3$ crystals previously formed in solution by a
dispersing action. Na$_2$SO$_4$ was added to get the same ionic strength as at the
start of a crystallization cycle.

Comparison of the results of the type 2 experiments with type 1
experiments shows that the most prominent influence of pretreatment is
observed in case of PAA. The adsorption of PAA on cotton is rather strong
because the effect of the pretreatment is still noticeable despite the
consecutively performed rinsing procedure. The incrustation, however, is still
comparable with the type 1 blank, indicating that the PAA molecules which
are adsorbed during the pretreatment do not cause sterical hindrance or
electrostatic repulsion or that the adherence of crystals does not affect the
incrustation significantly.

With PMA-PAMPS, PMA-PSS and PMAA-PSS only a minor reduction in
the incrustation was found compared to the experiments without
pretreatment. With PSS no difference was noticed between both types of
experiments, thus implying that the adsorption of PSS on cotton is probably
not important.

Again higher residual Ca$^{2+}$ concentrations were measured for PAA and
PMA-PAMPS.

*Type 3 experiments:*

As in the type 2 experiments the cotton is pretreated followed by a
rinsing procedure, but now the additive is not present during the
crystallization procedures.

None of the investigated polyelectrolytes affects the incrustation by
pretreatment alone. All values for the incrustation and for the residual Ca$^{2+}$
concentrations are about equal to the blank of the type 1 experiments as can be seen in figs.2.3 and 2.4. During the rinsing procedure performed after the pretreatment procedure any adsorbed polyelectrolyte molecule could in principle desorb from the cotton, but the result for PAA in the type 2 experiment shows that this is not always the case. Apparently, adsorption of the polyelectrolytes on cotton is either not strong enough to survive the rinsing procedure or is on its own not an essential step in influencing the incrustation. For PMA-PAMPS, PMA-PSS and PMAA-PSS these results are in contradiction with the results obtained in the type 2 experiments, where minor reductions of the incrustation were caused by the pretreatment. Quantitative adsorption experiments are thus necessary in order to reject or to sustain the found effects of the pretreatment with the different polyelectrolytes. The results of such experiments will be fully treated in chapter 5 and it will there be shown that PAA and PMA-PAMPS do adsorb onto cotton, while the other three polyelectrolytes do not. Since both PMA-PSS and PMAA-PSS do not adsorb onto cotton the observed minor reductions of the incrustation in the type 2 experiments cannot be assigned to their adsorption during the pretreatment. Only PAA and PMA-PAMPS could in principle diminish the incrustation by adsorption on cotton during the pretreatment in type 2 experiments. The negative result with PMA–PAMPS in a type 3 experiment makes it, however, questionable whether the adsorption of PMA–PAMPS on cotton really affects the incrustation.

Type 4 experiments:

In these experiments the crystallization of CaCO₃ was started in the absence of cotton, which was brought into the reactor five minutes after the start of the precrystallization procedure.
The aim of these experiments was to estimate the contribution to the in-crustation of entrapment or adherence of CaCO₃ crystals previously formed in solution compared to heterogeneous nucleation of CaCO₃ on the cotton. The in-crustation of the type 4 blank experiment, shown in fig.2.3, as well as the percentage deposited CaCO₃, given in table 2.6, are only about 10% of the values obtained in the type 1 blank. The in-crustation values resulting from a precrystallization procedure in the presence of the polyelectrolytes are lower than the in-crustation in the type 1 experiments with the same polyelectrolyte and all values are lower than the in-crustation in the type 1 blank.

Comparison of the in-crustation data for the type 4 experiments among themselves shows that PAA again increases the in-crustation compared to the blank experiment. In the type 4 experiments PMA-PAMPS also leads to a higher in-crustation than for the blank, although less high than PAA. In the other types of experiments PMA-PAMPS did not increase the in-crustation. Again it follows from the measured residual Ca²⁺ concentrations in the filtrate of the crystallization cycles that both PAA and PMA-PAMPS seem to inhibit the growth of CaCO₃.

With the other three PSS containing polyelectrolytes the in-crustation and the residual Ca²⁺ concentrations are comparable with the values for the type 4 blank experiment. The observed decrease of the in-crustation in the type 1 experiments in the presence of these polyelectrolytes is lost after the precrystallization procedure in the type 4 experiments.

The strong decrease of both the in-crustation and the corresponding percentage CaCO₃ deposited on the cotton in the type 4 experiments can be explained by two effects related to the precrystallization procedure.

1. Nucleation and growth of CaCO₃ largely occur during the first five minutes of the precrystallization procedure, so in the absence of cotton. Heterogeneous nucleation on cotton is strongly reduced because the
supersaturation is already decreased at the moment that the cotton is brought in the reactor.

(2) CaCO$_3$ particles which are entrapped by or adhere to the cotton may stick to the cotton during their further growth. In the experiments with precrystallization this sticking can only take place after the supersaturation has decreased due to nucleation and growth during the first five minutes. This reduces the chance that an entrapped particle will stick to the cotton.

It is thus not possible to draw a firm conclusion about the incrustation mechanism on the basis of the results of the type 4 experiments alone. The SEM micrographs discussed in section 2.4.2. indicated, however, that the incrustation most likely originates from heterogeneous nucleation of CaCO$_3$ on the cotton and is not predominantly determined by entrapment or adherence of CaCO$_3$ crystals formed in solution.

2.4.4. Experiments with the PAA-PVS (co)polymers from table 2.5.

The generic formulae of the PAA-PVS (co)polymers are given in table 2.5. Fig.2.5 gives the effect of these additives on the incrustation and on the mean residual Ca$^{2+}$-concentration in the filtrate of all crystallization procedures. Fig.2.5 shows a reduction of the residual Ca$^{2+}$ concentration when the percentage of PVS in the (co)polymer increases. As before, a high residual Ca$^{2+}$ concentration points at the occurrence of growth inhibition.

The (co)polymers which contain more than 20 % PVS all diminish the incrustation compared to the type 1 blank experiment (see section 2.4.3). The reduction of the incrustation becomes significant when a PAA-PVS (co)polymer has more than 50 % PVS groups in the structure. Above this percentage no clear correlation exists between the PVS content of the (co)polymer and the incrustation.
Figure 2.5  The influence of the PAA-PVS (co)polymers on the incrustation of cotton and on the residual $\text{Ca}^{2+}$ concentration.

The lowest incrustation for the PAA-PVS series is about equal to the incrustation observed in type 1 experiments in the presence of the three PSS containing (co)polymers in section 2.4.3. So, the addition of PVS or PSS containing polyelectrolytes leads to a decrease of the incrustation.

Table 2.8 shows the influence of the PAA-PVS (co)polymers on the modification of the precipitated $\text{CaCO}_3$. In the blank experiments the product was either predominantly calcite or vaterite. PAA stimulates the formation of calcite, whereas the PVS containing polyelectrolytes promote the precipitation of vaterite. The three PSS containing polyelectrolytes in section 2.4.3 also prompted the precipitation of vaterite (see table 2.7).


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Table 2.3  Influence of the PAA-PVS (co)polymers from table 2.5 on the modification of the precipitated CaCO$_3$.

<table>
<thead>
<tr>
<th>Additive</th>
<th>% Calcite</th>
<th>% Vaterite</th>
<th>% Aragonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>15 - 90</td>
<td>5 - 85</td>
<td>1 - 5</td>
</tr>
<tr>
<td>PAA</td>
<td>99</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>PAA-PVS 1</td>
<td>5</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>PAA-PVS 2</td>
<td>5</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>PAA-PVS 3</td>
<td>5</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>PAA-PVS 4</td>
<td>5</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>PVS</td>
<td>15</td>
<td>85</td>
<td>0</td>
</tr>
</tbody>
</table>

Apart from the importance of the adsorption of the polyelectrolytes onto cotton, only little attention has been paid yet to the mechanism(s) by which the polyelectrolytes affect the incrustation. This subject and the possible influence of the additives on the preferential development of either the metastable or the stable phase will be treated in the following section.

2.5. Potential mechanisms behind the effects of the polyelectrolytes on the incrustation

2.5.1 Scanning electron micrographs

On the basis of the SEM photographs discussed in section 2.4.2 the main cause of the severe incrustation in soda-based detergents was supposed to be heterogeneous nucleation of CaCO$_3$ on cotton. The entrapment by the textile fibres of CaCO$_3$ crystals previously formed in solution seems to be of minor importance for the incrustation.

Considering heterogeneous nucleation followed by growth to be the most acceptable explanation for the cause of the incrustation, it will now be
discussed how the polyelectrolytes can affect the degree of incrustation. The polyelectrolytes can be divided into two groups on the basis of their effect on the incrustation.

2.5.2 The first group: PAA and PMA-PAMPS

PAA and PMA-PAMPS do not significantly diminish the incrustation, with or without pretreatment of cotton. Both additives even lead to an increase of the incrustation in type 4 experiments compared to the blank. For PAA this effect was also noticed in type 1 experiments, while the incrustation with PMA-PAMPS was comparable to the blank. Both additives cause growth inhibition. The fact that the formation of calcite is promoted in the presence of PAA indicates that this additive especially inhibits the growth and/or nucleation of vaterite. Growth inhibition causes a relatively slow decrease of the supersaturation which extends the period of nucleation and heterogeneous nucleation on the fibres is apparently more favoured than nucleation in solution. Although the growth of these nuclei on the fibres is retarded by the growth inhibitor, their total surface area which is available for growth finally manages to consume sufficient supersaturation to cause considerable incrustation.

Apart from this mechanism, especially PAA and to a lesser extend PMA-PAMPS could act as coupling agents between cotton and CaCO₃ crystals since they are able to adsorb on both substrates. In chapter 5 the adsorption behaviour of the polyelectrolytes from table 2.4 on calcite and cotton and their effect on the zeta potential will be given. Calcite was chosen as a substrate in these experiments because the other CaCO₃ polymorphs were not available with the specific surface area and particle size distribution required in these experiments and because the transformation of the
CHAPTER 2

metastable phases into calcite could not be prevented during especially the adsorption experiments which lasted at least 24 hours. Since the adsorption experiments revealed that PAA and PMA-PAMPS adsorb on CaCO₃ as well as on cotton, the additives could act as coupling agents through attachment of free tails of polyelectrolyte molecules, adsorbed on one substrate onto the other. The relatively high incrustation levels could in this case be explained by the improved adherence of CaCO₃ particles to the cotton fibres by polymer bridging between the two substrates. Such a mechanism can also explain that the incrustation in the type 2 experiment in the presence of PAA is lower than in the type 1 experiment. During pretreatment PAA has enough time to adsorb with less dangling tails than during a crystallization cycle. Therefore PAA is no longer supposed to act as a coupling agent between cotton and CaCO₃ in the type 2 experiment.

It should be noted that the two mechanisms explaining the effects of PAA and PMA-PAMPS on the incrustation are connected with the two possible causes for the incrustation. Growth inhibition is related to the case that the incrustation mainly originates from heterogeneous nucleation of CaCO₃ on cotton. The bridging agent mechanism applies to the case that entrapment by or adherence to the fibres of CaCO₃ particles formed in solution is the major contribution to the incrustation. As said before, this last cause of incrustation was judged to be of minor importance making the bridging mechanism less likely, although it can not be fully rejected.

An increase of the incrustation in the presence of PAA was also reported by Hudson et al. [6]. They postulated that PAA slows down the precipitation in the solution but not on the cotton surface. The above given mechanisms seem to be more likely, because it is not clear why the growth of CaCO₃ on the textile will not be affected by the additive.
2.5.3 The second group: the PSS and PVS containing polyelectrolytes

The polystyrene sulfonic acid containing compounds in table 2.4 form the second group. PMA-PSS, PMAA-PSS and PSS diminish the incrustation significantly in type 1 and type 2 experiments. No indications for growth inhibition were observed. It will be shown in chapter 5 that PMA-PSS, PMAA-PSS and PSS do not adsorb on cotton, while PMAA-PSS also does not adsorb on CaCO₃.

Adsorption of PMA-PSS and PSS on CaCO₃ alone can already cause sterical hindrance for a close approach of CaCO₃ particles towards the cotton surface or electrostatic repulsion between cotton and CaCO₃ particles. These additives could thus act as dispersing agents, as they prevent the aggregation of the CaCO₃ crystals with the cotton fibres.

A dispersing mechanism is not likely for PMAA-PSS, which adsorbs neither on CaCO₃ nor on cotton. Another mechanism through an influence on the nucleation behaviour of CaCO₃ in solution might explain the observed effect of PMAA-PSS as well as of the other PSS and PVS containing polyelectrolytes on the incrustation. Dalas et al. observed that solid sulfonated polystyrene and sulfonated polystyrene divinylbenzene polyelectrolytes with a high specific surface area are strong adsorbents for Ca²⁺-ions [21]. These sulfonated polyelectrolytes were suitable substrates for the growth of CaCO₃. Addadi et al. proposed that sulfonates and carboxylates cooperate in the oriented nucleation of CaCO₃ in biomineralization [22]. Sulfonates, bound to polystyrene films, should concentrate calcium ions creating the supersaturation necessary for nucleation on structured carboxylate domains. Indications were given that Ca²⁺-ions are preferentially bound on a more than one-to-one basis to sulfonate groups [23]. All these observations concern experiments with solid substrates.
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The Ca\(^{2+}\) concentration in the neighbourhood of a sulfonate containing polyelectrolyte chain in solution will be higher than in the bulk, provided that Ca\(^{2+}\)-ions also have a strong affinity for sulfonate groups bound to dissolved polyelectrolyte chains. This makes it relatively easier to form nuclei in the neighbourhood of the polyelectrolytes than in the bulk of the solution. In this model sulfonate groups act as active sites, and accordingly the at this high pH value stretched polyelectrolyte chains act as templates for the nucleation of CaCO\(_3\). Such a general mechanism explaining the influence of all sulfonic acid containing polyelectrolytes on the incrustation is more logical than the dispersing agent mechanism which only applies to part of these compounds. In the template mechanism, nucleation in solution is favoured at the cost of the heterogeneous nucleation of CaCO\(_3\) on cotton, resulting in a lower incrustation.

The observations that PSS and PVS containing polyelectrolytes promote the development of the metastable polymorph vaterite sustains their proposed effect on the nucleation. As said in section 2.2, the formation of a metastable phase can by favoured by additives which stimulate the precipitation kinetics of this phase. The alternative mechanism in which the additives retard the growth of the stable polymorph is less likely here because the residual Ca\(^{2+}\) concentrations do not point at inhibition.

2.5.4. Structural matching between the additives and calcium carbonate

Geometric matching is often presumed to play a role in the effect of additives on the nucleation and growth kinetics. The investigated series of PAA-PVS (co)polymers provide a possibility to test the importance of structural matching for nucleation. The distance between the functional SO\(_3\) groups in PVS has been deduced to be 5 Å from a structural model of this
PRECIPITATION IN DETERGENT PERFORMANCE: PART I

compound [24]. In both the thermodynamically favoured polymorph calcite and the metastable polymorph vaterite the calcium and carbonate ions are arranged in alternate layers perpendicular to the threefold axis. All calcium ions in one layer are arranged at the corners of equilateral triangles having sites of 4.98 Å for calcite and 4.2 Å for vaterite [16,24]. From structural matching the formation of calcite is expected more than that of vaterite. Geometric matching thus seems to be of secondary importance for the investigated system.

Although the presence of sulfonic acid groups in a polyelectrolyte is essential for the stimulation of the nucleation by the template mechanism, the chemical surrounding of these groups in the polyelectrolyte chain also plays a role. This is illustrated by the negative results of PMA-PAMPS, where the sulfonic acid groups are bound to acrylamido methyl propane groups. In the other more effective sulfonate containing polyelectrolytes the sulfonate groups are bound to either styrene or vinyl groups. A second already discussed parameter seems to be the ratio between carboxylate and sulfonate groups in a copolymer. A significant reduction of the incrustation of cotton was only obtained with PAA-PVS (co)polymer containing more than 50 percent PVS.

The fact that additives are able to favour the nucleation of slightly soluble salts was also reported by Sarig et al. [25,26]. They observed that the precipitation of calcium oxalate was enhanced by low concentrations of glutamic acid. Furthermore Boyce [27] reported the initiation of calcium oxalate precipitation in kidney stone formation by a complex organic matrix, mostly composed of proteins.

A good structural matching between the additive and the precipitating salt is also believed to be one of the important factors for the retarding efficiency of the additive [24]. As mentioned before, the distance between the
CHAPTER 2

functional groups in PVS is about 5 Å. For PAA the distance between two adjacent carboxylic groups has been reported to be 3.0 Å [28]. For both PVS and PAA a small variance around the reported values can be tolerated due to the flexibility of the polyelectrolyte chain. From these distances and the above given Ca-Ca distances in calcite and vaterite PVS is expected to be a better growth retarder for both calcite and vaterite than PAA. The measured residual Ca$^{2+}$ concentrations shown in fig.2.5, however, point at a reverse trend: the highest residual Ca$^{2+}$ concentrations, indicating the best growth inhibition, are observed for the (co)polymers with a high percentage of PAA in the structure. According to our data PVS does not inhibit the growth of CaCO$_3$. Sarig et al. have reported that the precipitation of calcite is not affected by the addition of 5 ppm PVS [20], which is in good agreement with our findings. Apparently, structural matching is not the determining factor for explaining the retarding efficiency of the investigated type of copolymers.

The effect of some polymeric additives on the nucleation and growth of calcium carbonate in solution will be treated qualitatively in chapter 4 on the basis of their impact on the development of the particle size distribution in batch precipitation experiments. Furthermore it will be shown in chapter 8 how a combined analysis of induction time measurements in seeded and unseeded precipitation can provide quantitative information about the separate effect of polyelectrolytes on the nucleation and growth rates of vaterite.

It should be noted that the investigated combination of soda and the polyelectrolytes is just a very simple formulation of a soda-based detergent. It is therefore interesting to know whether the effects of the polyelectrolytes on the incrustation are still noticeable when this formulation is extended with some other frequently used components of soda-based detergents. This will be the subject of chapter 3 where the presently used formulation was extended with an anionic surfactant and/or a filler.
2.6. Conclusions

The incrustation in soda-based detergents is mainly caused by heterogeneous nucleation of CaCO₃ on cotton. Entrapment by the textile fibres of CaCO₃ crystals formed in solution seems to play only a minor role.

Table 2.9 summarizes the observed influence of the polyelectrolytes from table 2.4 on the incrustation and the related potential mechanisms.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Incrustation</th>
<th>Potential mechanism(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA</td>
<td>Higher</td>
<td>Growth inhibitor or coupling agent</td>
</tr>
<tr>
<td>PMA-PAMPS</td>
<td>Equal</td>
<td>Growth inhibitor or coupling agent</td>
</tr>
<tr>
<td>PMA-PSS</td>
<td>Lower</td>
<td>Nucleation stimulation or dispersing agent</td>
</tr>
<tr>
<td>PMAAA-PSS</td>
<td>Lower</td>
<td>Nucleation stimulation</td>
</tr>
<tr>
<td>PSS</td>
<td>Lower</td>
<td>Nucleation stimulation or dispersing agent</td>
</tr>
</tbody>
</table>

PAA and PMA-PAMPS inhibit the growth of CaCO₃, which results in a relatively slow decrease of the supersaturation. This increases the extent of nucleation on the fibres and could lead to a higher incrustation, when this phenomenon mainly arises from heterogeneous nucleation on cotton. A second option is that PAA and PMA-PAMPS, which adsorb on the cotton as well as on the CaCO₃ crystals, act as a coupling agents between the two, thus improving the adherence of CaCO₃ particles to the cotton fibres.

The PSS containing additives, which do not adsorb on cotton, could stimulate the nucleation in solution at the cost of the heterogeneous nucleation of CaCO₃ on cotton, resulting in a lower incrustation. PMA-PSS and PSS could prohibit the entrapment of CaCO₃ by the cotton fibres when their adsorption on CaCO₃ leads to extra sterical hindrance or electrostatic
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repulsion. This option is less likely than the nucleation stimulation because it only affects the adherence of CaCO₃ particles to the fibres, while other results indicate that entrapment is not the major cause of incrustation. Furthermore PMAA-PSS does not adsorb on CaCO₃ but had similar effects as PMA-PSS and PSS on the incrustation.

The PVS containing (co)polymers of the PAA-PVS series which contain more than 20 percent PVS groups reduced the incrustation. The reduction becomes significant when the (co)polymer has more than 50 percent PVS groups in the structure. The results of these additives are comparable to the PSS containing polyelectrolytes. It is thus likely that the PVS containing polyelectrolytes also stimulate the nucleation of CaCO₃ in solution.

The preferential formation of the metastable polymorph vaterite in the presence of the PVS and PSS containing polyelectrolytes is in good agreement with the proposed effect of these additives on the nucleation.

Sulfonic acid containing polyelectrolytes seem to be promising co-builders for soda-based detergents, also at elevated washing temperatures. The ratio between sulfonates and other monomers in the (co)polymer and the chemical structure of the sulfonic acid containing monomer are, however, important variables for their influence on the incrustation.

Acknowledgements

The authors are indebted to Household and Personal Care Research B.V., the Hague (The Netherlands), for financial support. The authors wish to thank E.G.P. Cornelissens and J. Pronk for stimulating discussions, and D. Stajcer, L. Maass, R. Nijhuis, M. Laldjising, W.F. Boeken and G. Demian for experimental assistance and analyses.
References

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PRECIPITATION IN DETERGENT PERFORMANCE
PART II: INFLUENCE OF AN ANIONIC SURFACTANT
AND A FILLER ON THE INCRUSTATION

Abstract

In chapter 2 various polyelectrolytes have been combined with sodium carbonate as a simple model for a soda-based detergent. The specific effects of the polyelectrolytes on the deposition of calcium carbonate (CaCO$_3$) on cotton, also called incrustation, have been determined.

In this chapter these simple detergent formulations have been extended systematically with an anionic surfactant and a filler material.

In the presence of the filler material, which was sodium sulfate (Na$_2$SO$_4$), a general increase of the incrustation was noticed compared to the simple system described in chapter 2. No difference is observed in the specific effects of the polyelectrolytes on the incrustation.

Addition of the anionic surfactant sodium dodecyl benzene sulfonate (SDBS) to the soda-polyelectrolyte combination resulted into a lower incrustation compared to the simple formulation. A more than average decrease of the incrustation was observed for those polyelectrolytes which were the least effective anti-incrustation agents in the most simple formulation.

Finally, the combination of soda with both SDBS, Na$_2$SO$_4$ and the polyelectrolytes revealed incrustation levels which are not significantly different from the formulation consisting of soda, SDBS and the polyelectrolytes. So the effect of SDBS on the incrustation prevails over that of Na$_2$SO$_4$.

The underlying mechanisms explaining the effects of Na$_2$SO$_4$ and SDBS on the incrustation will be proposed and related to the specific influences of the polyelectrolytes on the incrustation.
PREFCIPITATION IN DETERGENT PERFORMANCE: PART II.

3.1. Introduction

Detergent builders play a central role in the course of the washing process. Their function is largely that of supporting detergent action and of eliminating calcium and magnesium ions, which originate partly from the tap water and sometimes from soil and fabrics.

In chapter 2 soda was used as a builder and it was shown that the resulting precipitation of CaCO₃ leads to a troublesome deposition of CaCO₃ on the textile. Another name for this deposition is incrustation and this process is a major disadvantage of soda-based detergents. Low amounts of polyelectrolytes are therefore frequently added as co-builder in such detergents. The main task of a co-builder is to reduce the incrustation. The effect of combinations of soda with various polyelectrolytes on the degree of incrustation of cotton were determined in the previous chapter. It was found that polystyrene sulfonic acid (PSS) containing polyelectrolytes diminish the incrustation compared to the system without co-builder. (Co)polymers of polyacrylic and polyvinylsulfonic acid (PAA-PVS) also reduce the incrustation when the (co)polymer contains more than fifty percent vinyl sulfonic acid groups. The use of polyacrylic acid (PAA) as co-builder leads to an increased incrustation, while a copolymer of polymaleic acid and polyacrylamido methyl propane sulfonic acid (PMA-PAMPS) hardly affects the incrustation. The potential mechanisms causing the above effects of the polyelectrolytes on the incrustation were discussed in section 2.5.

As already mentioned in chapter 2, the combination of soda and a polymeric co-builder is in fact a too simple formulation for a soda-based detergent. This is exemplified by the general formulation of a European powdered detergent which is shown in table 3.1.

Other commonly used ingredients of powdered detergents, which are not
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Table 3.1  General formulation for an European powdered detergent [1].

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Composition</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactants</td>
<td>5 - 10 %</td>
<td>alkylbenzenesulfonates</td>
</tr>
<tr>
<td>Nonionic surfactants</td>
<td>3 - 6 %</td>
<td>alkyl poly(ethylene glycol) ethers</td>
</tr>
<tr>
<td>Builders</td>
<td>20 - 35 %</td>
<td>soda, zeolites</td>
</tr>
<tr>
<td>Co-builders</td>
<td>0 - 2 %</td>
<td>polyacrylates</td>
</tr>
<tr>
<td>Anticorrosion agents</td>
<td>5 - 12 %</td>
<td>sodium silicate</td>
</tr>
<tr>
<td>Optical brighteners</td>
<td>0.1 - 0.75 %</td>
<td>stilbenedisulfonic acid</td>
</tr>
<tr>
<td>Bleaching agents</td>
<td>15 - 30 %</td>
<td>sodium perborate</td>
</tr>
<tr>
<td>Enzymes</td>
<td>0 - 0.75 %</td>
<td>proteases, amylases</td>
</tr>
<tr>
<td>Fillers</td>
<td>5 - 45 %</td>
<td>sodium sulfate</td>
</tr>
</tbody>
</table>

included in the table, are: foam boosters (ethanolamides), foam depressants (silicones), anti-redeposition agents (sodium carboxymethyl cellulose), fabric softeners (quats and clays) and perfumes. It is thus clear that a detergent usually contains many other ingredients next to the builder and the co-builder. It was thus decided to extend the simple formulations investigated in chapter 2 with two other detergent components, namely a commonly used anionic surfactant and a filler material.

Surfactants play the essential role in the removal of soil from the textile. Modern detergents generally contain larger amounts of anionic than nonionic surfactants. For the anionic surfactant sodium dodecyl benzene sulfonate (SDBS) was selected. Furthermore, powdered detergents often contain large amounts of fillers to improve the flowability and to reduce the caking of the product. The most frequently used filler material in detergents is sodium sulfate ($\text{Na}_2\text{SO}_4$). There is, however, that it is a modern trend to formulate high density detergents without a filler.

In chapter 2 it was demonstrated that (co)polymers containing either PVS or PSS groups had similar effects on the incrustation and that these
PRECIPI TATION IN DETERGENT PERFORMANCE: PART II.

effects resulted from the same mechanism. It was therefore decided to use only the PSS containing polyelectrolytes as well as PAA and PMA-PAMPS as co-builders in the extended detergent formulations studied in this chapter.

The first objective of this chapter is to investigate whether other detergent components such as a surfactant and/or a filler affect the CaCO$_3$ incrustation. The second aim is to find out whether the effects of the polyelectrolytes on the incrustation of cotton, as observed in chapter 2, are still noticeable when the detergent formulation is extended with the anionic surfactant SDBS and/or the filler Na$_2$SO$_4$.

3.2. Experimental

AR grade chemicals, doubly distilled water and standard cotton for incrustation tests from TNO Delft were used in all experiments.

Adsorption of the anionic surfactant SDBS on cotton and/or CaCO$_3$ can in principle affect the incrustation. For this reason, adsorption isotherms of SDBS on CaCO$_3$ and cotton were determined by a depletion method. Calcium carbonate crystals (1.0 g, calcite with a specific surface area of 0.5 m$^2$/g) or a piece of cotton (0.5 g) were suspended in 50 ml of a solution with a known initial SDBS concentration, which was varied between 0.1 and 1.0 g/dm$^3$. The pH of the solutions was brought at a value of 10.0 and the samples were shaken in a thermostated waterbath at 25.0°C. The residual SDBS concentration after 24 hours was determined by means of UV derivative spectroscopy. SDBS has a characteristic absorbance pattern between 245 and 275 nm. The second derivative of this UV spectrum shows a maximum at 261 nm and a minimum at 265 nm and the difference in height between these extremes depends linearly on the SDBS concentration in the sample.

The equipment for the so-called incrustation experiments is shown in
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fig.2.1 of chapter 2. An incrustation experiment consists of three alternating crystallization and rinsing procedures. The experimental procedure, apart from the composition of the soda solution, is equal to the type 1 incrustation experiments in the previous chapter (see table 2.2). All experiments were started with a crystallization cycle by mixing 0.5 dm$^3$ 1.07x$10^{-2}$ M CaCl$_2$ with 0.5 dm$^3$ of a soda containing detergent solution in the presence of a cotton sheet. The first solution simulates tap water resulting in an initial water hardness in the reactor of 535 ppm as CaCO$_3$. The average hardness of European tap water is 250 ppm, but a higher value was chosen to include hardness arising from soil and fabrics.

Table 3.2 gives some brief information about the polyelectrolytes which are used as co-builder in the experiments with SDBS and Na$_2$SO$_4$. The generic formulae of these polyelectrolytes were shown in table 2.4.

The Na$_2$CO$_3$ and NaHCO$_3$ concentrations in the detergent solution before mixing were for all four types of experiments 2.27x$10^{-2}$ M and 3.39x$10^{-2}$ M, respectively. Except for the blanks a co-builder dosage of 100 ppm in the detergent solution was applied in all experiments. The polyelectrolytes selected as co-builders are listed in table 3.2 with their further used abbreviations and their molecular weights. In type B and type C experiments respectively 4.22x$10^{-2}$ M Na$_2$SO$_4$ and 1.43x$10^{-3}$ M SDBS were added to the detergent solution, while in type D experiments both Na$_2$SO$_4$ and SDBS were added (see table 3.3). The concentrations of the Na$_2$SO$_4$ and SDBS ingredients in these type 2D experiments are consistent with the average dosage of powdered detergents in Europe of 10 g/dm$^3$, and with an average detergent formulation of 30% builder, 0.5% co-builder, 5% anionic surfactant and 30% filler. Other ingredients, as e.g. bleaches, were not added to the formulation.
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Table 3.2  *The polyelectrolytes used as co-builders in the incrustation experiments with SDBS and Na₂SO₄. The generic formulae were shown in table 2.4.*

<table>
<thead>
<tr>
<th>Name of (co)polymer</th>
<th>Abbreviation</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyacrylic acid</td>
<td>PAA</td>
<td>5000</td>
</tr>
<tr>
<td>polymaleic acid - polycrylamido methyl propane sulfonic acid</td>
<td>PMA-PAMPS</td>
<td>7500</td>
</tr>
<tr>
<td>polymaleic acid - polystyrene sulfonic acid</td>
<td>PMA-PSS</td>
<td>13000</td>
</tr>
<tr>
<td>polymethacrylic acid - polystyrene sulfonic acid</td>
<td>PMAA-PSS</td>
<td>4310</td>
</tr>
<tr>
<td>polystyrene sulfonic acid</td>
<td>PSS</td>
<td>70000</td>
</tr>
</tbody>
</table>

Table 3.3  *Composition of the detergent solutions (before mixing) in the different experiments with SDBS and Na₂SO₄. The CaCl₂ concentration before mixing was always 1.07x10⁻² M.***

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Na₂CO₃ (g/dm³)</th>
<th>NaHCO₃ (g/dm³)</th>
<th>Na₂SO₄ (g/dm³)</th>
<th>SDBS (g/dm³)</th>
<th>polymer (mg/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>type A</td>
<td>2.4166</td>
<td>2.8560</td>
<td>0.0000</td>
<td>0.0000</td>
<td>100 *</td>
</tr>
<tr>
<td>type B</td>
<td>2.4166</td>
<td>2.8560</td>
<td>6.0000</td>
<td>0.0000</td>
<td>100 *</td>
</tr>
<tr>
<td>type C</td>
<td>2.4166</td>
<td>2.8560</td>
<td>0.0000</td>
<td>1.0000</td>
<td>100 *</td>
</tr>
<tr>
<td>type D</td>
<td>2.4166</td>
<td>2.8560</td>
<td>6.0000</td>
<td>1.0000</td>
<td>100 *</td>
</tr>
</tbody>
</table>

* In case of the blank experiments this concentration is zero.

The composition of the so-called detergent solution was varied systematically and its ingredient concentrations in the different experiments are given in table 3.3. The three crystallization procedures of each experiment were started by mixing of the CaCl₂ and the detergent solutions, almost instantaneously followed by the precipitation of CaCO₃, since the reactor contained a highly supersaturated CaCO₃ solution. After 30 minutes the resulting suspension was removed from the reactor and filtered. The
experiment was continued by filling the reactor with 1 dm$^3$ water. The aim of this so-called rinsing procedure, which also lasted 30 minutes, was to remove the CaCO$_3$ particles which were not tightly attached to the cotton. This procedure of crystallization followed by rinsing was repeated three times.

The residual Ca$^{2+}$ concentration in the filtrate of each crystallization procedure was measured with an inductively coupled plasma technique (Perkin Elmer Plasma 2 Spectrometer).

Infra red spectra were obtained of KBr tablets containing part of the crystals separated from the suspension after each crystallization procedure.

At the end of each incrustation experiment the cotton was dried and weighed. The cotton was then immersed in a 6% HCl-solution, thus dissolving the deposited CaCO$_3$. Measuring of the Ca$^{2+}$ concentration in this solution allowed calculation of the incrustation, expressed in mg CaCO$_3$ deposited per g cotton. In all cases the incrustation was determined from duplicate experiments.

3.3 Results

3.3.1 The supersaturation

The supersaturation S is defined as $[(\text{Ca}^{2+})(\text{CO}_3^{2-})/K_{\text{sol}}]^{1/2}$, where (Ca$^{2+}$) and (CO$_3^{2-}$) are activities of the free ions and $K_{\text{sol}}$ is the thermodynamic solubility product. The considered equilibria and the related values of the thermodynamic constants are summarized in table 3.4. This table gives the solubility products of both the thermodynamically stable polymorph calcite and of the metastable phase vaterite, since the X-ray diffraction analysis in chapter 2 showed that these CaCO$_3$ modifications were dominantly formed.
Table 3.4  Calcium carbonate equilibria and the corresponding equilibrium constants $K$ at 50°C.

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>$K$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$</td>
<td>$5.4739 \times 10^{-14}$ mole$^2$ dm$^{-6}$</td>
<td>[3]</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{HCO}_3^- = \text{H}_2\text{CO}_3^+$</td>
<td>$1.9305 \times 10^6$ dm$^3$ mole$^{-1}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$</td>
<td>$1.4961 \times 10^{10}$ dm$^3$ mole$^{-1}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3^0$</td>
<td>3235 dm$^3$ mole$^{-1}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+$</td>
<td>16.10 dm$^3$ mole$^{-1}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{OH}^- = \text{CaOH}^+$</td>
<td>199.5 dm$^3$ mole$^{-1}$</td>
<td>[5]</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4^0$</td>
<td>302 dm$^3$ mole$^{-1}$</td>
<td>[6]</td>
</tr>
<tr>
<td>$\text{CaCO}_3$ (calcite) $= \text{Ca}^{2+} + \text{CO}_3^{2-}$</td>
<td>$2.1806 \times 10^9$ mole$^2$ dm$^{-6}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$\text{CaCO}_3$ (vaterite) $= \text{Ca}^{2+} + \text{CO}_3^{2-}$</td>
<td>$6.9597 \times 10^9$ mole$^2$ dm$^{-6}$</td>
<td>[4]</td>
</tr>
</tbody>
</table>

Activity coefficients were calculated by the modified Debye-Hückel equation proposed by Davies (e.g.[2]). The complexes formed in solution were computed from the concentrations given in table 3.3 and mass- and charge-balance equations by iterative approximations of the ionic strength [2].

The thus-calculated supersaturation $S$ at the start of the crystallization procedures was 25.8 for the type A and type C experiments, and 23.9 for the type B and type D experiments related to the precipitation of calcite. For the formation of vaterite $S$ was 14.4 (type A and C), and 13.4 (type B and D).

3.3.2. Adsorption of SDBS on CaCO₃ and cotton

The adsorption isotherms of the anionic surfactant SDBS on both CaCO₃ and cotton are presented in fig.3.1 by plotting the amount of SDBS adsorbed (in mg/g substrate) versus the equilibrium concentration of SDBS in solution (in g/dm$^3$). Calcite was selected as CaCO₃ polymorph because no vaterite crystals were available with a sufficiently high specific surface area and because a transformation of vaterite into calcite was expected during the adsorption experiments.
Figure 3.1 Adsorption isotherms of SDBS on CaCO$_3$ and cotton.

Over the whole investigated SDBS concentration range the adsorption on cotton is higher than that on CaCO$_3$. The observed adsorption of SDBS on both cotton and CaCO$_3$ can in principle influence the incrustation by causing sterical hindrance for a close approach of the CaCO$_3$ crystals to the cotton or by increasing the electrostatic repulsion between the substrates.

3.3.3 Influence of SDBS and Na$_2$SO$_4$ on the incrustation of cotton

Fig.3.2 shows the effect of the co-builders on the incrustation of cotton in the presence and absence of SDBS and/or Na$_2$SO$_4$. Fig.3.3 shows their influence on the residual Ca$^{2+}$ concentration at the end of the crystallization procedures. The given values are the mean of all measured concentrations.
Figure 3.2  The incrustation of cotton in the different types of experiments with the detergent formulations from table 3.3.

Figure 3.3  The residual Ca^{2+} concentration in the filtrate of the crystallization procedures of the incrustation experiments.
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Type A experiments

In type A experiments the detergent solution is a combination of only the Na₂CO₃-NaHCO₃ builder system and, except for the blank experiment, one of the polyelectrolytes as a co-builder.

This is the most simple detergent formulation and the results of such systems have been discussed extensively as the type 1 incrustation experiments in chapter 2. A short summary of these results will be included here to facilitate the comparison with the more extended formulations in this section.

From the results of the incrustation experiments of chapter 2 it was concluded that incrustation of cotton mainly originates from heterogeneous nucleation of CaCO₃ on the rough cotton surface. The entrapment of CaCO₃ crystals, which were previously formed in solution, between the cotton fibres is of minor importance for the incrustation. The following results and potential mechanisms explaining the effects of the different polymeric co-builders on the incrustation were given in chapter 2.

PAA increases the incrustation compared to the blank experiment without co-builder, while PMA-PAMPS hardly affects the incrustation. From the relatively high residual Ca²⁺ concentrations it was concluded that both co-builders inhibit the growth of CaCO₃. Growth inhibition retards the deposition of CaCO₃ on the fibres. It also prolongs, however, the period of high supersaturation, thus promoting heterogeneous nucleation of CaCO₃ on the cotton surface. If this second effect dominates the deposition rate, by increasing the crystal surface available for growth, the incrustation can be increased in spite of the lower growth rate. This is apparently the case for PAA. Although the contribution of entrapment of crystals to the total incrustation is thought to be minor, this effect could become more important in the presence of PAA and PMA-PAMPS. Both co-builders can adsorb on
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CaCO₃ as well as on the cotton and a dispersing action is thus expected. This effect can, however, be counteracted, if the co-builders more act as coupling or bridging agents between the two substrates. Which action prevails is hard to decide from the available information.

The three PSS containing polyelectrolytes reduced the incrustation. This effect was attributed to a stimulation of the nucleation in solution at the cost of the heterogeneous nucleation on cotton. The presence of the sulfonic acid groups in the polymer was considered to be essential for this mechanism. Another, less likely, mechanism is that some of the PSS containing polymers which only adsorb on CaCO₃ crystals inhibit the entrapment of such crystals between the cotton fibres when their adsorption leads to sterical hindrance or to electrostatic repulsion of the crystals by the negatively charged cotton.

Type B experiments

The detergent solution in these experiments contained the Na₂CO₃-NaHCO₃ builder system, Na₂SO₄ as filler and , except for the blank experiment, one of the polymeric co-builders.

The degree of incrustation in the presence of Na₂SO₄ is in general higher than in the related type A experiments, but the effects of the polymeric co-builders on the incrustation follow the trends observed in the type A experiments. The addition of PAA again increases the incrustation compared to the type B blank experiment, PMA-PAMPS hardly affects the incrustation and, again, only in the presence of the PSS containing polyelectrolytes a significant reduction of the incrustation was observed. PMA-PSS is the only polyelectrolyte for which the degree of incrustation remains equal to that in the type A experiments in the absence of Na₂SO₄.

The extension of the detergent formulation with Na₂SO₄ leads to a
higher ionic strength in the reactor at the start of the crystallization procedures. Consequently the solubility of CaCO$_3$ increases, leading to a lower initial supersaturation than in the type A experiments, as was already shown by the calculations in section 3.3.1. This lower supersaturation will result in lower nucleation and growth rates of CaCO$_3$. Furthermore, it can be expected that at the lower supersaturation the relative contribution of heterogeneous nucleation increases at the cost of homogeneous nucleation, because this last process has a higher critical supersaturation limit than heterogeneous nucleation. It was discussed in chapter 2 that heterogeneous nucleation is the most probable origin of the incrustation. The higher incrustation levels in the type B experiments can thus be due to a relative increase of the heterogeneous nucleation of CaCO$_3$ on the cotton as a consequence of the effect of Na$_2$SO$_4$ on the supersaturation.

The highest residual Ca$^{2+}$ concentrations in the filtrate of the type B incrustation experiments are observed in the presence of PAA and PMA-PAMPS. These concentrations are also considerably higher than in the type A experiments with these co-builders. The higher residual Ca$^{2+}$ concentrations point at the occurrence of growth inhibition of CaCO$_3$ by PAA and PMA-PAMPS. The inhibiting effect of these additives seems to be stronger in the presence of Na$_2$SO$_4$. It is known that a growth inhibitor can become more effective at decreasing supersaturation (see e.g.[7]). This implies that the apparently better inhibition of PAA and PMA-PAMPS in the type B experiments can well be explained by the effect of Na$_2$SO$_4$ on the initial supersaturation. In the presence of the other polyelectrolytes the residual Ca$^{2+}$ concentrations were close to the value for the blank and they are comparable to the values obtained in the type A experiments. So no indications are present for the occurrence of growth inhibition by the PSS containing polyelectrolytes.
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The influence of the filler material on the incrustation and the residual Ca\textsuperscript{2+} concentration was related to its effect on the initial supersaturation, which has consequences for the nucleation and growth of CaCO\textsubscript{3}. But the addition of Na\textsubscript{2}SO\textsubscript{4} can also affect the entrapment of CaCO\textsubscript{3} crystals, formed in solution, between the cotton fibres. On the basis of the zeta potential measurements of CaCO\textsubscript{3} and cotton, which will be treated in chapter 5, it can be expected that both the CaCO\textsubscript{3} crystals and the cotton surface are negatively charged at the relatively high pH value of 10.0 in the reactor. Since both surfaces are negative, the entrapment of CaCO\textsubscript{3} crystals between the cotton fibres will be hindered by electrostatic repulsion. The extra Na\textsuperscript{+} ions from Na\textsubscript{2}SO\textsubscript{4} can screen part of the negative charge, as was e.g. shown for the effect of Na\textsubscript{2}SO\textsubscript{4} on the zeta potential of cotton in a SDBS solution [8]. A similar impact on the zeta potential of cotton was noticed when NaCl was added as background electrolyte [9]. It can thus be expected that the electrostatic repulsion between CaCO\textsubscript{3} and cotton will decrease in the presence of Na\textsubscript{2}SO\textsubscript{4}, making it relatively easier for CaCO\textsubscript{3} crystals to approach the fibres. The resulting increase of the amount of entrapped CaCO\textsubscript{3} crystals can provide another explanation for the observed effect of Na\textsubscript{2}SO\textsubscript{4} on the incrustation.

Type C experiments

The ingredients of the detergent solution in this type of experiments were the Na\textsubscript{2}CO\textsubscript{3}-NaHCO\textsubscript{3} builder system, the anionic surfactant sodium dodecyl benzene sulfonate (SDBS) and, except for the blank experiment, one of the polymeric co-builders.

Fig.3.2 shows that the incrustation in this type of experiments is in all cases lower than in the type A experiments, where the detergent solution only consisted of a combination of the builder system with one of the
CHAPTER 3

core-builders. So the extension of the detergent formulation with SDBS leads to a decrease of the incrustation. The adsorption of SDBS on both cotton and CaCO₃, which was shown in fig.3.1, might affect the incrustation. In the first place, the adsorption of SDBS on cotton can prevent part of the heterogeneous nucleation of CaCO₃ on the textile, which process was thought to give the largest contribution to the incrustation. Secondly, the C₁₂H₂₅ alkane chains of adsorbed SDBS molecules can cause steric hindrance for a close approach of the CaCO₃ crystals to the cotton. Such a mechanism will reduce the entrapment of CaCO₃ crystals between the cotton fibres.

The observed decrease of the incrustation can also be caused by the precipitation of Ca(DBS)₂. The precipitation of Ca(DBS)₂ in a 0.5 g/dm³ solution of SDBS was observed above a critical Ca²⁺ concentration of 10 ppm [10]. Taking into account the formation of the complexes given in table 3.4, the initial free Ca²⁺ concentration in the type C experiments is calculated to be 25 ppm. Precipitation of Ca(DBS)₂ can thus be expected under the given experimental conditions. The infra red spectra of the precipitate in the type C experiments indeed showed some extra peaks compared to the spectra of the experiments without SDBS. These peaks, which are indicated in fig.3.4, are presumably due to the precipitation of Ca(DBS)₂.

It must be noted that precipitation of Ca(DBS)₂ is an unwanted process because the resulting loss of surfactant reduces the efficiency of detergent action. In addition, the Ca(DBS)₂ precipitate may also cause incrustation on the textile [9]. In the presence of SDBS part of the supersaturation is consumed by the formation of Ca(DBS)₂ crystals and relatively less CaCO₃ is formed. If Ca(DBS)₂ has a lower affinity for cotton than CaCO₃, its chance to be deposited on or adhered to the cotton is lower than for CaCO₃, which may explain the overall observed reduction of the incrustation in the presence of SDBS. No experimental data neither from literature nor from our own work are, however, available to sustain or reject this assumption.
Figure 3.4 *Infra red spectra of the precipitate in the incrustation experiments in the absence and presence of SDBS.*

The type B experiments with Na$_2$SO$_4$ revealed higher incrustation values but the effects of the co-builders on the incrustation were similar to the trends found in the most simple formulation (type A experiments). In the presence of SDBS, however, the influence of some of the investigated polyelectrolytes on the incrustation is different from their behaviour in the formulation without SDBS. Until now, the use of PAA as co-builder always resulted in an increase of the incrustation compared to the blank experiment. In combination with SDBS a small reduction of the incrustation is observed, but compared to the other investigated co-builders the effect of PAA is still the lowest. The largest difference is observed in case of the addition of PMA-PAMPS, which hardly affected the incrustation in the previous types of experiments. In combination with SDBS, however, the
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incrustation is about similar to that for the PSS containing polyelectrolytes which were the most effective co-builders in chapter 2 and in the type A and type B experiments. As in the other experiments the PSS containing co-builders reduce the incrustation with about 50 percent compared to the type C blank experiment.

The use of PAA and PMA-PAMPS again leads to relatively high residual Ca\(^{2+}\) concentrations, but the difference compared to the blank and the other co-builders is smaller than in the first two types of experiments. Apparently, the retarding effect of PAA and PMA-PAMPS on the growth of CaCO\(_3\) and the related consequence for the incrustation are less pronounced in the presence of SDBS, which might be due to the dispersing action of SDBS.

Type D experiments

The detergent formulation in these experiments contained both the anionic surfactant and the filler material, next to the always present builder system. With the exception of the blank, one of the co-builders was also used.

The addition of the filler Na\(_2\)SO\(_4\) was studied in the type B experiments and resulted in an increase of the incrustation compared to the experiments with the most simple detergent formulation. The incrustation levels in the presence of the anionic surfactant SDBS were lower than in the related type A experiments, which served as reference. In the type D experiments, where the detergent solution contains SDBS as well as Na\(_2\)SO\(_4\), the values for the incrustation and the residual Ca\(^{2+}\) concentration are of the same order of magnitude as in the presence of solely SDBS (type C experiments), and thus lower than in the simple formulations. This implies that the effect of SDBS on the precipitation of CaCO\(_3\) and the resulting incrustation overrules the influence of Na\(_2\)SO\(_4\). It has been reported that detergent components as sodium silicate, sodium sulfate, nonionic surfactants and anionic surfactants do not influence the degree of incrustation in soda-based detergents [11].

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This is in contradiction with the results of the experiments in this chapter, which unequivocally point at a direct effect of both Na₂SO₄ and SDBS on the incrustation.

The trends of the effects of the individual co-builders on the incrustation is comparable to the type C experiments. The highest incrustation is measured for the blank experiment. PAA is the least effective co-builder, while the strongest reduction of the incrustation is observed in the presence of PMA-PAMPS and the three PSS containing polyelectrolytes.

3.4 Conclusions

The simple detergent formulations consisting of a Na₂CO₃/NaHCO₃ builder system in combination with a polymeric co-builder have been systematically extended with the anionic surfactant SDBS and the filler material Na₂SO₄.

The addition of Na₂SO₄ resulted in general in an increase of the incrustation compared to the simple formulations, while the specific effects of the different investigated co-builders were preserved. Potential causes for these observations are the influence of Na₂SO₄ on the nucleation and growth of CaCO₃ via the supersaturation or the reduction of electrostatic repulsion forces due to the screening of the negative surface charges of cotton and CaCO₃ by the Na⁺ ions.

The anionic surfactant SDBS caused an overall decrease of the degree of incrustation compared to the experiments with the simple formulation. Changes in the behaviour of the polymeric co-builders were noticed, especially for those which were less effective or even had a controversial influence in the simple formulation and in the experiments in the presence of Na₂SO₄. The measured adsorption of SDBS on both cotton and CaCO₃
CHAPTER 3

provides the first explanation for the observed general trend. The adsorption on cotton can reduce the extent of heterogeneous nucleation of CaCO₃ on the textile which is the most plausible cause of incrustation. Furthermore adsorption of SDBS on both substrates can result in sterical hindrance for a close approach of CaCO₃ crystals to the cotton, thus decreasing the chance of entrapment of the crystals between the fibres, which is an alternative cause of incrustation. The last effect of SDBS on the incrustation is related to the precipitation of Ca(DBS)₂. Although this process is essentially unwanted, it may lead to a lower incrustation level when the deposition of Ca(DBS)₂ on cotton is less severe than that of CaCO₃.

The experiments with formulations which contained both Na₂SO₄ and SDBS showed that the effect of SDBS on the incrustation prevailed over that of Na₂SO₄, so that a general decrease of the incrustation was observed compared to the most simple formulation.

Acknowledgements

The authors are indebted to Household and Personal Care Research B.V., The Hague, for financial support and to E.G.P. Cornelisseens and J. Pronk for stimulating discussions. They are most grateful to R.C. van Landschoot, R. Nijhuis and M.S. de Jonge for practical assistance and analyses.

References


PECIPITATION IN DETERGENT PERFORMANCE: PART II.


CHAPTER 4

THE EFFECT OF ADDITIVES ON THE PARTICLE SIZE DISTRIBUTION OF CALCIUM CARBONATE IN BATCH PRECIPITATION EXPERIMENTS.

Abstract

Batch precipitation experiments of CaCO$_3$ were done at 50°C in the presence of low amounts of different polyelectrolytes. The development of the particle size distribution was followed with time by an on-line forward light scattering technique.

The polymeric additives reduced the size and increased the number of the precipitated particles. The time needed to obtain the final distribution was also affected by the polymers. The residual calcium concentration provided an indication for the extent of growth inhibition.

A qualitative evaluation of the influence of additives on processes such as nucleation, growth and agglomeration was made, and the consequences for some relevant experimentally accessible parameters are given. Comparison of the so-predicted shifts in parameter values caused by additives with the experimentally obtained data revealed the potential mechanisms by which the polyelectrolytes act on the precipitation of CaCO$_3$.

The results were also used to support the explanation of the previously observed behaviour of these polyelectrolytes as performance additives in soda-based detergents.

THE EFFECT OF ADDITIVES ON THE PARTICLE SIZE DISTRIBUTION

4.1. Introduction

Additives are often applied in batch as well as in continuous crystallization. Some of their applications are control of the particle size and improvement of the filterability of the product [1]. An example of a process where polymeric additives are frequently used for the control of the negative effects caused by the water hardness is the washing process with soda-based detergents. The reduction of the free calcium concentration in the washing liquor by applying such detergents is in principle a batch precipitation of CaCO₃.

Water hardness in the form of calcium and magnesium ions has a significant influence on the results of the washing process with laundry detergents. A high calcium ion concentration in the water hinders the removal of pigment soil, while calcium ions also form insoluble salts with anionic surfactants, which are usually a main constituent of detergents. These effects decrease the detergency. A detergent will therefore often contain a substance, usually called a builder, with the task to lower the calcium ion concentration in the washing liquor.

Until recently sodium triphosphate has been used as the main builder in modern detergents. Sodium triphosphate acts as a sequestering agent for calcium ions and has several other benefits on detergency. During the last decades it has been recognised that sodium triphosphate may lead to overfertilization of standing and slow flowing waters, which in turn leads to extreme algae growth [2]. Therefore the use of phosphates in detergents has been banned in various countries.

Much work has been done in order to find suitable replacements. These can be other sequestering agents like nitrilo tri acetic acid (NTA) [3], either alone or in combination with ion exchangers as zeolites [4], or precipitating
agents as sodium carbonate [5].

The use of sodium carbonate, also called soda, as a detergent builder results in the removal of calcium ions by precipitation of CaCO₃. The residual calcium ion concentration after precipitation is sufficiently low to obtain a good detergency. Another advantage of soda is that it provides a mild alkalinity, which favours detergency because fibres and soil become more negatively charged as the pH increases, resulting in an increased mutual repulsion. But soda also leads to troublesome depositions of CaCO₃ on both laundry and laundering apparatus, especially at high washing temperatures, due to the inverse solubility of CaCO₃.

Logically there are two possible mechanisms which both could lead to the deposition of CaCO₃ on textile. The first one is that the crystals are formed in the solution after which they get entrapped in the fabric and stick to it by means of growth. The second possibility is that the crystals are already formed on the textile surface by means of heterogeneous nucleation, which generally occurs easier than homogeneous nucleation.

Low amounts of polyelectrolytes are frequently added to soda-based detergents in order to diminish the deposition of CaCO₃ on cotton. Former work, described in chapter 2 and in ref.[6], has shown the influence of several types of (co)polymers on the deposition of CaCO₃ on cotton. The names of these polymers, their further used abbreviations as well as their molecular weights are given in table 4.1. The generic formulae of these compounds are given in table 2.2 of chapter 2.

Polyacrylic acid (PAA) increased and a copolymer of polylactide acid with polyaclrylamido methyl propane sulfonic acid (PMA-PAMPS) did not affect the deposition of CaCO₃ on cotton in simple soda-based detergents. PAA and PMA-PAMPS were assumed to be able to form polymer bridges between CaCO₃ crystals and cotton and also did inhibit the growth of CaCO₃.
THE EFFECT OF ADDITIVES ON THE PARTICLE SIZE DISTRIBUTION

Table 4.1 The added (co)polymers, their abbreviations and their mean molecular weights (MW).

<table>
<thead>
<tr>
<th>Name of (co)polymer</th>
<th>Abbreviation</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylic acid</td>
<td>PAA</td>
<td>5000</td>
</tr>
<tr>
<td>Polymaleic acid - polyacrylamido methyl propane sulfonic acid</td>
<td>PMA-PAMPS</td>
<td>7500</td>
</tr>
<tr>
<td>Polymaleic acid - polystyrene sulfonic acid</td>
<td>PMA-PSS</td>
<td>13000</td>
</tr>
<tr>
<td>Polymethacrylic acid - polystyrene sulfonic acid</td>
<td>PMAA-PSS</td>
<td>4300</td>
</tr>
<tr>
<td>Polystyrene sulfonic acid</td>
<td>PSS</td>
<td>70000</td>
</tr>
</tbody>
</table>

The three other polymers which all contain styrene sulfonic acid groups reduced the deposition. Several mechanisms have been forwarded to explain this observed phenomenon for the PSS containing polymers. They either promote the primary nucleation of CaCO₃ in the solution, or act as dispersing agents for CaCO₃, or they do both.

Some of the above mentioned mechanisms, which explain the influence of the additives on the deposition, are related with the adsorption of the additives on CaCO₃ or cotton and/or their subsequent effect on the zeta potential of these substrates. These subjects will be extensively treated in chapter 5.

Other mechanisms are associated with processes such as nucleation, growth and agglomeration of CaCO₃. Together they determine the final particle size distribution (P.S.D.) and each step could be influenced by an additive. Monitoring the development of the P.S.D. of CaCO₃ during batch precipitation experiments could therefore be a useful tool to find evidence for some of the above mentioned mechanisms or even to discriminate between them. In the following we will only consider primary nucleation since the amount of solids is too low for secondary nucleation.

The P.S.D. in batch precipitation experiments is mainly determined by the following processes: nucleation, growth and agglomeration. Additives can in principle affect all these processes either directly or indirectly, as will be demonstrated below.

In the first place polymers can form soluble complexes with the precipitating cations and thus reduce their free ionic concentration. This causes an indirect effect on the above given processes since the supersaturation, being the driving force for the processes, will decrease. Because additives are present here only at ppm levels, their effect on the supersaturation through sequestration can be neglected and the influence of additives on the precipitation merely proceeds through other mechanisms.

In table 4.2 possible effects of additives on P.S.D. determining processes are given, together with their consequences for the experimentally measured parameters when only that particular process is affected by the additive. If the additive simultaneously influences more than one process, the prediction of the consequences for the parameters is not straightforward because two processes can impose opposite effects on the given parameters.

The following experimentally accessible parameters are given in table 4.2. The (median) size of the particles is characterized by the diameter $d_{50} \ (\mu m)$ under which value 50 volume percent of the P.S.D. is measured, as is illustrated in fig.4.2. Another parameter related to the P.S.D. is $t_r \ (s)$, defined as the time after which no further change was noticeable in the measured distribution. This time $t_r$ was always much shorter than the total reaction time, which was 30 minutes. For the number density of particles in the reactor after 30 minutes reaction time the symbol $N \ (# \ dm^{-3})$ is used. Furthermore the parameters $[Ca]_{res}$ and $[Add.]_{res}$ represent respectively the
residual Ca$^{2+}$ and additive concentration in the reactor after 30 minutes reaction time.

We will now proceed with describing how additives can affect the processes mentioned in table 4.2.

The classical formula for the steady state primary nucleation rate $J$ reads:

$$J = K_J S \exp(-\Delta G^*/kT) = K_J S \exp \left[-\beta \sigma^3 v^2/(kT)^3 \delta^2 \ln^2 S\right]$$  (1)

where $\Delta G^*$ is the Gibbs free energy of formation of a critical nucleus and $K_J$ is a practically supersaturation $S$ independent kinetic factor, which among other factors consists of the frequency of attachment $f^*$ of building units to the nuclei. $J$ is linearly dependent on $f^*$. One of the terms in the thermodynamic exponential part is $\sigma$, which is the surface free energy of the nucleus/solution interface. Nucleation can in principle be inhibited or stimulated by additives, as will be elucidated below.

Nucleation inhibition has been related with adsorption of additives on subcritical nuclei [7]. This reduces the available surface for attachment of building units to the subcritical nuclei and thus decreases $f^*$ and the
nucleation rate $J$. But adsorption of additives onto the nucleus also reduces the surface free energy $\sigma$ in the exponential term, which according to eq.(1) leads to an increase of the nucleation rate [8]. The final effect of additives on $J$ will be determined by the competition between the influence on the kinetic term by means of $f^*$ and the impact on the thermodynamic part via surface free energy $\sigma$.

Nucleation stimulation in solution has also been reported for cases, where the precipitating cations have a strong affinity for the negatively charged groups of a polymeric additive [9-11]. This results in an energetically less costly formation of clusters around the additive than in the bulk of the solution. The additive molecules can thus be regarded as templates and accordingly the negatively charged groups as active sites for the nucleation of the salt. The structural matching between the active groups of the additive and the distance between the cationic sites on one of the crystallographic faces of the precipitating salt could thereby play a role.

In most cases the crystal growth rate decreases in the presence of additives. CaCO$_3$ growth inhibition by additives is caused by adsorption of additives on active growth sites through ionic bonding with calcium ions and/or hydrogen bridging with carbonate ions at the crystal surface [12]. Only for a few systems the presence of additives resulted in an increase of the growth velocity [13]. This effect is contributed to a reduction of the edge free energy due to the adsorption of the additives.

Also the degree of agglomeration of the developing crystals can be affected by additives. Prevention of agglomeration by the dispersing action of an additive is based on its adsorption at the crystal surface, which leads to either sterical hindrance or increased electrostatic repulsion [14]. An additive can also stimulate agglomeration either by the formation of bridges between crystals, or when its adsorption leads to a decrease in charge of the
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crystals. Rather high surface coverages of the crystals with adsorbed additive molecules seem to be needed to influence the extent of agglomeration by either of these mechanisms. A relatively strong consumption of the initial additive concentration is therefore to be expected, if such a mechanism is operative.

The mentioned mechanisms all indicate how additives can directly influence nucleation, growth and agglomeration of crystals. These processes are, however, interrelated via physical parameters such as the supersaturation. Also the surface area of the formed particles is a factor which indirectly influences the precipitation process. An additive can therefore directly affect one process and indirectly another, through its influence upon a physical parameter.

4.3. Experimental

Batch precipitation experiments of CaCO₃ were performed in duplicate at 50°C and pH=10. The experimental equipment is shown in fig.4.1.

European tap water was simulated by a 2.5x10⁻³ M CaCl₂ solution, corresponding with a water hardness of 7.0°dH after mixing of the solutions in the reactor. A simple detergent formulation was simulated by a mixed NaHCO₃/Na₂CO₃ solution, with respective concentrations of 3.39x10⁻² and 2.27x10⁻² M. This solution also contained 100 ppm of one of the polyelectrolytes, except for the blank experiment. In a thermostated double walled reactor 0.5 dm³ of both solutions were mixed.

The development of the P.S.D. of CaCO₃ in the presence or absence of additives was monitored continuously. The content of the reactor was pumped through the flow cell of a Malvern Master Sizer. With this apparatus the P.S.D. can be measured in the size range between 0.1 to 600 μm by
Figure 4.1  Equipment for on-line P.S.D. measurements during the batch precipitation of CaCO₃.

means of a forward light scattering technique. The measurement principle is based on the fact that small particles diffract light at larger angles than large particles. The light intensity pattern over a range of scattering angles contains information about the P.S.D. The measurement of one P.S.D. was completed in 15 seconds.

After 30 minutes the experiment was stopped and three samples were taken from the reactor. Two samples were filtered, and the residual Ca²⁺-concentration in the filtrate of one of the samples was determined by Inductively Coupled Plasma (Perkin Elmer Plasma 2). The residual concentrations of the styrene sulfonic acid containing polymers were determined by measuring the UV absorbance of the filtrate of the second sample at 225 nm in case of PMA-PSS and PSS or at 255 nm for PMAA-PSS
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[15]. The final concentrations of PAA and PMA-PAMPS were determined turbidimetrically using Hyamine 1622 from BDH. Hyamine 1622 forms stable suspensions with polycarboxylic acids and the extinction at 420 nm is linearly dependent on the polymer concentration [16]. Calibration curves were made prior to each measurement.

The number density of particles present in the third sample taken from the crystallizer after 30 minutes was counted immediately with a Coulter Counter Multisizer. A measurement tube with a hole of 70 μm, previously calibrated with a standard latex suspension, was used.

4.4. Results

After mixing of both solutions the precipitation of CaCO$_3$ started immediately due to the relatively high initial supersaturation. This supersaturation S of the a-stoichiometric solution with an excess of carbonate ion is defined as $\sqrt{[(Ca^{2+})(CO_3^{2-})/K_{sol}]}$, where (Ca$^{2+}$) and (CO$_3^{2-}$) are the activities of the free ions and $K_{sol}$ is the thermodynamic solubility product. The complexes formed in solution and the supersaturation S were calculated from mass-balance and charge-balance equations by successive approximations for the ionic strength [17]. The considered equilibria and the values of the thermodynamic constants were obtained from Plummer and Busenberg [18]. With $K_{sol}$ = 2.1806x10^{-9} mole$^2$dm$^{-6}$ for calcite and 6.9597x10^{-9} mole$^2$dm$^{-6}$ for vaterite (from ref.[18]), the supersaturation S was calculated to be 12.6 and 7.1 with respect to calcite and vaterite, respectively.

The development of the P.S.D. for a blank experiment with time is shown in fig.4.2. Scanning electron micrographs revealed that the product in the different experiments consisted of mixtures of individual crystals and agglomerates.
Figure 4.2 Undersize P.S.D. for a blank experiment as a function of time.

The diameter \(d_{50}\) will be used to characterize the size of the particles. The value of this parameter has been indicated in fig.4.2 for the P.S.D. obtained after 180 s, in order to illustrate the meaning of \(d_{50}\).

The parameter \(t_f\) can also be deduced from the P.S.D. measurements. In the example shown in fig.4.2 all P.S.D. curves for reaction times longer than 180 s coincided with the distribution measured at 180 s. So in this example \(t_f\) equals 180 s.

The number density of particles in the reactor, \(N\) (\(\#\ \text{dm}^{-3}\)), was determined with the Coulter Counter after 30 minutes reaction time.

The values for \(d_{50}\), \(t_f\) and \(N\) in the presence of the polyelectrolytes are given in comparison with these data for the blank experiment in fig.4.3. The residual \(\text{Ca}^{2+}\)- and additive-concentrations after 30 minutes are presented in fig.4.4. The initial additive concentration amounted in all cases 50 ppm.
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![Graph showing the effect of additives on particle size distribution.](image)

Figure 4.3 Influence of polyelectrolytes on the parameters $d_{50}$, $t_r$ and $N$ in batch precipitation experiments of CaCO$_3$.

![Graph showing residual Ca-ion and additive concentrations.](image)

Figure 4.4 Residual Ca-ion and additive concentrations in batch precipitation experiments of CaCO$_3$. 

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4.5. Discussion

At the start of a batch experiment nucleation and subsequent growth take place, which cause the supersaturation $S$ to decrease. When $S$ drops below a critical value primary nucleation almost stops and the process will be mainly controlled by growth. Provided that agglomeration and secondary nucleation are of minor importance, the number of particles $N$ formed in a batch process is given by

$$N = \bar{J} \, t_c$$  \hspace{1cm} (2)

where $\bar{J}$ is the mean nucleation rate and $t_c$ is the time needed to reach the critical supersaturation. Fig.4.2 shows that during the experiment the distribution changed in the direction of larger particle sizes, which is caused by growth of the previously nucleated particles. After a certain period, called $t_c$, the measured distribution did not change noticeably.

In figs.4.3 and 4.4 the polyelectrolytes have already been divided into two groups. Group I consists of PAA and PMA-PAMPS, while the polystyrene sulfonic acid (PSS) containing additives form group II. The additives within a group show qualitatively a similar effect on the measured parameters compared with the data obtained for the blank, as will be discussed below.

1) PAA and PMA-PAMPS lead to smaller particles as follows from the smaller values for $d_{50}$. The number density $N$ is high compared to all other experiments. It took a relatively long time $t_r$ to obtain the final distribution. The residual $\text{Ca}^{2+}$-concentrations are significantly higher than in the other experiments, which can only partially be caused by complexation of the $\text{Ca}^{2+}$-ions by the polyelectrolytes. Widely differing literature data can be found on the complexation of $\text{Ca}^{2+}$ ions by PAA. Experimental data in ref.[19] indicate that 50 ppm PAA can complex about 6 ppm $\text{Ca}^{2+}$-ions of the total residual $\text{Ca}^{2+}$-concentration under the present experimental conditions, while it was stated in ref.[20] that
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polyacrylates do not form complexes with Ca\(^{2+}\) ions. All effects of the polyelectrolytes on the measured parameters match with the consequences, shown in table 4.2, in case of growth inhibition. The increase in the number of particles is caused by the fact that growth inhibition leads to a relatively slow decrease of the supersaturation. This increases \(t_c\) in eq.(2), and thus \(N\). The residual and starting concentrations of the additives are almost equal. Growth inhibition has been reported to occur already at surface coverages of only a few percent, so growth inhibition might even take place at hardly decreasing additive concentrations [21].

2) Addition of the styrene sulfonic acid (PSS) containing polymers also results in a decrease of \(d_{60}\). The number density \(N\) is again higher than for the blank, but lower than in the experiments with PAA and PMA-PAMPS. The final distribution was obtained faster than in all other experiments. The residual Ca\(^{2+}\)-concentrations are about equal to that for the blank, which excludes growth inhibition. Comparison of these data with the predicted effects in table 4.2 demonstrates that they match with two mechanisms, namely: prevention of agglomeration by a dispersing action or nucleation stimulation. Both mechanisms lead to shifts of the parameter values in a similar direction, but a differentiation between the two mechanisms is still possible from additional information, as will be demonstrated below.

a) When the PSS containing polymers act as dispersing agents for CaCO\(_3\), the number of particles increases. Consequently, the available surface area for growth increases, leading to smaller particles and to a faster decrease of the supersaturation, provided that no growth inhibition occurs. Relatively high surface coverages, close to a monomolecular layer, are in general needed to achieve a dispersing action. Fig.4.4 shows that PMAA-PSS does not exhibit the relatively low residual additive
concentration required for a dispersant. The PMA-PSS and PSS concentrations, on the other hand, decrease noticeably during the precipitation probably due to adsorption on CaCO₃. Such an adsorption could cause sterical hindrance or electrostatic repulsion. Scanning electron micrographs, however, showed at least the same extent of agglomeration in the presence of PSS containing polymers as for the blank experiment. The PSS containing polymers therefore do not seem to act as dispersing agents for CaCO₃. They neither retard the precipitation, as follows from the relatively short $t_r$ values, in spite of their apparent adsorption at the particle surface. It thus seemed relevant to gain more insight in the specific adsorption behaviour of all the used additives as well as in their effect on the zeta potential of CaCO₃ and cotton. A separate study on these phenomena will be presented in chapter 5.

b) Nucleation and growth of CaCO₃ can be favoured when specific interactions between crystals and polymers reduce the surface free energy of the crystals. As mentioned before this effect on the nucleation rate $J$ can be counterbalanced by the fact that these interactions unavoidably reduce the available surface for attachment of building units to the crystals. This could lead to a lower nucleation rate. The decrease of the additive concentration in this model will be relatively small. The effect of PMA-PSS on the nucleation and surface free energy of CaCO₃ will be treated in chapter 8. Growth stimulation by the additives can be excluded because this would increase the particle size, which is in contradiction with the experimental findings.

c) Another possibility for nucleation stimulation by additives is that they act as templates during the nucleation of CaCO₃, due to the strong affinity of calcium ions for the styrene sulffonic acid groups. As mentioned before, this makes it relatively easier to form nuclei in the neighbourhood of the polymers than in the bulk of the solution. The polyelectrolytes probably
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have a stretched structure at the prevailing high pH value of 10.0, so that almost all active groups are available for the template action. As a consequence of the mechanism more particles will be formed, because \( J \) in eq.(2) increases. This leads to smaller particles, a faster decrease of the supersaturation and an earlier reached final distribution. Template polymer chains will be incorporated in the crystals or remain attached to the surface of the crystals, but the expected decrease of the polymer concentration should be lower than if they act as dispersing agents. Azoury et al. have proposed a stimulation of the nucleation of calcium oxalate by a template action of low amounts of glutamic acid [9]. None of the presently obtained results is in contradiction with a template action of the PSS containing polymers.

There seems to be a correlation between the size of the particles, depicted by the parameter \( d_{50} \) in fig.4.3, and the molecular weight (MW) of the PSS containing polymers, given in table 4.1. The largest particles are formed in the presence of the polymer with the highest MW. No firm explanation for this phenomenon can be given, but possibly the chance that a nucleus forms and subsequently grows along the template increases with the number of styrene sulfonic acid groups per chain, and thus with MW. Another possibility is that more nuclei can be formed and grown along a chain. Each nucleus can not form an individual crystal, because it is connected with the others through the polymer chain. The number of nuclei per chain and the final size of the particle, which can be considered as the result of several intergrowing crystals, could then increase with MW.

For the PSS containing additives it can be concluded that a stimulation of the nucleation of CaCO\(_3\) is the most likely mechanism. This can be caused either by a reduction of the surface free energy of the nuclei due to specific interactions, or by a template action of the additives.

The discussion presented above shows that the influence of additives on
CHAPTER 4

the P.S.D. determining processes on the basis of measured parameters can sometimes be explained by more than one mechanism. Taking all available information into account it can, however, be concluded that PAA and PMA-PAMPS inhibit the growth of CaCO$_3$, while the PSS containing additives most likely stimulate the nucleation of CaCO$_3$. It is now interesting to see whether the effects of the additives on the here considered processes also provide an explanation for their specific influence on the deposition of CaCO$_3$ on cotton, which has been determined in chapter 2. This subject will be treated in the following section.

4.6. Relation with incrustation experiments.

The above proposed mechanisms for the effects of the additives on nucleation, growth and agglomeration will be correlated with their influence on the deposition of CaCO$_3$ on cotton in soda-based detergents. This last phenomenon is also known as incrustation.

As already mentioned in the introduction, heterogeneous nucleation of CaCO$_3$ on the cotton surface is one of the possible causes for incrustation. The amount of CaCO$_3$ deposited on the cotton will be determined by the competition between the nucleation in solution and the heterogeneous nucleation on the textile. Heterogeneous nucleation will in general require a lower free energy change ($\Delta G_{\text{het}}^*$) than the free energy change related to homogeneous nucleation in the bulk solution ($\Delta G^*$). An often used relation between the two factors is of the form

$$\Delta G_{\text{het}}^* = \phi \Delta G^*$$  \hspace{1cm} (3)

with $0 < \phi < 1$ (e.g.[22]), where $\phi$ is given by

$$\phi = (2+\cos \theta)(1-\cos \theta)^2/4$$  \hspace{1cm} (4)

Here $\theta$ (0°<\theta<180°) is the contact angle between the crystal and the foreign substrate. Evaluation of eqs.(1), (3) and (4) teaches that heterogeneous
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nucleation proceeds at least as fast as or faster than homogeneous nucleation.

PAA and PMA-PAMPS were found to inhibit the growth of CaCO₃. Consequently, the supersaturation decreases slower than in a blank experiment and the time where nucleation plays a role is prolonged. This would increase the incrustation, if it is caused by heterogeneous nucleation on cotton. In spite of the growth inhibition the larger total surface area available for growth leads to a larger amount of deposited CaCO₃. This would explain why PAA increased the incrustation (see chapter 2). From the measurements of $d_{50}$, N and the residual Ca$^{2+}$-concentration it can be concluded that PAA is a better growth inhibitor for CaCO₃ than PMA-PAMPS. This may be one of the reasons that the incrustation is not increased but remained equal to the blank in the presence of PMA-PAMPS.

For the PSS containing polymers a mechanism was proposed where nucleation in solution is stimulated by the additives. A reduction of the incrustation is expected when the additives stimulate nucleation in solution at the cost of the heterogeneous nucleation on cotton. Adsorption of the polymers on cotton could also enhance the nucleation there, thus counterbalancing the effect of stimulation of nucleation in solution. The PSS containing polymers, however, do not adsorb on cotton as will be treated in chapter 5. So, the observation in chapter 2 that the incrustation decreased in the presence of the PSS containing additives (see chapter 2) can be explained by this mechanism.

It can thus be concluded that the results obtained in this chapter are consistent with the conclusions reached in chapter 2.

4.7. Conclusions

- Following the development of the Particle Size Distribution with time can
be an useful tool in the determination of the influence of additives on processes as nucleation, growth and agglomeration.

- PAA and PMA-PAMPS inhibit the growth of CaCO$_3$, thus prolonging the primary nucleation period in solution. This eventually leads to smaller particles.

- The styrene sulfonic acid containing polymers seem to stimulate the nucleation of CaCO$_3$, which leads to smaller particles and a faster decrease of the supersaturation.

- The proposed mechanisms can explain the effects of the additives on the incrustation, when it is assumed that heterogeneous nucleation of CaCO$_3$ on textile is an essential step in the deposition of CaCO$_3$.

Acknowledgements

The authors are indebted to Household and Personal Care Research B.V., the Hague, for financial support. The authors wish to thank E.G.P. Cornelissens and J. Pronk for stimulating discussions and are most grateful to D. Stajcer, W.F. Boeken and L. Maass for experimental assistance.

References

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CHAPTER 5

ADSORPTION OF POLYELECTROLYTES, THEIR EFFECT ON THE
ZETA POTENTIAL AND THE RELATION WITH THE DEPOSITION OF
CALCIUM CARBONATE ON COTTON IN DETERGENTS

Abstract

The influence of five different polyelectrolytes on the deposition of calcium carbonate on cotton in a simple soda-based detergent has been quantified previously (see chapter 2). This phenomenon is also called incrustation.

In the present study the adsorption isotherms of these polyelectrolytes on calcium carbonate and cotton have been measured for polyelectrolyte concentrations from 0 to 100 ppm. Furthermore the effects of the polyelectrolytes on the zeta potential of calcium carbonate and cotton was determined. Negative zeta potentials were found for all systems, and the polyelectrolytes affected the zeta potential of calcium carbonate, but not that of cotton. A good correlation is found between the adsorption behaviour of the polyelectrolytes and their influence on the zeta potential.

The degree of adsorption of the polyelectrolytes on calcium carbonate and cotton and the impact of the polyelectrolytes on the zeta potential of calcium carbonate and cotton give an indication for the likelihood of improved sterical hindrance or higher electrostatic repulsion forces in incrustation experiments, respectively. Comparison of the adsorption behaviour of the polyelectrolytes and their influence on the zeta potential with their specific effects on the incrustation leads to the conclusion that electrostatic repulsion and/or sterical hindrance are not likely to play the predominant role in determining the incrustation in soda-based detergents.

D. Verdoes and G.M. van Rosmalen, to be submitted for publication in Journal of Colloid and Interface Science.
ADSORPTION AND ZETA POTENTIAL

5.1. Introduction

Since the end of the sixties, the use of phosphates in laundry detergents has met with public criticism because of their contribution to eutrophication of standing or slow flowing surface waters. The search for environmental and economic alternatives in detergents has continued unabated since then. Nowadays, several countries have limits on phosphates in detergents. Water hardness controlling agents (detergent builders) are used in synthetic detergents to diminish the free hardness (the calcium and magnesium ion concentration) which is responsible for reduced cleaning. The builders most commonly used are of three major types: (1) sequestrants; (2) precipitant builders, and (3) ion exchange builders [1].

Sodium carbonate, trivially called soda, belongs to the second type of builders and causes the precipitation of calcium carbonate. A disadvantage of soda is that part of the precipitated CaCO₃ crystals adhere to the textile surface, especially to cotton, and to the hot parts of the washing machine. This phenomenon is called incrustation. Small amounts of specific polyelectrolytes are known to diminish the incrustation [2,3]. Adsorption of these polyelectrolytes on cotton and CaCO₃ and the resulting increase of electrostatic repulsion forces and/or sterical hindrance has been mentioned as a potential mechanism for the reduction of the incrustation in the presence of the polyelectrolytes.

In chapter 2 it was shown that especially polystyrene sulfonic acid containing polyelectrolytes reduce the deposition of CaCO₃ on cotton in simple soda-based detergents, while other (co)polymers, as e.g. polyacrylic acid, hardly affect or even increase the incrustation.

In this study, adsorption experiments on CaCO₃ and cotton were carried out with some of the polyelectrolytes which were previously tested in
incrustation experiments. Furthermore, the influence of these compounds on the zeta potential of CaCO$_3$ and cotton was determined. The aim is to investigate whether the different effects of the polyelectrolytes on the incrustation can be correlated with their degree of adsorption and/or their influence on the zeta potential.

5.2. Background information on polyelectrolyte adsorption

The theory describing the adsorption of uncharged polymers is rather well developed and it is in general in good agreement with experimental data and it even gives some insight on the structure of the adsorbed layer. The theory includes the effects of the most important parameters as e.g. the molecular weight of the polymer, the influence of the solvent and the polymer-surface interaction.

The adsorption theory for charged polyelectrolytes is more complicated than that for the uncharged polymers. Recently, however, considerable progress has been made in the theoretical description of the adsorption of polyelectrolytes. The lattice theories for polymer adsorption of Roe [4] and of Scheutjens and Fleer [5] have been extended for polyelectrolyte adsorption by including electrical free energy contributions [6,7]. The main differences between the adsorption of polymers and polyelectrolytes are the importance of electrolytes and the structure of the adsorbed layer. Background electrolytes are important for the adsorption of polyelectrolytes because of their ability to screen the electrical contributions of the charged polyelectrolyte groups, which are absent in polymers, to the adsorption energy. Furthermore a polyelectrolyte (at low electrolyte concentration) adsorbs rather flat on the surface because the formation of loops and tails, which is often observed in the adsorption of polymers, is suppressed because
the mutual repulsion between the like charges on the polyelectrolyte chain inhibits strong accumulation of segments, except in the flatly adsorbed trains where this repulsion is compensated by the adsorption energy [8]. The adsorbed layers of polyelectrolytes at low electrolyte concentrations are therefore very thin, whereas at higher electrolyte concentrations more loops and tails are formed, thus increasing the thickness of the adsorbed layer, which in this case looks like that of an uncharged polymer.

The consequences of the electrical free energy contributions on the structure of an adsorbed polyelectrolyte layer and on the adsorption mechanism can be illustrated with some experimental results for the adsorption of polyacrylic acid (PAA) on various mineral salts. It has been concluded from adsorption experiments on calcite that the PAA molecules lie in a relatively flat configuration on the surface with more than one segment attached to it but having, nevertheless, some extension into the solution [9]. The configuration of adsorbed spin-labelled PAA on barium sulfate has been studied with electron spin resonance (ESR) measurements, showing that at low ionic strength the polyelectrolytes are flatly adsorbed with more than 90% of the segments associated with the surface [10]. In this last case, the carboxylate groups of PAA were not closely associated with barium ions in the surface and the adsorption of PAA was accompanied by desorption of SO\textsubscript{4}\textsuperscript{2-} from the surface, though this does not necessarily mean that the carboxyl groups occupy SO\textsubscript{4}\textsuperscript{2-} positions. Adsorption experiments with PAA on calcium phosphate with a varying amount of Ca\textsuperscript{2+} in the crystal surface showed that PAA adsorption increased when the surface had a higher Ca\textsuperscript{2+} ion density, indicating that the adsorption of PAA via interactions of its carboxylate groups with Ca\textsuperscript{2+} ions in the surface [11].

It can thus be concluded that polyelectrolytes adsorb flatly upon the surface at low background electrolyte concentrations and that ions in the mineral surface can play a role in the adsorption process.
5.3. Experimental

AR grade chemicals, doubly distilled water and standard cotton for incrustation tests from TNO Delft were used in all experiments. The five tested polyelectrolytes, their abbreviations and molecular weights (MW) are: polyacrylic acid (PAA, MW=5000), polymaleic acid - polyacrylamido methyl propane sulfonic acid (PMA-PAMPS, MW=7500), polymaleic acid - polystyrene sulfonic acid (PMA-PSS, MW=13000), polymethacrylic acid - polystyrene sulfonic acid (PMAA-PSS, MW=4310) and polystyrene sulfonic acid (PSS, MW=70000).

Supersaturated CaCO_3 solutions were prepared by mixing CaCl_2 and Na_2CO_3 solutions, with concentrations and at conditions equal to those used in the incrustation experiments in chapter 2, namely at T=50°C and pHeq=10. After precipitation of CaCO_3 the suspension was filtered and the filtrate was used as a saturated CaCO_3 solution in all experiments. This procedure was followed in order to have a solution of about the same composition as the solution in the incrustation experiments. It contained about 4x10^{-5} M Ca^{2+}, 4x10^{-2} M Na^+, 1x10^{-2} M Cl^- and 2.3x10^{-2} M total carbonate, resulting in an ionic strength of about 0.045.

Calcium carbonate crystals were prepared by bubbling carbon dioxide through a solution of Ca(OH)_2. The CaCO_3 crystals were removed by filtration and ripened for at least one week in a saturated solution at 25°C. The crystals were then separated and dried in air at 50°C. The specific surface area of the crystals was 10 m^2/g, as determined by BET measurements with N_2 gas. X-Ray diffraction showed that the crystals were purely calcite.

Pieces of cotton for adsorption experiments and streaming potential measurements were taken from the same batch of cotton as was used in the incrustation experiments.
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Adsorption isotherms were determined by measuring the difference in polyelectrolyte concentration in the solution before and after adsorption. Either CaCO$_3$ crystals (0.25 g) or a piece of cotton (1.0 g) were suspended in 50 ml of the saturated CaCO$_3$ solution with a known added concentration of the polyelectrolyte. The concentration of the polyelectrolytes in the adsorption experiments was in the range between 0 and 100 ppm (mg/l). All adsorption experiments were done at least in duplicate. When necessary, the pH of the solutions was brought at a value of 10.0 $\pm$ 0.1 with a NaOH solution. The samples were shaken in a thermostated waterbath at 25 $\pm$ 1°C for 24 hours. This time lapse was sufficient to reach adsorption equilibrium.

The concentrations of the styrene sulfonic acid containing polyelectrolytes after adsorption were determined by measuring the UV absorbance at 225 nm (PMA-PSS and PSS) or 255 nm (PMAA-PSS) [12]. The concentrations of PAA and PMA-PAMPS were determined by using the quaternary salt Hyamine 1622 from BDH, which forms stable suspensions with polycarboxylic acids. The turbidity of these suspensions measured at 420 nm is linearly dependent on the concentration of the polycarboxylate [13]. Separate calibration curves were determined for each adsorption experiment.

Calcium carbonate suspensions for the zeta potential measurements were prepared by adding 50 mg CaCO$_3$ crystals to 45.0 ml saturated CaCO$_3$ solution. To these suspensions either 5.0 ml of a pure saturated CaCO$_3$ solution was added for the blank or 5.0 ml of a saturated CaCO$_3$ solution containing 500 ppm polyelectrolyte. This resulted in an initial concentration for the polyelectrolytes of 50 ppm. All samples were brought at pH 10.0 and were shaken in a thermostated waterbath at 25°C for 24 hours. The zeta potential of the CaCO$_3$ crystals was calculated from electrophoretic mobility data based on measured Doppler shifts of scattered laser light, as obtained with a Malvern Zetasizer 3. These shifts were caused by CaCO$_3$ crystals moving in an applied electric field [14].

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The zeta potential of cotton in saturated CaCO$_3$ solutions with or without various concentrations polyelectrolytes was determined from streaming potential measurements. A porous plug of cotton, containing about 1 g of cotton, was placed between perforated platinum electrodes, allowing passage of the saturated CaCO$_3$ solution contained by two reservoirs on both sides of the plug holder. Another pair of platinum plate electrodes was mounted in the reservoirs. A detailed description of the equipment is given elsewhere [15]. All experiments were performed at 25 ± 0.1°C and pH 10.0. A saturated CaCO$_3$ solution was forced from one reservoir into the other through the plug by nitrogen pressure. The streaming potential (i.e. the potential difference over the plug electrodes) was recorded at various pressure differences between 5.0 and 30.0 cm Hg. The conductivity of the bulk solution was measured with a Philips PW 9510 conductance cell (cell constant 0.78 cm$^{-1}$) and a Wayne Kerr B642 universal bridge. The conductivity of the plug, needed to calculate the cell constant of the plug, was determined from the measured potential difference over the plug during passage of an accurately known d.c. current between the plate electrodes in the reservoirs.

Each series of measurements was done on one cotton plug. Within one series the polyelectrolyte concentration was gradually increased from 0 to 50 ppm in steps of 10 ppm, and from 50 to 100 ppm, in steps of 25 ppm.

5.4. Results and discussion of the adsorption experiments

5.4.1 Comments on the experimental conditions

The experimental conditions in the adsorption and incrustation experiments will here be compared because the adsorption experiments are
done in order to provide information about the effects of the polyelectrolytes on the incrustation.

The applied polyelectrolyte concentration in the incrustation experiments in chapter 2 was 50 ppm, which is just in the middle of the investigated range in the adsorption experiments where the polyelectrolyte concentration is varied between 0 and 100 ppm.

In an incrustation experiment the amount of precipitated CaCO₃ is about 0.5 g/dm³, while the specific surface area of the final precipitate is about 0.3 m²/g. The added amount of CaCO₃ and the specific surface area in the adsorption experiments are much higher, namely 5.0 g/dm³ and 10.0 m²/g. These conditions were chosen in order to obtain a measurable amount of adsorbed polyelectrolyte in the adsorption experiments. Calcite crystals were chosen as a substrate firstly because the other CaCO₃ polymorphs were not available with the required specific surface area and particle size. Secondly, the transformation of the metastable phases into calcite could not be prevented during the experiments which lasted at least 24 hours. Furthermore it must be noted that the surface area of CaCO₃ in the incrustation experiments is changing with time because the crystals are there precipitated in the reactor. That this can have a significant consequence for the amount of adsorbed polyelectrolyte is e.g. shown in chapter 4. The batch precipitation of CaCO₃ described there is comparable to the incrustation experiments and among other things the residual additive concentration in the reactor was measured after 30 minutes reaction time. These results are presented in fig.4.4, which shows e.g. that the PMA-PSS concentration in the reactor, which was initially 50 ppm, decreased to 37 ppm in the mentioned time lapse. This decrease is higher than it would be expected on basis of the amount of precipitated CaCO₃ and the measured specific surface area of the precipitate. Despite of the discrepancies between
the incrustation and the adsorption experiments, the last experiments give at least a qualitative sequence for the adsorption behaviour of the polyelectrolytes.

The pieces of cotton in the incrustation and adsorption experiments were taken from the same batch and the mass of the cotton was in both cases about 1 g, which was high enough to result in a measurable decrease of the polyelectrolyte concentration in the adsorption experiments.

5.4.2 Polyelectrolyte adsorption on calcium carbonate

Fig. 5.1 shows the adsorption isotherms of the polyelectrolytes on calcium carbonate.

![Graph showing adsorption isotherms of polyelectrolytes on CaCO\textsubscript{3}. Points corresponding with a starting concentration of 50 ppm are marked with "s".]

**Figure 5.1** Adsorption of polyelectrolytes on CaCO\textsubscript{3}. Points corresponding with a starting concentration of 50 ppm are marked with "s".
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The isotherms are given as plots of $\Gamma$, which is the amount of polyelectrolyte adsorbed in mg/m$^2$ or mg/g, versus the equilibrium concentration of the polyelectrolyte in ppm.

At the given pH of 10.0, it can be expected that almost all acidic groups of the polyelectrolytes are dissociated. Considering the relatively low ionic strength an extensive screening of the negatively charged polyelectrolyte groups by background electrolyte seems unlikely and the adsorption behaviour of the added compounds will probably more resemble that of charged polyelectrolytes than that of uncharged polymers.

For CaCO$_3$ it can be expected that the association of negatively charged polyelectrolyte groups with Ca$^{2+}$ ions in the surface and/or the formation of hydrogen bridges with CO$_3^{2-}$ groups in the surface determine the adsorption behaviour. Furthermore Ca$^{2+}$ ions can form bridges between groups in the polyelectrolyte chain and surface ions, which are both negatively charged.

The sequence in degree of adsorption of the polyelectrolytes on CaCO$_3$, given by their decreasing $\Gamma$, is: PMA-PSS > PSS > PMA-PAMPS $\approx$ PAA > PMAA-PSS = 0 mg/m$^2$. The isotherm of PMA-PSS is characterized by a steep initial part, which levels off to a plateau at about 0.4 mg PMA-PSS adsorbed per m$^2$ at an equilibrium concentration of 10 ppm. The shape of this isotherm is of the high affinity type. The slope of the isotherm for PSS at low concentrations is less steep and the plateau of about 0.2 mg/m$^2$ is reached at an equilibrium concentration of 30 ppm. The amount of PMA-PAMPS adsorbed is 0.05 mg/m$^2$ for the total concentration range above 10 ppm. PAA adsorbs in about equal amounts as PMA-PAMPS below an equilibrium concentration of 70 ppm, but above this concentration the isotherm an increase of $\Gamma$ is observed. For PMAA-PSS no adsorption could be detected in the added concentration range.

Adsorption experiments performed by Adam and Robb [12] with PAA
(MW 2.5x10^5) and PSS (MW 5x10^5) on CaCO_3 showed that PAA adsorbed in higher amounts than PSS in pure water as well as in the presence of 0.5 M NaCl background electrolyte. Competitive adsorption experiments in water of PAA and PSS, with a lower and a higher MW than PAA, showed that PAA was preferentially adsorbed onto CaCO_3 [12].

Fig.5.1. shows a lower adsorption for PAA (0.05 mg/m^2) than for PSS (0.20 mg/m^2) at equilibrium concentrations below 70 ppm. The main differences between the experiments in ref.[12] and the present work are the ionic strength, the molecular weights of the investigated polyelectrolytes and the concentration range, which were all much higher in ref.[12] than in the present study. The number of bonding possibilities per molecule is proportional to the molecular weight of the polyelectrolytes. Higher adsorption levels are therefore expected when MW increases, which may explain the lower adsorption of PAA here. Furthermore, the adsorption of PAA increases at concentrations above 70 ppm, and approaches γ for PSS at a concentration of 90 ppm, thus indicating that at higher concentrations the adsorption of PAA onto CaCO_3 will be higher than that of PSS.

The sequence of the MW of the polyelectrolytes does not correlate with the observed sequence of γ in this work. This is not surprising, considering the structural differences between the polyelectrolytes. The three styrene sulfonic acid containing polyelectrolytes have very different γ values for the adsorption on CaCO_3, ranging from 0.4 mg/m^2 for PMA-PSS to no detectable adsorption for PMAA-PSS. This probably indicates that the other monomer in the PSS containing copolymers has a great influence on the adsorption behaviour of the compound.

The adsorption results for the polyelectrolytes on both CaCO_3 (section 5.4.2) and cotton (section 5.4.3) will be correlated with their influence on the zeta potential in section 5.5. The consequences of both adsorption and zeta
potentials on the effects of the polyelectrolytes on the incrustation will be discussed in section 5.6.

5.4.3 Polyelectrolyte adsorption on cotton

In fig.5.2 the adsorption isotherms of the polyelectrolytes on cotton are shown as plots of $\Gamma$, here in mg polyelectrolyte adsorbed per g cotton, versus the equilibrium concentration of the polyelectrolyte in ppm.

![Graph showing adsorption isotherms](image)

**Figure 5.2** Adsorption of polyelectrolytes on cotton.

For cotton the following sequence in adsorption level is observed: PMA-PAMPS > PAA > PMA-PSS = PMAA-PSS = PSS = 0 mg/m². The amount of PMA-PAMPS adsorbed per g cotton raises sharply up to an equilibrium concentration of 20 ppm. This is followed by a less steep part
until an equilibrium concentration of 50 ppm, after which \( \Gamma \) again raises sharply, without indications that a plateau level will be reached soon. For PAA \( \Gamma \) raises until an equilibrium concentration of 20 ppm, after which a plateau level is reached at 0.4 mg PAA adsorbed per gram cotton. For the other three polyelectrolytes, all containing sulfonic acid groups, no measurable adsorption on cotton was found in the selected concentration range.

5.5. Results and discussion of the zeta potential measurements

5.5.1 Influence of polyelectrolytes on the zeta potential of calcium carbonate

Fig.5.3 shows the influence of an initial concentration of 50 ppm of the polyelectrolytes on the zeta potential of \( \text{CaCO}_3 \) calculated from the measurements with the Malvern Zetasizer 3. The observed differences in the zeta potential are significant, since they are larger than the standard deviation of the individual measurements which is in the order of 1 mV.

The mean zeta potential of \( \text{CaCO}_3 \) in the blank experiment without polymeric additives was \(-5.6\) mV. In the presence of 50 ppm polyelectrolyte the zeta potential of \( \text{CaCO}_3 \) decreased to values between \(-6.7\) and \(-11.9\) mV, as shown in fig.5.3. The zeta potential became more negative in the following sequence: blank \( \rightarrow \) PMAA-PSS \( \rightarrow \) PMA-PAMPS \( \rightarrow \) PAA \( \rightarrow \) PSS \( \rightarrow \) PMA-PSS.

In fig.5.1 the results for the adsorption experiments with a initial polyelectrolyte concentration of 50 ppm are marked with the sign "s". For all polyelectrolytes these signs lie on the first adsorption plateau. For experimental reasons, the samples for the zeta potential measurements contained less \( \text{CaCO}_3 \) crystals, and thus have less surface available for adsorption, than the samples in the adsorption experiments. For that reason
Figure 5.3  Influence of polyelectrolytes on the zeta potential of CaCO₃.

The actual concentration of the polyelectrolytes in the samples for the zeta potential measurements will lie between the with "s" indicated equilibrium concentration and the initial concentration of 50 ppm. Fig 5.1 shows that this has no consequences for the observed sequence of adsorption which was, starting with the highest measured ζ: PMA-PSS > PSS > PMA-PAMPS ≈ PAA > PMAA-PSS. Comparison of this sequence with the effects of the polyelectrolytes on the zeta potential of CaCO₃ shows that the following correlation seems to exist: the higher the adsorption the lower the zeta potential. For PMA-PAMPS and PAA, however, equal values of ζ were observed, while addition of these polyelectrolytes leads to significantly different zeta potentials. PMAA-PSS, which did not adsorb in detectable amounts on CaCO₃ does change the zeta potential somewhat compared to the blank, but less than for the other polyelectrolytes.
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The more negative zeta potentials obtained in the systems with polymeric additives are probably caused by adsorption of the, at pH 10, negatively charged polyelectrolytes on CaCO₃. The adsorption is likely to be governed by electrostatic interactions.

The surface electrical properties of CaCO₃ dispersed in aqueous solutions have been studied by a number of different electrokinetic techniques. Widely differing zeta potential values, including differences in sign, have been reported for calcite [16-19]. Values for the pH of the isoelectric point of calcite have been reported to vary between 5.4 and 10.8. Attempts have been made to explain the variations in terms of the origins of different samples, but no satisfactory correlation between sample source and surface electrical properties has been found. Investigations of the origin of the electrical charge at the calcite-aqueous solution interface have also led to conflicting opinions [16-18]. A number of studies have indicated Ca²⁺ and CO₃²⁻ as important surface ions, while it has also been claimed that H⁺, OH⁻, HCO₃⁻, CaOH⁺ and CaHCO₃⁺ play either major or minor roles in the surface charging mechanism.

A positive zeta potential has been reported for calcite particles suspended in a 5x10⁻⁴ M CaCl₂ solution, while the zeta potential measured in a 5x10⁻³ M NaCl solution was negative [18]. Electrokinetic measurements revealed that the zeta potential of calcite in 0.01 M KNO₃ changed from positive in the absence of orthophosphate to negative in the presence of low amounts of orthophosphate due to the adsorption of the negatively charged phosphate species onto calcite [19].

5.5.2. Influence of polyelectrolytes on the zeta potential of cotton

Each series of measurements was done on one cotton plug. Within a
series the polyelectrolyte concentration in the saturated CaCO$_3$ solution was gradually increased from 0 to 100 ppm. It was hereby assumed, that the adsorption equilibrium is not affected by prior adsorption of the polyelectrolyte at a lower concentration level.

The zeta potential of cotton in the absence of polyelectrolyte has been determined at the start of each series. The mean zeta potential of cotton in a pure saturated CaCO$_3$ solution (blank) obtained from these multiple measurements is $-12.6 \pm 2.0$ mV. The influence of PAA and PMA-PAMPS on the zeta potential of cotton is depicted in fig.5.4.

In the presence of PAA and of the three styrene sulfonic acid (PSS) containing polyelectrolytes a more or less constant zeta potential was measured for the whole applied concentration range. The standard deviation from the mean value for the zeta potential in the measurement series with these compounds was less than 1 mV. The measurements for the PSS containing polyelectrolytes are not given in fig.5.4 for reasons of clarity. The mean zeta potential of cotton in the presence of the PSS containing polyelectrolytes are: $-14.5$ mV for PMA-PSS, $-11.4$ mV for PMAA-PSS and $-11.0$ mV for PSS. All values, including that of PAA with a mean zeta potential of $-13.4$ mV, fall within the range observed for the blank. It can thus be concluded that the zeta potential of cotton is not significantly influenced by PAA, PMA-PSS, PMAA-PSS or PSS. Only for PMA–PAMPS the zeta potential of cotton seemed to change as a function of the added concentration. In this case the zeta potential remained constant between 0 and 50 ppm, but started to decrease at higher concentrations. It must, however, be noted that even in the presence of 100 ppm PMA-PAMPS the measured zeta potential is just outside the uncertainty range of the blank.

Logically, no effect on the zeta potential was expected for the PSS containing polyelectrolytes, because no measurable adsorption of these
compounds on cotton could be detected (see fig. 5.2). The observed adsorption of PAA on cotton (0.4 mg/g) apparently does not affect the zeta potential of this substrate. The effect of PMA-PAMPS on the zeta potential corresponds with the adsorption isotherm of this compound on cotton, which showed that the adsorption raises sharply above 50 ppm. Below this concentration the adsorption of PMA-PAMPS on cotton is comparable to that of PAA, so that similar to PAA no effect on the zeta potential is expected. Above 50 ppm the adsorption of PMA-PAMPS is significantly higher than that of PAA. This is also the concentration above which PMA-PAMPS starts to affect the zeta potential.

Cotton is a cellulose derivate, with a polyacidic character, due to the presence of carboxylic acid groups in the structure. At high pH values OH\textsuperscript{-}ions can deprotonate these groups, which results in a negatively charged
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surface. The influence of pH on the zeta potential of cotton linters has been investigated by Herrington [20] in the presence of various concentrations NaCl as background electrolyte. The isoelectric point of cotton was found at pH 2, and at pH 10 the zeta potential in $1 \times 10^{-2}$ M NaCl was $-11$ mV, which is comparable with the value for the blank in the present study.

In the following section the adsorption behaviour of the polyelectrolytes and their effect on the zeta potential will be correlated with their previously determined influence on the incrustation.

5.6. Consequences of adsorption and zeta potential for the incrustation 

The influence of the polyelectrolytes on the incrustation of cotton in simple soda-based detergents has been determined in chapter 2. The incrustation decreased in the sequence: PAA > blank $\approx$ PMA-PAMPS $>$ PMA-PSS $\approx$ PMAA-PSS $>$ PSS. In the following we will discuss whether these results can be correlated with the adsorption behaviour of the polyelectrolytes or their influence on the zeta potential of CaCO$_3$ and cotton.

Adsorption of polymers leads to stabilization of dispersions, when the following conditions are fulfilled: (i) There should be a more or less complete coverage of the particle by the adsorbed polymer, leading to sterical hindrance. If this is not the case bridging flocculation may arise; (ii) The polymer molecules need to be strongly adsorbed to prevent desorption during particle collisions [21]. Polyelectrolytes are also applied to reduce particle adhesion in fouling, where penetration of adsorbed polymer layers should prevent collision and hence adhesion, by sterical hindrance [22].

Table 5.1 gives $r$ for both CaCO$_3$ and cotton for the samples with a polyelectrolyte starting concentration of 50 ppm together with the effects of the same polyelectrolyte concentration on the incrustation of cotton.

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Table 5.1  *Amount of polyelectrolyte adsorbed on CaCO₃ and cotton from a polyelectrolyte starting concentration of 50 ppm, together with their effects on the incrustation (in mg CaCO₃ deposited per g cotton, see chapter 2).*

<table>
<thead>
<tr>
<th>Polyelectrolyte</th>
<th>$\gamma$ (CaCO₃)</th>
<th>$\gamma$ (cotton)</th>
<th>Incrustation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>----</td>
<td>----</td>
<td>175 mg/g</td>
</tr>
<tr>
<td>PAA</td>
<td>0.04 mg/m²</td>
<td>0.4 mg/g</td>
<td>275 mg/g</td>
</tr>
<tr>
<td>PMA-PAMPS</td>
<td>0.05 mg/m²</td>
<td>0.5 mg/g</td>
<td>150 mg/g</td>
</tr>
<tr>
<td>PMA-PSS</td>
<td>0.4 mg/m²</td>
<td>0.0 mg/g</td>
<td>100 mg/g</td>
</tr>
<tr>
<td>PMAA-PSS</td>
<td>0.0 mg/m²</td>
<td>0.0 mg/g</td>
<td>95 mg/g</td>
</tr>
<tr>
<td>PSS</td>
<td>0.2 mg/m²</td>
<td>0.0 mg/g</td>
<td>75 mg/g</td>
</tr>
</tbody>
</table>

The points corresponding with a polyelectrolyte starting concentration of 50 ppm have been indicated in the different adsorption isotherms for CaCO₃ shown in fig.5.1.

Considering the requirements for sterical hindrance and the amounts of polyelectrolytes adsorbed, the present results can only explain the low incrustation obtained with PMA-PSS. The adsorption levels of PMAA-PSS and PSS on CaCO₃ are, however, much lower, while the incrustation with these polyelectrolytes is comparable to the incrustation with PMA-PSS. Sterical hindrance due to adsorbed polyelectrolyte molecules is therefore certainly not the only reason for the decrease of incrustation observed with the PSS containing polyelectrolytes.

In the type 2 incrustation experiments in chapter 2 the cotton was first immersed for a period of 30 minutes in a 50 ppm solution of the polyelectrolytes. This preadsorption procedure diminished the incrustation from 275 to 175 mg CaCO₃ per g cotton in case of PAA, thus indicating adsorption of PAA on cotton. The present experiments confirm the presumed adsorption of PAA on cotton.
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One of the potential mechanisms given in chapter 2 for the observation that PAA increased the incrustation was that PAA forms bridges between CaCO₃ particles and cotton by means of free tails of PAA molecules which are only partly adsorbed on one of the substrates. In type 4 incrustation experiments described in chapter 2, where during the first five minutes the precipitation of CaCO₃ occurred in the absence of cotton, the addition of both PAA and PMA-PAMPS resulted in relatively high incrustation levels. This was also attributed to the above described bridging mechanism. The present work shows that only PAA and PMA-PAMPS adsorb on both substrates, as required in case of a bridging mechanism. Both additives have a relatively low molecular weight, while bridging is in general observed with high molecular weight polymers. It has, however, been reported that even low molecular weight poly(ethylene oxide) and PAA (MW ≥ 10⁹ to 2x10⁴) can induce flocculation of a stable polystyrene latex due to a bridging mechanism [23]. For the three PSS containing polyelectrolytes, which all reduced the incrustation, no adsorption on cotton, and for PMAA-PSS also no adsorption on CaCO₃, could be detected. This makes a bridging mechanism for this type of polyelectrolytes unlikely.

Electrostatic interactions between CaCO₃ and cotton can also affect the incrustation. The effect of 50 ppm of the polyelectrolytes on the zeta potential (ζ) of both CaCO₃ and cotton is therefore compared with their influence on the incrustation in table 5.2.

Table 5.2 shows that negative zeta potentials were obtained for both CaCO₃ and cotton in the absence or presence of 50 ppm of the polyelectrolytes. It is therefore likely that cotton and CaCO₃ are negatively charged during incrustation experiments. Higher electrostatic repulsion forces between CaCO₃ and cotton, and thus a lower incrustation, can be expected for those polyelectrolytes which cause very low zeta potential values.
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Table 5.2  The effect of 50 ppm polyelectrolyte on the zeta potential of CaCO₃ and cotton and the influence of the polyelectrolytes on the incrustation, given as mg CaCO₃ deposited per g cotton.

<table>
<thead>
<tr>
<th>Polyelectrolyte</th>
<th>ζ (CaCO₃)</th>
<th>ζ (cotton)</th>
<th>Incrustation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>- 5.6 mV</td>
<td>- 12.6 mV</td>
<td>175 mg/g</td>
</tr>
<tr>
<td>PAA</td>
<td>- 10.4 mV</td>
<td>- 13.2 mV</td>
<td>275 mg/g</td>
</tr>
<tr>
<td>PMA-PAMPS</td>
<td>- 8.4 mV</td>
<td>- 10.7 mV</td>
<td>150 mg/g</td>
</tr>
<tr>
<td>PMA-PSS</td>
<td>- 11.9 mV</td>
<td>- 14.5 mV</td>
<td>100 mg/g</td>
</tr>
<tr>
<td>PMAA-PSS</td>
<td>- 6.7 mV</td>
<td>- 13.2 mV</td>
<td>95 mg/g</td>
</tr>
<tr>
<td>PSS</td>
<td>- 10.5 mV</td>
<td>- 11.7 mV</td>
<td>75 mg/g</td>
</tr>
</tbody>
</table>

Addition of 50 ppm of PMA-PSS and PSS resulted in the lowest zeta potentials for CaCO₃ while both additives diminished the incrustation. PMAA-PSS, however, also decreased the incrustation, although it hardly affects the zeta potential of CaCO₃. The zeta potential of CaCO₃ in the presence of 50 ppm PAA is comparable to the values obtained with PMA-PSS and PSS. In the presence of PAA, however, the highest incrustation was found, even higher than in the blank experiments. The sequence of the zeta potentials of CaCO₃ is thus different from the observed sequence in incrustation.

Table 5.2 shows that the zeta potential of cotton slightly changes in the presence of the polyelectrolytes but none of these effects is significant, as is already discussed in section 5.5.2. Thus the influence of the polyelectrolytes on the incrustation cannot be related with their impact on the zeta potential of cotton.

Because of the reasons given above it can be concluded that sterical hindrance or electrostatic repulsion forces, caused by adsorption of the polyelectrolytes on CaCO₃ and/or cotton, are not likely to play the predominant role in determining the incrustation. Another more logical
mechanism is that the polyelectrolytes affect the incrustation by influencing
the nucleation and growth of CaCO₃.

5.7. Conclusions

- The sequence in degree of adsorption of the polyelectrolytes on CaCO₃
  is: PMA-PSS > PSS > PMA-PAMPS = PAA. PMAA-PSS did not adsorb
  in measurable amounts.
- Addition of 50 ppm of the polyelectrolytes affected the zeta potential of
  CaCO₃. In all cases negative zeta potentials were found and the zeta
  potential became more negative in the following sequence: blank >
  PMAA-PSS > PMA-PAMPS > PAA > PSS > PMA-PSS.
- The following correlation seems to exist: the higher the polyelectrolyte
  adsorption on CaCO₃ the lower the zeta potential.
- For the degree of adsorption on cotton the following sequence is
  observed: PMA-PAMPS > PAA. For PMA-PSS, PMAA-PSS and PSS no
  adsorption could be detected.
- A negative zeta potential of cotton was found in all experiments and the
  polyelectrolytes had no significant effect on the zeta potential of cotton
  in the added concentration range.
- The zeta potential of cotton did not change as a function of the
  polyelectrolyte concentration, expect for the addition of PMA-PAMPS
  between 50 and 100 ppm. This effect can be correlated with the
  measured adsorption isotherm of this compound on cotton.
- A bridging mechanism has been proposed in chapter 2 as an explanation
  for some of the effects of PAA and PMA-PAMPS on the incrustation of
  cotton. It is shown here that only these two polyelectrolytes adsorb on
  both CaCO₃ and cotton.
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- Sterical hindrance due to the adsorption of the polyelectrolytes on CaCO₃ and/or cotton can not explain the measured effects of the polyelectrolytes on the incrustation.
- The differences in the effects of the various polyelectrolytes on the incrustation of cotton can neither be attributed to their influence on the zeta potential of CaCO₃ or cotton.

Acknowledgements

The authors wish to thank Household and Personal Care Research, The Hague, for financial support. They are indebted to E.P.G. Cornelisens and J. Pronk for the stimulating discussions and to J. Oldenburg for the zeta potential measurements of CaCO₃. They are also grateful to D. Stajcer, L. Maass, M.S. de Jonge, J. Timmerman, M. Lentelink and V. Arkesteijn for their practical assistance.

References

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CHAPTER 6

INDUCTION TIME AND METASTABILITY
LIMIT IN NEW PHASE FORMATION

Abstract

An analysis is made of the induction time $t_i$ in new phase formation, i.e. of the time elapsing before the onset of the process. A general formula for $t_i$ is proposed which is valid for any number of nuclei appearing and growing in the parent phase and which unites the known expressions for $t_i$ only applicable when either one or a statistically large number of nuclei are involved in the process. This formula for $t_i$ is used for determination of the metastability limit in new phase formation, i.e. of the critical (or maximum) supersaturation below which the parent phase can stay long enough in metastable equilibrium.

INDUCTION TIME AND METASTABILITY LIMIT

6.1. Introduction

The potentiality to realise thermodynamically metastable states is a characteristic feature of the first-order phase transitions. Upon supersaturating the parent phase, a certain induction time (or period) $t_i$ may elapse before an appreciable amount of the new phase is formed. This time is a measure of the "ability" of the system to remain in metastable equilibrium and can, therefore, be used to determine the metastability limit of the parent phase, i.e. the critical (or maximum) supersaturation below which this phase can stay long enough without losing its metastability.

So far, two approaches have been most widely used for the theoretical determination of $t_i$. The first one is based on the assumption that the appearance of the first nucleus is the event that brings the system out of its metastable equilibrium [1-9]. In this case, as in growth of crystals by two-dimensional (2D) nucleation (e.g. [10]), one can speak of a mononuclear (MN) mechanism of losing metastability. The second approach [10-14] relies on the presumption that the formation of a statistically large number of nuclei and their growth to detectable sizes are responsible for the breakdown of the metastable equilibrium. Accordingly, it can be said that in this case the metastability is lost by a polynuclear (PN) mechanism which is known (e.g. [10]) to be operative also in the nucleation-mediated growth of crystals.

Although in their own right both the MN and the PN approaches are correct, they lead to different expressions for $t_i$, since they describe only the two limiting cases of nucleation that can be encountered in practice. For instance, under otherwise identical conditions, the MN and PN mechanisms are operative for smaller and larger volumes, respectively, of the studied metastable phase, because the number of nuclei formed in it increases with its volume. It should be noted as well that, experimentally, it is not always
possible to know a priori whether given $t_i$-data have to be interpreted in terms of the MN or the PN mechanism. It is thus clear that a more comprehensive theoretical description of the induction time is desirable in order to unite the MN and PN approaches and facilitate the analysis of experimental data. Progress in treating the two approaches from a unified point of view has recently been made in the cases of crystallization of small particles and droplets [15] and of nucleation-mediated growth of crystals [16].

The aim of the present paper is (i) to derive a general formula for the induction time $t_i$ valid irrespective of whether metastability is lost by the appearance of one, several or many nuclei of the new phase, and (ii) to apply this formula for determination of the critical supersaturation of vapours and solutions below which they can stay long enough in metastable equilibrium.

6.2. The induction time

The present analysis is restricted only to the case when a parent phase of fixed volume $V$ is held at constant supersaturation $\Delta \mu$ established at the initial moment $t = 0$. We assume also that the nuclei of the new phase form progressively at a constant nucleation rate $J$ ($m^{-3}s^{-1}$) and that they grow in one, two or three dimensions without changing a given regular shape.

6.2.1 The mononuclear approach

Let us first consider the MN mechanism. The probability $P_1$ that at least one nucleus is formed in the system within time $t$ is known to be of the form [17]

$$P_1(t) = 1 - \exp(-J\mu t)$$  \hspace{1cm} (1)

and the mean time $t_{MN} = \int_0^\infty t \, dP_1(t)$ for appearance of the first nucleus is,
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therefore, given by [17]
\[ t_{MN} = \frac{1}{JV}. \] 

(2)

Since it is postulated that the system loses its metastability just at the moment when the first nucleus comes into being, the induction time \( t_i \) for new phase formation coincides with \( t_{MN} \), i.e. (refs.[1-9])
\[ t_i = \frac{1}{JV}. \] 

(3)

This equation gives \( t_i \) in the scope of the MN approach. Strictly speaking, it can be used for analysis of \( t_i \)-data only if they are obtained by an experimental technique allowing detection of the presence of microscopic volumes of the order of the volume of the nucleus which, typically, consists of about 10 to 100 atoms (or molecules). If the \( t_i \)-data are obtained by a method involving three-dimensional (3D) growth of the nucleus to a registrable macroscopic volume \( V_{macr} \) which is a fixed fraction \( \alpha = V_{macr}/V \) of the volume of the parent phase and if \( G \) is the growth rate, the experimental error vanishes only when \( G \to \infty \), since then the growth time \( t_G \approx V_{macr}^{1/3}/G = (\alpha V)^{1/3}/G \to 0 \). The requirement \( t_G << t_{MN} \) sets up the limit of applicability of eq.(3) to \( t_i \)-data based on volume-registering techniques:
\[ V << \alpha^{-1/4}(G/J)^{3/4}. \] 

(4)

For example, with a typical value for \( \alpha = 10^{-4} \) and with a rather high growth rate \( G = 1 \, \mu m \, s^{-1} \) and rather low nucleation rate \( J = 1 \, cm^{-3} \, s^{-1} \), it follows from (4) that if the condition \( V << 10 \, mm^3 \) is not satisfied experimentally, the use of eq.(3) is not legitimate.

6.2.2 The polynuclear approach: 3D growth at constant rate

Let us now consider the PN mechanism. It is operative in the opposite extreme, i.e. when
\[ V >> \alpha^{-1/4}(G/J)^{3/4}, \] 

(5)
as then more nuclei have time to come into being while the first nucleus
grows to a macroscopic size. The probability $P$ that the phase transformation
is accomplished within time $t$ is equal to the ratio $V_{\text{new}}(t)/V$, where $V_{\text{new}}(t)$
is the volume of the new phase at time $t$. According to Kolmogorov [18] and
Avrami [19], most generally,

$$P(t) = 1 - \exp[-V_{\text{ex}}(t)/V]$$  \hspace{1cm} (6)

where $V_{\text{ex}}$ is the so-called extended volume of the new phase, i.e. the volume
that this phase would have if there were no contacts between the growing
particles. When nucleation proceeds at constant rate $J$, $V_{\text{ex}}$ is given by the
expression

$$V_{\text{ex}}(t) = c_m JV_0 \int_0^t r^m(t',t) \, dt'$$  \hspace{1cm} (7)

in which $m = 1, 2, 3$ is the dimensionality of growth, $c_m$ is a shape factor
(see Table 6.1), and $r(t',t)$ is the radius at time $t$ of the particles nucleated
at time $t' \leq t$.

**Table 6.1** The power $n$ and the shape factor $a_n$ for parabolic ($v = 1/2$) and
linear ($v = 1$) 1D growth of needles with constant cross-sectional
area $A$, 2D growth of disks or squares with constant thickness $H$
and 3D growth of spheres or cubes.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$n$</th>
<th>$a_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D growth ($m = 1$, $c_1 = 2A$ (needles))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>3/2</td>
<td>4A/3</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>$A$</td>
</tr>
</tbody>
</table>

| 2D growth ($m = 2$, $c_2 = \pi H$ (disks), 4H (squares)) |     |                |
| 1/2      | 2   | $\pi H/2$ a)  |
| 1        | 3   | $\pi H/3$ a)  |

| 3D growth ($m = 3$, $c_3 = 4\pi/3$ (spheres), 8 (cubes)) |     |                |
| 1/2      | 5/2 | $8\pi/15$ c)   |
| 1        | 4   | $\pi/3$ c)     |

a) Disks, b) Squares, c) Spheres, d) Cubes.
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In the case considered in this subsection of 3D growth obeying the law 
\( r(t', t) = G(t-t') \), using \( m = 3 \) in eq.(7) and substituting the resulting \( V_{\text{ex}}/V \) in 
(6) yields [18,19]

\[
P(t) = 1 - \exp(-aJG^3t^4) \tag{8}
\]

where \( G \) is the growth rate and \( a_4 = c_3/4 \) is a numerical shape factor (see Table 6.1). Hence, in this case of growth the mean time \( t_{\text{PN}} = \int_0^\infty t \, dP(t) \) for 
formation of new phase by the PN mechanism reads

\[
t_{\text{PN}} = \frac{\Gamma(5/4)}{(aJG^3)^{1/4}} \tag{9}
\]

where \( \Gamma(5/4) \approx 0.91 \) (\( \Gamma \) is the complete gamma-function).

Since, physically, \( t_{\text{PN}} \) may be considered as the induction time for new 
phase formation, eq.(9) can be used for definition of \( t_i \) in the scope of the PN 
approach. Recalling, however, that experimental \( t_i \)-data are also obtained by 
techniques sensitive to the presence of a certain macroscopic volume \( V_{\text{macr}} \leq V \) 
of the new phase, it is more appropriate to define \( t_i \) as the time needed for 
the formation of this volume which, as already mentioned, is a specified 
fraction \( \alpha = V_{\text{macr}}/V \) of \( V \). Thus, from the definition equality \( V_{\text{new}}(t_i) = V_{\text{macr}} \) 
presented in the form \( P(t_i) = \alpha \) and from (8) it follows that [11,14]

\[
t_i = (\alpha/aJG^3)^{1/4} \tag{10}
\]

provided \( \alpha < < 1 \) (then \( \ln(1-\alpha) \approx -\alpha \)). It is seen that \( t_i \) differs trivially from \( t_{\text{PN}} \) 
by a numerical factor.

Eq.(10) gives \( t_i \) in the scope of the PN mechanism when nucleation and 
3D growth occur at constant rates. As seen, it predicts a much weaker 
dependence of \( t_i \) on \( J \) than does eq.(3) of the MN approach and, besides, a 
dependence on \( G \), but no dependence on \( V \). The question, therefore, arises 
about passing from eq.(3) to eq.(10) when the experimental conditions change 
from satisfying (4) to satisfying (5), i.e. about finding a general formula for 
\( t_i \) applicable also when several nuclei, and not only one or many, bring about 
the metastability breakdown.
6.2.3 General formula for $t_\varepsilon$: 3D growth at constant rate

The answer of essentially the same question as the one above has already been given in the case of nucleation-mediated growth of atomically smooth crystal faces [10,16]. It has been established by Monte Carlo simulation techniques that the crystal growth rate $R$ (m s$^{-1}$) resulting from the birth and spread of one, several or many 2D nuclei of monoatomic height $h$ (m) can be expressed as (see eqs.(1), (2) and (7) of Ref.16)

$$
1/R = 1/R_{MN} + 1/R_{PN}
$$

(11)

where $R_{MN}$ and $R_{PN}$ are, respectively, the growth rates corresponding to the MN and PN mechanisms when only one or statistically many 2D nuclei appear on the crystal surface. The steady state growth rate according to the MN mechanism is given by (e.g. [10,16])

$$
R_{MN} = hJ_{2D}A
$$

(12)

where $J_{2D}$ (m$^{-2}$s$^{-1}$) is the 2D nucleation rate and $A$ (m$^2$) is the area of the crystal face. The expressions derived for the steady state growth rate according to the PN mechanism have the general form (e.g.[10,16])

$$
R_{PN} = h\beta(bJ_{2D}v^2)^{1/3}
$$

(13)

where $\beta$ is a constant numerical factor close to unity, $b$ is a geometrical shape factor for the 2D nuclei and $v$ (m s$^{-1}$) is the spreading velocity of the 2D nuclei.

The mean time $\theta$ (s) to build up a single monolayer by any number of 2D nuclei is by definition

$$
\theta = h/R = h/R_{MN} + h/R_{PN}
$$

(14)

The mean times $\theta_{MN}$ and $\theta_{PN}$ to build up a monolayer by only one or statistically many 2D nuclei can be written as

$$
\theta_{MN} = h/R_{MN} = 1/J_{2D}A
$$

(15)

$$
\theta_{PN} = h/R_{PN} = 1/[\beta b^{1/3}(J_{2D}v^2)^{1/3}]
$$

(16)
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Physically, there is a full analogy between the 2D problem solved in the case of nucleation-mediated growth of crystals and the 3D problem considered here. Accordingly the derived expressions for both cases are very similar. Compare e.g. eqs.(2) and (9) related with respectively the MN and PN mechanisms for the 3D system with eqs.(15) and (16) for the 2D system. By using eqs.(15) and (16) we can rewrite eq.(14), which has been verified by Monte Carlo simulations [16], in the form \( \theta = \theta_{MN} + \theta_{PN} \). Adapting this equation for the 3D system results in \( t_i = t_{MN} + t_{PN} \). Substitution of eqs.(3) and (10) into this last equation gives

\[
t_i = \frac{1}{JV} + \left( \frac{\alpha}{a_f G^3} \right)^{1/4}
\]

(17)

Eq.(17) is the sought general formula for \( t_i \) valid irrespectively of whether one, several or many nuclei cause the loss of metastability of the supersaturated parent phase. In the limiting case of MN mechanism, i.e. when (4) is fulfilled, eq.(17) simplifies to (3). In the opposite extreme specified by (5), eq.(17) passes into eq.(10) of the PN mechanism.

Shown in fig.6.1 is \( t_i \) from (17) as a function of the volume \( V \) of the metastable parent phase for values of \( J=1 \) and \( 10^6 \text{ cm}^{-3}\text{s}^{-1} \) and \( G=0.1 \) and \( 1 \mu\text{m s}^{-1} \) (as indicated) provided \( \alpha=10^{-4} \) and \( a_t=\pi/3 \). The inclined and horizontal linear portions of the \( t_i(V) \) dependence correspond to eqs.(3) and (10), respectively, of the MN and PN mechanisms. Extrapolation of these portions up to crossing yields the \( V \)-values above which the MN formula (3) cannot be used, since it predicts too short induction times.

Fig.6.2 depicts the dependence (17) of \( t_i \) on \( J \) for a supersaturated phase of volume \( V=10^6 \text{ cm}^3 \). The possible change in \( G \) while changing \( J \) (e.g. by changing the supersaturation) is neglected and again \( G=0.1 \) and \( 1 \mu\text{m s}^{-1} \) (as indicated) as well as \( \alpha=10^{-4} \) and \( a_t=\pi/3 \) are used. The more and less steeply inclined linear portions of the \( t_i(J) \) dependence represent, respectively, the MN and PN formulae (3) and (10). Extrapolating the MN linear portion to
Figure 6.1
Dependence of the induction time from eq.(17) on the volume of the parent phase for $J = 1$ and $10^6$ cm$^{-3}$s$^{-1}$ and $G = 0.1$ and 1 μm s$^{-1}$ (as indicated). The inclined and horizontal linear portions correspond to eqs.(3) and (10), respectively, of the mononuclear and polynuclear mechanisms.

Figure 6.2
Dependence of the induction time from eq.(17) on the nucleation rate for $G = 0.1$ and 1 μm s$^{-1}$ (as indicated) and $V = 10^{-6}$ cm$^3$. The MN and PN linear portions correspond to eqs.(3) and (10), respectively, of the mononuclear and polynuclear mechanisms.
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higher J-values shows that even for a system with relatively small size of \( V^{1/3} = 100 \ \mu m \), the MN mechanism is not operative when \( J > 10^5 \ \text{cm}^{-3}\text{s}^{-1} \). Accordingly, using eq.(3) could then lead to a very erroneous determination of \( t_i \).

6.2.4 General formula for \( t_i \): 1D, 2D or 3D growth

It is worth generalizing eq.(17) to cover other possible cases of growth of the nucleated particles as well. A typical growth law is of the form (e.g. [10])

\[
    r(t',t) = G'(t-t')^v
\]

where \( v > 0 \) is a number ranging usually from 1/2 to 1, and G may be called growth constant (when \( v = 1 \), G is merely the growth rate). For instance, \( v = 1/2 \) or 1 in some cases of growth controlled by volume diffusion or by surface incorporation. Thus, for growth specified by (18), using (7), we find from (6) that

\[
    P(t) = 1 - \exp(-a_n J G^{n-1} t^n) \tag{19}
\]

where \( n = m v + 1 \) and \( a_n = c_m / n \). The shape factors \( c_m \) and \( a_n \) and the values of \( n \) for \( v = 1/2 \) and 1 are presented in Table 1 in the cases of 1D growth of needles with constant cross-sectional area \( A \), 2D growth of disks or square plates with constant thickness \( H \) and 3D growth of spheres or cubes. In all these cases \( P \) from (19) is a sigmoidal function of \( t \), since \( n \) has values greater than unity.

From (19) and the definition equality \( P(t_i) = \alpha \) we can again determine \( t_i \) in the scope of the PN mechanism (\( \alpha < < 1 \)):

\[
    t_i = (a_n J G^{n-1})^{1/n}. \tag{20}
\]

Hence, as before, expressing \( t_i \) as a sum of the right-hand sides of eqs.(3) and (20) leads to the following general formula for the induction time valid regardless of the number of nuclei in the metastable phase provided that
they appear at constant rate $J$ and grow in one, two or three dimensions according to the growth law (18):

$$t_i = 1/JV + (\alpha/a_nJG^{n-1})^{1/n}.$$  \hspace{1cm} (21)

As seen, in the case of 3D growth at constant rate (then $n=4$, since $m=3$ and $v=1$) eq.(21) passes into (17). Also, when

$$V << (a_n/\alpha)^{1/n}(G/J)^{(n-1)/n},$$  \hspace{1cm} (22)

eq(21) reduces to eq.(3) of the MN approach. In the other extreme, i.e. when $V \to \infty$, $J \to \infty$ and/or $G \to 0$, eq.(21) takes the form of eq.(20) of the PN approach.

6.3. The metastability limit

The above considerations show how the induction time depends on the two basic kinetic parameters of the process of new phase formation - the nucleation rate $J$ and the growth constant (or, in particular, growth rate) $G$. Since both $J$ and $G$ are functions of the supersaturation $\Delta \mu$ imposed on the parent phase, eq.(21) actually gives implicitly the dependence of $t_i$ on $\Delta \mu$ in the case when $\Delta \mu$ is kept constant. For that reason, eq.(21) can be used for determination of the critical supersaturation $\Delta \mu_c$ below which the parent phase may remain in metastable equilibrium an arbitrarily long, previously specified time $\tau$. Thus, by definition, $\Delta \mu_c$ is the solution of the equation

$$t_i(\Delta \mu_c) = \tau$$  \hspace{1cm} (23)

and has the physical meaning of metastability limit of the parent phase. It should be emphasized, however, that rather than having universal thermodynamic validity, the so-defined $\Delta \mu_c$ is a quantity of essentially kinetic nature, because it is sensitive not only to the particular dependences of $J$ and $G$ on $\Delta \mu$, but also to the arbitrary choice of the time ($\tau$) and space ($V$) scales. In the following, we shall determine $\Delta \mu_c$ in the case of isothermal formation
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of droplets or crystallites in supersaturated vapours or solutions.

Let us first determine the dependence of $t_i$ on $\Delta \mu$. For both vapours and solutions $\Delta \mu$ is known to be given by (e.g. [4,10])

$$\Delta \mu = kT \ln S$$  \hspace{1cm} (24)

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $S$ is the supersaturation ratio: $S = p/p_e$ for vapours and $S = a/a_e$ for solutions, $p$ and $a$ being, respectively, the actual vapour pressure and solute activity, and $p_e$ and $a_e$ being their equilibrium values. In classical approximation, the $S$-dependence of $J$ is of the form (e.g. [4])

$$J = K_J S \exp(-B/\ln^2 S)$$  \hspace{1cm} (25)

where $K_J$ and $B$ can be regarded as practically $S$-independent kinetic and thermodynamic parameters, respectively. As to the dependence of $G$ on $S$, we choose the formula

$$G = K_G (S-1)$$  \hspace{1cm} (26)

known to hold in various cases of growth of condensed phases [5,10] ($K_G$ is a constant factor). From eq.(21) we thus get

$$t_i(S) = (K_J V)^{-1} S^{-1} \exp(B/\ln^2 S)$$

$$+ \left( \alpha/a_e K_J K_G^{-1} \right)^{1/n} [S(S-1)^{n-1}]^{-1/n} \exp(B/n \ln^2 S).$$  \hspace{1cm} (27)

This dependence of $t_i$ on $S$ is shown in fig.6.3 by the solid curves. The calculation is done for 3D growth of spherical particles with $n=4$, $a_i = \pi/3$, $a = 10^{-4}$, $V = 1 \text{ cm}^3$, $K_J = 10^{25} \text{ cm}^{-3} \text{ s}^{-1}$, $K_G = 0.1 \mu \text{m s}^{-1}$ and $B = 30$ and 300 (as indicated). These $B$-values correspond, respectively, to relatively low and high specific surface free energies of the new phase/parent phase interface.

As seen from (27), for smaller $S$-values the MN mechanism is operative and then this equation reduces to the known formula (e.g. [6])

$$t_i(S) = (K_J V)^{-1} S^{-1} \exp(B/\ln^2 S)$$  \hspace{1cm} (28)

which follows also from (3) and (25). When $S$ is higher, however, the PN mechanism is effective and eq.(27) takes the form

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Figure 6.3
Dependence of the induction time from eq.(27) on the supersaturation ratio for \( B = 30 \) and 300 (as indicated). The dotted (MN) and dashed (PN) curves represent eqs.(28) and (29), respectively, of the mononuclear and polynuclear mechanisms.

\[
t_i(S) = \left( \frac{\alpha}{a_n K_J K_G^{n-1}} \right)^{1/n} \left[ S(S-1)^{n-1} \right]^{-1/n} \exp(B/n \ln^2 S) \tag{29}
\]

which can be obtained from (20), (25) and (26) as well. The supersaturation ratio \( S_i \), limiting the regions of validity of eqs.(28) and (29) can be found by equalizing the two summands on the right-hand sight of (27) and putting \( [S_i(S_i-1)^{n-1}]^{1/n} \approx S_i; \)

\[
S_i = \exp[(n-1)B/\ln(\alpha V^{n}K_J^{n-1}/a_n K_G^{n-1})]^{1/2} \tag{30}
\]

The same result for \( S_i \) follows upon using (25) and (26) in (22) when this is regarded as an equality. We note as well that \( S_i \) is sensitive to the volume of the parent phase: with the above values of \( n, a_p, \alpha, K_J, K_G \) and with \( B=300 \), for instance, we find that \( S_i = 12.3 \) and 8.4 when \( V = 10^{-6} \) and 1 cm\(^3\), respectively. The dotted and dashed curves in fig.6.3 represent eqs.(28) and (29), respectively, and visualize the change from stronger to weaker \( t_i(S) \) dependence occurring with increasing \( S \) when the MN mechanism is replaced.
by the PN one. It is clearly seen that the error in $t_i$ may be very large if the
MN formula (28) is used when $S > S_i$.

With the help of the $t_i(S)$ dependence (27) and eq.(23) we can now
determine the critical supersaturation ratio $S_c$ which, according to (24), is
related to $\Delta \mu_c$ by $\Delta \mu_c = k T \ln S_c$. The resulting formula for $S_c$ reads:

$$(K_j V)^{-1} S_c^{-1} \exp(B/\ln^2 S_c) + \left(\alpha/a_n K_j K_G^{-n-1}\right)^{1/n} [S_c(S_c-1)^{n-1}]^{-1/n} \exp(B/n \ln^2 S_c) = \tau \quad (31)$$

Unfortunately, this algebraic equation for $S_c$ has no exact analytical
solution and only gives $S_c$ implicitly. We shall, therefore, find explicit
approximate formulae for $S_c$ only in the two limiting cases when either the
MN or the PN mechanism is operative. Neglecting the second summand on
the left-hand side of (31) and putting $S_c \approx 1$ in the pre-exponential factor we
arrive at the familiar expression (e.g.[1,4,20])

$$S_c = \exp[B/\ln(K_j V \tau)]^{1/2} \quad (32)$$
valid for $S_c < S_i$ and pertinent to the MN mechanism. In the opposite extreme,
 omission the first summand on the left-hand side of (31) and approximating
$[S_c(S_c-1)^{n-1}]^{1/n}$ by 2, we find that

$$S_c = \exp[B/\ln(2^n a_n K_j K_G^{-n-1} \tau^n / \alpha)]^{1/2} \quad (33)$$
provided $S_c > S_i$ so that the PN mechanism is operative. The above two
formulae can also be derived from eqs.(23), (28) and (29).

Three points are worth making in respect to eqs.(32) and (33). First,
these show that both the MN and the PN mechanisms lead to the same
dependence of $S_c$ on the specific surface free energy $\sigma$ of the parent
phase/new phase interface. Indeed, since according to the classical nucleation
theory [1,4] $B \propto \sigma^3$, both (32) and (33) yield the known result (e.g. refs.
[4,21]) $\ln S_c \propto \sigma^{3/2}$. Second, while the MN formula (32) predicts a dependence
of $S_c$ on $V$, according to (33) there is no such dependence in the PN case.
Finally, it is seen from eqs.(32) and (33) that for a given system, numerically,$S_c$ can be very different (especially for higher $B$-values) depending on
whether it is calculated on the basis of the MN or the PN mechanism. For example, with \( \tau = 1 \text{ s}, n = 4 \) and the values of \( a_4, \alpha, K_J \) and \( K_G \) used above, from (33) it follows that \( S_c = 2.5 > S_t = 2.0 \) and \( 18.6 > S_t = 8.4 \) for \( B = 30 \) and 300, respectively, so that (as \( S_c > S_t \)) it is the use of this equation that is legitimate. If instead of (33) the MN formula (32) is employed, with \( V = 1 \text{ cm}^3 \) and the same \( \tau \) and \( K_J \) values the result is an erroneous, significantly reduced \( S_c = 2.1 \) and 9.8 for \( B = 30 \) and 300, respectively. Since so far comparison between experimental and theoretical \( S_c \)-values has usually been made by means of eq.(32) (e.g. refs.[1,4,20]) the above example shows that this comparison needs a revision on the basis of eq.(33) in those cases when the experimental \( S_c \)-data have been obtained by registration of many droplets or crystallites in the parent phase. Among the numerous results in ref.[20], for instance, while \( S_c = 4.9 \) from experiments [21] on crystallization of \( \text{Ba(IO}_3)_2 \), theoretically [20], \( S_c = 3.7 \) from eq.(32) with \( K_J = 10^{26} \text{ cm}^{-3}\text{s}^{-1}, V = 1 \text{ cm}^3, \tau = 1 \text{ s} \) and \( B = 104 \). According to eq.(33), however, using the above parameter values along with \( n = 4, a_4 = \pi/3, \alpha = 10^{-4} \) and \( K_G = 0.1 \mu\text{m s}^{-1} \) leads to an appreciably higher theoretical metastability limit \( S_c = 5.7 \).

6.4. Conclusions

The analysis made provides a general formula, eq.(21), for the induction time \( t_i \) in new phase formation, which is valid for any number of nuclei taking part in the process and which reduces to the known expressions for \( t_i \), derived in the scope of either the MN or the PN mechanism. This formula is applicable when the nucleation rate is time-independent and the growth law is given by eq.(18). The limit of validity of eq.(3) of the MN approach is specified by the condition (22) which leads to the conclusion that, typically, the MN mechanism is unlikely to be operative in supersaturated phases of
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volume $V>10$ mm$^3$ and that this number can often be much smaller. Unjustified application of the MN formula (3) to cases when the PN mechanism is in force (e.g. for larger V- and/or J-values) could yield very erroneous, low $t_i$-values.

The use of eq.(21) for determination of the metastability limit in new phase formation results in the general formula (31) for the critical supersaturation ratio $S_c$ of the parent phase. Explicit expressions, eqs.(32) and (33), follow from (31) only for lower ($S_c<S_p$) or higher ($S_c>S_p$) values of $S_c$ when either the MN or the PN mechanism is operative, respectively. The limiting supersaturation ratio $S_i$ is given by eq.(30) and depends on the volume $V$ of the parent phase. In both the MN and the PN cases $S_c$ is proportional to $\sigma^{3/2}$ but the $S_c$-value itself could be much lower (particularly for higher B, i.e. $\sigma$-values) if incorrectly calculated from the classical MN formula (32) in cases when the PN mechanism is in force. Provided the experimentally detectable volume fraction $\alpha$ is the same, according to eq.(33) of the PN mechanism, $S_c$ does not change with the volume of the parent phase.

Acknowledgement

The authors wish to thank Dr. J.P. van der Eerden of the University of Nijmegen, the Netherlands, for the stimulating discussions.

References

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1967) 419.


CHAPTER 7

THEORY OF INDUCTION TIME IN SEEDED AND UNSEEDED PRECIPITATION

Abstract

General expressions are derived for the induction time in seeded and unseeded precipitation. These expressions are used for finding the dependence of the induction time on the supersaturation for different growth mechanisms. It is shown how the nucleation and growth rates of the crystallites can be determined separately by a combined analysis of the induction time in both seeded and unseeded precipitation. Such an analysis allows the effect of additives on the nucleation and growth rates to be also separately studied.

INDUCTION TIME IN SEEDED AND UNSEEDED PRECIPITATION

7.1. Introduction

Sparingly soluble salts can be precipitated via primary nucleation and growth from supersaturated aqueous solutions. The supersaturation is mostly achieved by rapid mixing of stable solutions containing the precipitating ions. A commonly used parameter to characterize the precipitation process is the induction time, which is generally defined as the time elapsing between the creation of the supersaturation and the formation of a detectable quantity of the precipitate. To determine the induction time several techniques are applied, e.g. visual observation [1], measurement of turbidity [2-4] or of a concentration-dependent property such as the solution conductivity [5], and recording of one of the reacting species by an ion-selective electrode [6].

So far, the theoretical description of the induction time has been devoted mostly to the case of unseeded precipitation, when crystallites nucleate and grow during the whole process [2,7-12]. In this case both the rate of primary nucleation and the growth rate of the crystallites determine the induction time. Recently, Söhnel and Mullin [10] have analyzed the induction time resulting from various nucleation and growth mechanisms.

Experimental induction times are usually obtained from unseeded precipitation [1-6,8,13,14]. As has already been pointed out by Mullin [9, p.221], however, it should in principle also be possible to find induction times in other types of crystallization experiments, which we will call seeded precipitation. Here crystallites with a given number density are already present at the start of the process, which can be realized for example by extremely rapid (instantaneous) primary nucleation or by addition of seeds with negligible sizes. Thus, in this case the induction time is determined by the growth rate only. It is a well-established fact that the formation of primary nuclei can be suppressed by the addition of seeds. Addition of a
sufficient number of seeds can even eliminate completely the induction time (e.g.[15,16]). In these cases the growth rate can be obtained for instance from the desupersaturation curve.

Additives are well-known to have a great impact on the precipitation kinetics of mineral salts. Especially their effect on the growth kinetics has been thoroughly investigated by many authors [9,17-25]. In general, it can be concluded that additives mostly retard the crystal growth by their preferential adsorption onto the crystal surface. In some cases, however, a stimulation of the growth by additives has been reported [26].

Much less information can be found in the literature about the impact of additives on nucleation. Inhibition [27] as well as stimulation [28] of the nucleation by different types of additives have been observed. Blockage of the attachment sites on the nucleus surface by the additive has been suggested as a mechanism in the case of inhibition. Nucleation can be stimulated when additive adsorption lowers the surface free energy of the nucleus or when the additives provide active sites for the nucleation. Since additives are increasingly applied in many industrial processes, it will be important to know their precise effect on the nucleation kinetics. So far, such information has been deduced from unseeded precipitation experiments. As already mentioned, however, the commonly applied registration techniques cannot differentiate between nucleation and growth. We therefore suggest in this study to combine experiments on the induction time in seeded and unseeded precipitation in order to analyze the nucleation and the growth processes separately. Such a combined analysis can also reveal the effect of the additives on each of these two processes independently.

The aim of this chapter is: to find theoretical expressions for the induction time in both seeded and unseeded precipitation, which are applicable in both the absence and presence of additives.
7.2. Theory

7.2.1. Seeded precipitation

We consider a system with a given volume $V$ at constant absolute temperature $T$ and constant supersaturation $\Delta \mu$, which is the difference in the chemical potential of the precipitating species in the supersaturated and in the saturated solution. At the initial moment $t=0$, crystallites of supernucleus size are generated either by instantaneous primary nucleation or by introduction of microscopically small seeds of the phase to be formed in the system. It is assumed that during the whole process only growth of these initial crystallites takes place and that neither secondary nucleation nor agglomeration occurs. Secondary nucleation has been reported to be irrelevant for the precipitation of sparingly soluble substances [29]. It is more difficult to predict the agglomeration behaviour, since this process is strongly dependent on the precipitating salt and the composition of the solution. In general, agglomeration is found to be of minor importance when the particles are charged [30]. The charge of the particles can be shielded by background electrolyte addition. For instance, for calcium oxalate it was shown [6] that high NaCl concentrations enhance agglomeration. Below 0.1 M background electrolyte no agglomeration was noticed.

According to the theory of Kolmogorov [31] and Avrami [32], most generally, the volume $V_{\text{new}}$ of the new phase at time $t$ is given by

$$V_{\text{new}}(t)/V = 1 - \exp[-V_{\text{ex}}(t)/V], \quad (1)$$

where $V_{\text{ex}}$ is the so-called extended volume of the new phase, which is the volume this phase would have if there were no contacts between the growing crystallites.

When all crystallites have initially the same radius $r_{s}$, $V_{\text{ex}}$ can be
represented as

\[ V_{sx}(t) = V \cdot N \cdot c_m [r^m(t) - r_s^m] \].

(2)

Here \( N(\text{m}^{-3}) \) is the number density of the crystallites in the solution, \( m = 1, 2 \) or 3 is the dimensionality of growth, \( c_m \) is a shape factor (see Table 7.1), assumed to be the same for the seeds and the growing crystallites, and \( r \) is the crystallite radius at time \( t \). Both \( r_s \) and \( r \) are effective quantities: for instance, when \( m = 1 \) (one dimensional (1D) growth of needle-like crystallites), they are the seed and crystallite half-lengths, respectively.

A typical growth law is of the form (e.g. [7,9,33])

\[ r(t) = r_s + G^v t^v \],

(3)

where \( v > 0 \) is a number ranging usually from 0.5 to 1 and \( G \) may be called growth constant. When \( v = 1 \), \( G(\text{m s}^{-1}) \) is merely the growth rate. For instance (see Table 7.2), \( v \) is equal to 0.5 or 1 in some cases of growth.

<table>
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<tr>
<th>( v )</th>
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<tr>
<td>1D growth (( m = 1 ))</td>
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<td>2D growth (( m = 2 ))</td>
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<td>1</td>
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<td>3D growth (( m = 3 ))</td>
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<td>1</td>
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INDUCTION TIME IN SEEDED AND UNSEEDED PRECIPITATION

controlled by volume diffusion or surface incorporation, respectively (e.g.[7,9,33]).

After combining eqs. (1) to (3), we find the following expression
\[ V_{\text{new}}(t)/V = 1 - \exp(-c_mN[(r_s + G^v t^n)^{m-1} - r_s^{m-1}]). \]  (4)

Experimentally, induction times are often obtained by techniques sensitive to the formation of a certain macroscopic volume \(V_{\text{macro}}<V\) of the new phase. We therefore define the induction time \(t_s\) in seeded precipitation, as the time needed for the formation of this volume which is a specified fraction \(\alpha=V_{\text{macro}}/V\) of \(V\).

From eq.(4) and the definition equality \(V_{\text{new}}(t_s)=V_{\text{macro}}\), the following general formula for \(t_s\) is obtained upon using the fact that for precipitation \(\alpha<<1\) (since then \(\ln(1-\alpha)\approx -\alpha\))
\[ t_s = \left\{ r_s \left[ (1 + \alpha/c_mr_s^{mN})^{1/m} - 1 \right] \right\}^{1/v}/G. \]  (5)

Two limiting cases concerning the total volume fraction \(c_mr_s^{mN}\) of the seeds can be recognized, in which the above expression for \(t_s\) is simplified. When this fraction is small enough, i.e. when
\[ c_mr_s^{mN} << \alpha, \]  (6)
it follows from eq.(5) that
\[ t_s = (\alpha/c_mr_s^{mN})^{1/mv}/G. \]  (7)
The opposite extreme belongs to the case that the volume fraction of the seeds is not negligibly small, i.e. when
\[ c_mr_s^{mN} >> \alpha. \]  (8)
Using the approximation \((1 + \alpha/c_mr_s^{mN})^{1/m} = 1 + \alpha/mc_mr_s^{mN}\), which is justified for small values of \(\alpha/c_mr_s^{mN}\), leads in combination with eq.(5) to
\[ t_s = (\alpha/mc_mr_s^{m-1N})^{1/v}/G. \]  (9)
Comparison of eqs.(7) and (9) shows that these equations are identical for \(m=1\) (1D growth) and that in this case the value of \(r_s\) is of no importance for the precipitation process. For \(m=2\) or 3, however, eqs.(7) and (9) represent
the two different limiting cases concerning the seed volume fraction.

Fig. 7.1 shows the dependence of \( t_s \) on \( N \), calculated from the general dependence (5), from eq. (7) for the limiting case of negligibly small volume fraction of the seeds and from eq. (9) for the opposite extreme belonging to the case that the volume fraction of the seeds is not negligibly small. The following parameters were used in the calculations: \( m = 3 \), \( \nu = 1 \), \( \alpha = 5 \times 10^{-8} \), \( c_s = 4\pi/3 \), \( r_s = 0.1 \, \mu m \) and \( G = 1 \, \text{nm/s} \).

Fig. 7.1 shows that the \( t_s(N) \) dependence is determined by the relative magnitudes of the volume fraction of the seeds, and of the smallest detectable volume fraction \( \alpha \) of the newly formed phase. In the calculations for fig. 7.1 the volume fraction of the seeds was changed by varying the number density \( N \) of the seeds, while \( \alpha \) was kept constant.

![Figure 7.1](image-url)

The dependence of the induction time \( t_s \) on the seed number density \( N \) computed from the general dependence (5), indicated by the solid curve, and the limiting cases of small volume fraction of the seeds (eq. (7), dashed line) and of large volume fraction of the seeds (eq. (9), dotted line).
INDUCTION TIME IN SEEDED AND UNSEEDED PRECIPITATION

The induction time $t_s$ is proportional to $N^p$, where the power $p$ is equal to the slope of the $t_s(N)$ dependence in a plot of $\log t_s$ versus $\log N$. Fig.7.1 shows that $p$ changes from 1/3 in case of a negligibly small volume fraction of the seeds, as predicted by eq.(7), to $p=1$ for the opposite extreme belonging to the case where the volume fraction of the seeds is not negligibly small, as can be seen from eq.(9). In the intermediate region where neither inequality (6) nor inequality (8) is satisfied, the general $t_s(N)$ dependence (5) has to be used, which passes smoothly from the first to the second limiting case with $1/3 < p < 1$.

Eqs.(7) and (9) are the sought general relations between the induction time $t_s$ and the growth constant or growth rate $G$. It is, however, also important to have a dependence of $t_s$ on the supersaturation. This can be obtained by introducing the dependence of $G$ on the supersaturation for various growth models. As known [10,14,34], the supersaturation $\Delta \mu$ which is the thermodynamic driving force per molecule of the precipitate, can be expressed as

$$\Delta \mu = \delta k T \ln S.$$  \hspace{1cm} (10)

Here $k$ is the Boltzmann constant, $\delta$ is the number of ions in the formula unit, and $S$ is the commonly used supersaturation ratio introduced for brevity by

$$S = (\Pi / \Pi_s)^{1/6},$$  \hspace{1cm} (11)

where $\Pi$ is the ionic activity product, and $\Pi_s$ is the thermodynamic solubility product.

For crystal growth from solution various growth models can be distinguished. Generally, the relationship between $G$ and $S$ is of the form

$$G(S) = K_G f(S),$$  \hspace{1cm} (12)

where $K_G$ is a $S$-independent factor, and $f(S)$ is a given function of $S$.

Combination of eqs.(7), (9) and (12) yields the following general $t_s(S)$
CHAPTER 7

dependence:

\[ t_s(S) = A_s/f(S), \quad (13) \]

the S-independent kinetic factor \( A_s \) being given by

\[ A_s = (\alpha/c_m N)^{1/m_v}/K_G, \quad (14) \]

for small volume fraction of the seeds, and

\[ A_s = (\alpha/m_c r_s^{-m-1} N)^{1/n}/K_G, \quad (15) \]

for large volume fraction of the seeds. Either of these equations for \( A_s \) is applicable when \( m=1 \).

We will now specify \( f(S) \) for the most relevant growth models in order to use it in eq.(13) for obtaining \( t_s \) as a function of \( S \).

Normal growth

For an atomically rough crystal face every site constitutes a growth site and growth proceeds by the so-called normal growth mechanism [33]. In this case \( v=1 \) and the growth rate \( G \) is determined by the net flux of growth units to the crystal surface which is proportional to \( (S-1) \), so that

\[ f(S) = (S-1) \quad (16) \]

and from (13)

\[ t_s(S) = A_s/(S-1). \quad (17) \]

Spiral growth

When screw dislocations emerge on the crystal surface, growth can be initiated by dislocations [35]. In this so-called parabolic rate model \( v=1 \) and the \( S \)-dependence of the growth rate \( G \) is determined by two factors. The first factor allows for the density of steps on the surface, which is proportional to \( \ln S \). The second factor takes into account the net flux of growth units to the surface, which is proportional to \( (S-1) \). The combination of these two factors leads to \( f(S) = (S-1)\ln S \), which for \( S \approx 1 \) transforms into
INDUCTION TIME IN SEEDED AND UNSEEDED PRECIPITATION

\[ f(S) = (S-1)^2. \]  \hspace{1cm} (18)

Nielsen [36], however, reported that experimental data can often be fitted by this parabolic law, even when lnS deviates markedly from (S-1). He therefore proposed that in those cases the integration of growth units into the kinks, and thus the kink density on the surface, is growth rate determining. Accounting for this effect, he showed that eq.(18) can be used in a wider range of S, and not only for S≈1. Assuming the validity of this, we will use eq.(18) for \( f(S) \), which after combination with eq.(13) yields

\[ t_s(S) = A_0/(S-1)^2. \]  \hspace{1cm} (19)

This \( t_s(S) \) dependence is the same as the one already given by Sühnel and Mullin [10] for the case when only growth and not nucleation determines the induction time.

Two-dimensional (2D) nucleation-mediated growth

Growth on atomically smooth surfaces can occur by formation and lateral growth of 2D nuclei. A rather general expression for the stationary 2D-nucleation rate \( J_{2D} \) is (e.g. [37])

\[ J_{2D} = K_{2D}S \exp(-B_{2D}/\text{ln}S), \]  \hspace{1cm} (20)

where \( K_{2D} \) is a kinetic factor, which is a weak function of S, and

\[ B_{2D} = \beta_{2D}\kappa^2a/\delta(kT)^2. \]  \hspace{1cm} (21)

Here \( \beta_{2D} \) is a numerical 2D shape factor (e.g. \( \pi \) for circles), \( \kappa \) (J m\(^{-1}\)) is the specific edge free energy of the nucleus and \( a \) is the molecular area.

For \( K_{2D} \) various dependences on S have been given in the literature [34,38,39], but in general the value of \( J_{2D} \) is dominated by the exponential term in eq.(20). For that reason hereafter \( K_{2D} \) will be considered as S-independent.

For the growth of large enough crystallites, the so-called polynuclear or "birth and spread" mechanism is operative, according to which each
monolayer of the crystal is built up via the appearance and spreading of numerous individual 2D nuclei. In this case \( v = 1 \) and the dependence of the growth rate \( G \) on the spreading velocity \( v \) and \( J_{2D} \) is given by the expression (e.g. [7])

\[
G = \epsilon dv^{2/3} J_{2D}^{1/3},
\]

(22)
in which \( \epsilon \approx 1 \), and \( d \) is the molecular diameter. Assuming a \( v(S) \) dependence of the normal growth type, \( v \propto (S-1) \), from eqs.(12), (20) and (22) it follows that

\[
f(S) = (S-1)^{2/3} S^{1/3} \exp(-B_{2D}/3\ln S),
\]

(23)
which is close to the \( f(S) \) dependence obtained in reference [39]. Upon using this \( f(S) \) function in eq.(13), the following expression for \( t_s \) is found:

\[
t_{s}(S) = A_s (S-1)^{-2/3} S^{-1/3} \exp(B_{2D}/3\ln S).
\]

(24)
A similar equation has been proposed by Söhnel and Mullin [10] for the case when only growth and not nucleation determines the induction time.

**Volume diffusion-controlled growth**

Growth can also be determined by transport of the solute through the solution to the crystal surface by diffusion or convection or both. For small crystals (< about 5 \( \mu m \)) convection has been reported to be a negligible factor [7,40]. Since the crystals in both seeded and unseeded precipitation are, by assumption, below this limit we will only consider pure diffusion-controlled growth. The diffusion flux of growth units is proportional to the difference between the bulk concentration and the concentration close to the crystal surface. In this case \( v = 1/2 \) and the \( f(S) \)-dependence for this mechanism can be represented as (e.g.[7,9,33])

\[
f(S) = (S-1).
\]

(25)
This leads (see also [7]) to the same \( t_s(S) \) relation as given by eq.(17) for normal growth
INDUCTION TIME IN SEEDED AND UNSEEDED PRECIPITATION

\[ t_u(S) = \frac{A_u}{(S-1)}, \]  

(26)

except that \( A_u \) from eqs. (14) and (15) for these two growth mechanisms differs in the value of \( \nu \) and in the parameters constituting \( K_0 \).

7.2.2. Unseeded precipitation

We consider the same system as in the seeded precipitation, but now we have progressive primary nucleation, with a stationary nucleation rate \( J (m^{-3} \ s^{-1}) \), instead of instantaneous primary nucleation or seeding. Nucleation is in principle a non-stationary process, because a certain time has to elapse between the creation of supersaturation and the achievement of the steady-state cluster distribution [11,37,41]. After this time, called nucleation time-lag, the steady-state nucleation rate is achieved. The time-lag effect on the induction time in unseeded precipitation has been analyzed elsewhere [11]. It was estimated by Söhnlen and Mullin [10] that the time-lag is often negligible for the precipitation of slightly soluble salts and we shall disregard it hereafter.

Recently, a general expression for the induction time in unseeded precipitation, \( t_u \), has been proposed [12] which is valid for any number of nuclei appearing and growing in the supersaturated solution. This expression for \( t_u \) reads

\[ t_u = \frac{1}{J \nu} + \left( \frac{\alpha}{a_n J G^{n-1}} \right)^{1/n}, \]  

(27)

where \( a_n = c_m / n \) is a shape factor and \( n = m \nu + 1 \).

The above equation contains two terms. The first one originates from the induction time for the mononuclear mechanism, operative provided the system loses its metastability when the very first nucleus is born (e.g. [7,9,10,42]). When metastability is lost by nucleation and growth of a statistically large number of nuclei, i.e. by the polynuclear mechanism, the
induction time can be described by the second term [2,7,10,11]. It follows from eq.(27) with typical values of $V$, $\alpha$, $J$ and $G$ for precipitation of mineral salts from solutions that the first term is often negligible with respect to the second one, so that

$$t_u = \left(\frac{\alpha}{a_n G^{n-1}}\right)^{1/n}.\quad (28)$$

To find the $t_u(S)$ dependence from this equation we shall use again the classical formula for the steady state nucleation rate which for 3D nucleation reads (e.g. [37])

$$J = K_j S \exp(-B/\ln^2 S),\quad (29)$$

where $K_j$ is a practically $S$-independent kinetic factor and

$$B = \beta \sigma^3 n^2/(kT)^3 \delta^2.\quad (30)$$

Here $\beta$ is a numerical shape factor (e.g. $16\pi/3$ for spheres), $n$ is the molecular volume, and $\sigma$ ($Jm^{-2}$) is an effective specific surface free energy. In the case of homogeneous nucleation $\sigma$ equals the specific surface free energy $\sigma_{homo}$ of the nucleus/solution interface, but it is smaller than $\sigma_{homo}$ when nucleation is heterogeneous.

With eqs.(12), (28) and (29) the following general expression for $t_u$ is found

$$t_u(S) = A_u \left[f(S)\right]^{-(n-1)/n} S^{-1/n} \exp(B/\ln^2 S),\quad (31)$$

in which the nucleation and growth pre-factors $K_j$ and $K_G$ are combined into the single $S$-independent kinetic factor

$$A_u = \left(\frac{\alpha}{a_n K_j K_G^{n-1}}\right)^{1/n}.\quad (32)$$

For $f(S)$ the same $S$-dependences have to be used as for the seeded precipitation. This leads to the following expressions for $t_u$ corresponding to the different growth mechanisms:

**Normal growth**

Combination of eqs.(16) and (31) results in $n = m + 1$

$$t_u(S) = A_u (S - 1)^{-(n-1)/n} S^{-1/n} \exp(B/\ln^2 S).\quad (33)$$

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INDUCTION TIME IN SEEDED AND UNSEEDED PRECIPITATION

Spiral growth

Using eqs. (18) and (31) gives \( n = m + 1 \)

\[
t_u(S) = A_u (S-1)^{-2(n-1)/n} S^{-1/n} \exp(B/n \ln^2 S).
\]  

(34)

2D nucleation-mediated growth

Substitution of eq. (23) into (31) leads to the expression \( n = m + 1 \)

\[
t_u(S) = A_u (S-1)^{-2(n-1)/3n} S^{-(n+2)/3n} \exp((n-1)B_{2D}/3n \ln S + B/n \ln^2 S),
\]  

(35)

which is similar to the one given by Söhnel and Mullin [2,10], for the particular case of 3D growth \( n = 4 \).

Volume diffusion-controlled growth

For this mechanism the same expression for \( t_u \) as given by eq.(33) is obtained after combining eqs.(25) and (31) (see also [8,10]), but now \( n = (m/2) + 1 \). Both normal growth and diffusion-controlled growth thus show the same dependence of \( t_u \) on \( S \), but with different kinetic factors \( A_u \) because of the difference in the values of \( n \) and in the parameters constituting \( K_J \) and \( K_G \) in eq.(32).

7.3. Procedure to analyze experimental data

In the following we will show how information can be obtained about growth and nucleation from experimentally measured induction times. The data from seeded precipitation allow the operating growth mechanism to be revealed and can be used for full determination of \( G \), including \( K_G \). The analysis of the data from unseeded precipitation gives direct information about the nucleation rate \( J \) when the induction time is determined by the appearance of the first nucleus only. When the induction time, however, is controlled by both nucleation and growth of many nuclei it is not possible to
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calculate the nucleation and growth pre-factors \( K_J \) and \( K_G \) separately. In this case only the thermodynamic parameters \( B_{2D} \) and/or \( B \) of nucleation and possibly the growth mechanism can be deduced from the experimental data.

A combined analysis of the induction time in seeded and unseeded precipitation is therefore necessary to obtain full information about \( G \) and \( J \), including the pre-factors \( K_G \) and \( K_J \). Furthermore, this combined analysis is even more important when the effect of an additive on nucleation and on growth has to be revealed independently.

7.3.1. Seeded precipitation

In the case of seeded precipitation the experimentally obtained \( t_s(S) \) data can be used to distinguish between the growth mechanisms and for the determination of \( G \) itself. To analyze the \( t_s(S) \) dependence it is convenient to represent \( t_s(S) \) in \( \ln t_s \)-vs.-\( \ln (S-1) \) coordinates. According to eqs. (17), (19) and (26), a straight line should then result, its slope being \(-1\) for normal and volume diffusion-controlled growth and \(-2\) for spiral growth. From the intercept, \( A_s \) can be calculated making thus possible the computation of \( K_G \) from eqs. (14) and (15) provided that \( m, v, c_m, \alpha, r_s \) and \( N \) are known. However, a different representation of the \( t_s(S) \) data is necessary in the case of 2D nucleation-mediated growth. According to eq.(24)

\[
F_s(S) = \ln A_s + B_{2D}/3\ln S,
\]

where

\[
F_s(S) = \ln [S^{1/3} (S-1)^{2/3} t_s].
\]

Thus a straight line is obtained when \( F_s \) is plotted vs. \( 1/\ln S \). The slope of this line is \( B_{2D}/3 \) and allows calculation of the edge energy \( \kappa \) and the number \( n_{2D}^* \) of molecules in the 2D nucleus by means of the known formula

\[
n_{2D}^* = B_{2D}/6\kappa \ln^2 S \quad (e.g. \ [7]).
\]

As before, \( K_G \) can be obtained from eqs. (14) and (15) by using the \( A_s \)-value determined from the intercept.

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7.3.2. Unseeded precipitation

In this case, experimentally obtained $t_u(S)$ data can be used to determine the operative growth mechanism and some physical parameters as the effective specific surface energy $\sigma$ and the number $n^*$ of molecules in the 3D nucleus.

A common procedure is to treat $t_u$ as determined by the appearance of the very first nucleus. Then, according to eq.(27), $t_u$ is simply equal to $1/\bar{J}V$, the term corresponding to the mononuclear mechanism. Using eq.(29) then yields

$$t_u(S) = (K_J V S)^{-1} \exp(B/\ln^2 S). \tag{38}$$

The constants $K_J$ and $B$ are given, respectively, by the intercept and the slope of $\ln(t_u S)$ vs. $1/\ln^2 S$. Knowing $B$, $\sigma$ can be calculated from eq.(30), and $n^*$ can be evaluated from the known relation (e.g.[7])

$$n^* = 2B/\delta \ln^3 S. \tag{39}$$

More complicated becomes the determination of $\sigma$ and $n^*$ in the case of the polynuclear mechanism when both primary nucleation and growth control the induction time. In this case eq.(31) has to be applied. For analysis of the experimental data, the value of $n = mv + 1$ and the $f(S)$ function (i.e. the operating growth mechanism) have to be known. A value for $m$ can be obtained by observation of the crystal growth shape. As an alternative to find $n$ and the operating growth mechanism a fitting procedure could be applied, as described below.

Eq.(31) can be rearranged into

$$F_u(S) = \ln A_u + B/n \ln^2 S \tag{40}$$

by defining the experimentally accessible quantity $F_u$ as

$$F_u(S) = \ln \{S^{1/n} [f(S)]^{(n-1)/n} t_u\}. \tag{41}$$

For normal, spiral and volume diffusion-controlled growth, possible values for $\nu$, $m$, $n$ and the related $F_u$ from eq.(41), are given in Table 7.2.
Table 7.2  Possible values for the power $v$ in the growth law, for the dimensionality $m$ of growth and for $n = mv + 1$, as well as the related $F_u$ functions for unseeded precipitation.

<table>
<thead>
<tr>
<th>Growth mechanism</th>
<th>$v$</th>
<th>$m$</th>
<th>$n$</th>
<th>$F_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal growth</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>$\ln [t_u (S - 1)^{1/2} S^{1/2}]$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td></td>
<td>$\ln [t_u (S - 1)^{2/3} S^{1/3}]$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td></td>
<td>$\ln [t_u (S - 1)^{3/4} S^{1/4}]$</td>
</tr>
<tr>
<td>Spiral growth</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>$\ln [t_u (S - 1)^{1/2} S^{1/2}]$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td></td>
<td>$\ln [t_u (S - 1)^{1/3} S^{1/3}]$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td></td>
<td>$\ln [t_u (S - 1)^{3/2} S^{1/4}]$</td>
</tr>
<tr>
<td>Diffusion-controlled growth</td>
<td>1/2</td>
<td>1</td>
<td>3/2</td>
<td>$\ln [t_u (S - 1)^{1/3} S^{2/3}]$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td></td>
<td>$\ln [t_u (S - 1)^{1/2} S^{1/2}]$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5/2</td>
<td></td>
<td>$\ln [t_u (S - 1)^{3/5} S^{2/5}]$</td>
</tr>
<tr>
<td>2D nucleation-mediated growth</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>$\ln [t_u (S - 1)^{1/3} S^{2/3}]$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td></td>
<td>$\ln [t_u (S - 1)^{4/9} S^{5/9}]$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td></td>
<td>$\ln [t_u (S - 1)^{1/2} S^{1/2}]$</td>
</tr>
</tbody>
</table>

Plots of $F_u$ vs. $1/\ln^2 S$ for the above three mechanisms and the possible values of $n$ have to be fitted by a straight line with intercept $\ln A_u$ and slope $B/n$. The quality of the fit, characterized by for instance the squared correlation coefficient, may give information about the operating growth mechanism and the most likely value of $n$. The constant $B$ can then be obtained from the slope of the best fit line and $\sigma$ and $n^*$ can be calculated from $B$ as specified before.

However, according to eq.(32) the intercept only allows calculation of a combination of the nucleation and growth pre-factors $K_J$ and $K_G$. Thus, in unseeded precipitation when the induction time is determined by the polynuclear mechanism it is not possible to fully evaluate the nucleation and growth rates separately.
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For 2D nucleation-mediated growth a somewhat different procedure has to be followed. Rearranging eq.(35) leads to

\[ F_u(S) = \ln A_u + (n-1)B_{2D}/3n\ln S + B/n\ln^2 S, \]  

where

\[ F_u(S) = \ln [(S-1)^{(n-1)/3n} S^{(n+2)/3n} t_u]. \]

Possible values for \( n \) and the related \( F_u \) from eq.(43) are also presented in Table 7.2. Plots of \( F_u \) vs. \( 1/\ln S \) for the different values of \( n \) should be fitted by a parabolic dependence. Comparison of the squared correlation coefficients should indicate the best value for \( n \). With \( n \) thus determined, \( \sigma \) and \( n^* \) along with \( \kappa \) and \( n^*_{2D} \) can be calculated from the coefficients of the quadratic and the linear \( 1/\ln S \) terms in eq.(42), resulting from the best fit. The first term in eq.(42) yields the value of \( A_u \), which also in this case does not allow the separate calculation of \( K_J \) and \( K_G \).

7.3.3 Combined analysis of seeded and unseeded precipitation

The above analysis shows that while in seeded precipitation it is possible to obtain full information about \( G \) from \( t_u(S) \) data, in the case of unseeded precipitation by the polynuclear mechanism \( G \) and \( J \) cannot be determined separately, because the pre-factors \( K_G \) and \( K_J \) enter the \( t_u(S) \) dependence (31) through the single parameter \( A_u \). In this case complete determination of \( J \) from \( t_u(S) \) data can be done only if \( G \) is known independently. Since such a knowledge about \( G \) is obtainable from \( t_g(S) \) data, it is clear that a combined analysis of the induction times in both seeded and unseeded precipitation (preferably in the same \( S \)-range) can be very useful for the complete determination of \( J \).

Provided both \( t_g \) and \( t_u \) are independently known, for such an analysis it is convenient to use the ratio \( t_u^n / t_g^{n-1} \), since according to eqs.(7), (9) and (28)
CHAPTER 7

This ratio is determined by J only:
\[ t_u^n / t_s^{n-1} = K_c / J, \]  \hspace{1cm} (44)

where for a small total volume fraction \( c_m r_s^{m-1} N \) of the seeds
\[ K_c = n N, \]  \hspace{1cm} (45)

and for large total volume fraction of the seeds
\[ K_c = n (c_m / a)^{m-1} (m r_s^{m-1} N)^m \]  \hspace{1cm} (46)

With the aid of eq.(29), eq.(44) can be represented as
\[ F_c(S) = \ln(K_c / K_j) + B / \ln^2 S, \]  \hspace{1cm} (47)

where the experimentally accessible quantity \( F_c \) is defined by
\[ F_c(S) = \ln(S t_u^n / t_s^{n-1}). \]  \hspace{1cm} (48)

Eq.(47) shows that a plot of \( F_c \) vs. \( 1 / \ln^2 S \) should give a straight line with slope \( B \) and intercept \( \ln(K_c / K_j) \). Thus, the slope yields directly the thermodynamic parameter \( B \) from which \( \sigma \) and \( n^* \) can be evaluated, and the intercept allows the separate calculation of the nucleation pre-factor \( K_j \).

In the case of precipitation in the presence of an additive it may be sufficient to know separately only the \( G_a / G \) and \( J_a / J \) ratios of the growth rates (or constants) \( G_a \) and \( G \) and nucleation rates \( J_a \) and \( J \) in the presence and absence of the additive, respectively. Again, this information can be obtained by combining the corresponding induction times \( t_{sa}, t_{ua}, t_s \) and \( t_u \) for seeded additive-containing, unseeded additive-containing, seeded blank and unseeded blank experiments. Provided the growth dimensionality \( m \), the power \( \nu \) in the growth law, the shape factor \( c_m \) and the inequalities (6) and (8) do not change in the presence of the additive, from eqs.(7), (9) and (44) it follows that
\[ G_a / G = t_u / t_{sa}, \]  \hspace{1cm} (49)
\[ J_a / J = (t_{sa} / t_u)^{n-1} (t_u / t_{ua})^n. \]  \hspace{1cm} (50)

These expressions show that it is possible to study the relative change of both the growth and the nucleation rates with \( S \) and/or the additive
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concentration by measuring independently the four induction times as functions of these two experimentally controllable parameters.

7.4. Conclusions

The analysis made provides the general dependence of $t_s$ on $N$ and $G$ for seeded precipitation, eqs.(7) and (9), and of $t_u$ on $J$ and $G$ for unseeded precipitation involving stationary primary nucleation of many crystallites, eq.(28). The various growth mechanisms lead to a number of simple explicit $t_s(S)$ and $t_u(S)$ dependences. While $t_s(S)$ data can be used for complete determination of the growth mechanism and $G$, $t_u(S)$ data can only yield information about the thermodynamics of nucleation and, possibly, about the mechanism of growth. Complete determination of $J$ is possible only when $t_s(S)$ and $t_u(S)$ data (preferably in the same $S$-range) are available simultaneously and the combined analysis proposed in section 7.3.3 shows a way to do such a determination. The general expressions for $t_s$ and $t_u$, eqs.(7), (9) and (28), as well as eqs.(44), (49) and (50) resulting from the combined analysis of $t_s$ and $t_u$ are fully applicable to precipitation in the presence of additives and may be successfully used for accessing their effect on $G$ and $J$.

References

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CHAPTER 8

DETERMINATION OF NUCLEATION AND GROWTH RATES FROM INDUCTION TIMES IN SEEDED AND UNSEEDED PRECIPITATION OF CALCIUM CARBONATE

Abstract

Theoretical expressions for the supersaturation dependence of the induction time in seeded and unseeded precipitation are derived for different mechanisms of crystallite growth. On the basis of the theory a combined analysis of the induction time in both seeded and unseeded precipitation is presented, which allows separate determination of the nucleation and growth rates.

Induction times in both seeded and unseeded precipitation of calcium carbonate in the absence and presence of additives are measured and interpreted in the light of the proposed theory. The analysis provides full information about the growth and nucleation rates in the investigated systems.

The analysis points at heterogeneous primary nucleation of vaterite in both the absence and presence of an additive. Growth in the absence of an additive proceeds via the spiral growth mechanism. In the presence of the additives a change to two dimensional nucleation mediated growth may occur, or the mechanism remains spiral growth but the effect of the additives on the growth changes with the supersaturation.

NUCLEATION AND GROWTH RATES OF CALCIUM CARBONATE

8.1. Introduction

Calcium carbonate can be found in different polymorphs which in order of increasing solubility are calcite, aragonite, vaterite, calcium carbonate monohydrate and calcium carbonate hexahydrate.

The precipitation of calcium carbonate (CaCO$_3$) is of considerable importance in a wide variety of fields. The formation of CaCO$_3$ can be unwanted, e.g. when it is formed as a crystalline scale in heat exchangers or cooling towers or during geothermal energy production, desalination of seawater, or oil and gas recovery [1]. On the other hand CaCO$_3$ is a useful mineral which can be applied as filler material in paints, paper and rubber [2]. Also, from a biological point of view CaCO$_3$ is an important substance which is present in e.g. mollusk and egg shells [3]. In soda-based laundry detergents the free calcium ion concentration in the washing liquor is reduced by the precipitation of CaCO$_3$ [4]. A disadvantage of such detergents is that part of the precipitated CaCO$_3$ is deposited on the textile surface and on parts of the washing machine. The CaCO$_3$ deposition during washing is also called incrustation.

In many of these processes polymers play an important role. These compounds can either be present in the system or added on purpose, mostly in relatively low concentrations compared to those of the growth units. Known, for example, is the use of polyelectrolytes as anti-scalants [1,4], and the role of acidic proteins in the formation of shells [3].

It is therefore important to know how additives influence the precipitation process. Very often their effect can be attributed to the changes they bring about in the nucleation and/or the growth of the precipitate. Much information is available about the impact of additives on growth, mostly deduced from seeded growth experiments [5]. It is more difficult,
however, to determine the influence of additives on nucleation. One way to obtain this information is to measure the so-called induction time which is the time elapsing until the moment at which the onset of precipitation can be detected. In general, the induction time has been related to unseeded precipitation [6,7], but in principle an induction time can also be observed when seeds are added in the solution [7,8]. While the induction time in seeded precipitation can provide full information about the growth rate, in unseeded precipitation involving the formation of many nuclei it cannot be used for unravelling the rates of nucleation and growth. A combined analysis of the induction times in both types of precipitation is therefore needed to obtain separate information about the nucleation and growth rates.

The aim of this work is (i) to present a theoretical method for such a combined analysis of induction times in seeded and unseeded precipitation and (ii) to obtain and analyze experimental data for the induction times in CaCO$_3$ precipitation, in the absence and presence of additives.

### 8.2. Theory

In both seeded and unseeded precipitation we consider a system with a given volume $V$ at constant absolute temperature $T$ and constant supersaturation $\Delta \mu$. For precipitation, the supersaturation is normally achieved by changing the concentrations (and thereby the activities) of the reactants. A generally known relation between $\Delta \mu$ and the supersaturation ratio $S$ is (e.g. [6])

$$\Delta \mu = \delta k T \ln S,$$

where $k$ is the Boltzmann constant, and $\delta$ is the number of ions in the formula unit. For CaCO$_3$ precipitation $\delta=2$, and $S$ is defined as

$$S = \left( \frac{\left( \text{Ca}^{2+} \right) \left( \text{CO}_3^{2-} \right)}{K_{\text{sol}}} \right)^{1/2}.$$
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Here (Ca\(^{2+}\)) and (CO\(_3\)^{2-}\) are notations for the activities of free Ca\(^{2+}\) and CO\(_3\)^{2-}\) ions, respectively, and K\(_{\text{sol}}\) is the thermodynamic solubility product of CaCO\(_3\).

General expressions for the induction times in seeded and unseeded precipitation were derived in chapter 7. In the following we present only results relevant for the analysis of the experimental data reported here. These results are valid for growth in three dimensions and for spherical crystallites.

8.2.1. Seeded precipitation

In this type of precipitation, seeds of the phase to be formed are introduced in the system at the initial moment \(t = 0\) by addition of crystallites of supernucleus size. It is assumed that all seed crystallites have the same radius \(r_s\), and that during the whole process only growth of these crystallites occurs.

The dependence of the induction time on the supersaturation is governed by the relationship between the growth rate \(G\) and the supersaturation ratio \(S\), which is of the form (e.g.[6,7])

\[ G(S) = K_G \cdot f(S). \] (3)

Here \(K_G\) is a S-independent factor, and \(f(S)\) is a given function of \(S\), related to the growth mechanism of the crystallites. This function reads

\[ f(S) = (S - 1), \] (4)

for normal growth (e.g.[9,10]),

\[ f(S) = (S - 1)^2, \] (5)

for spiral growth (e.g.[10,11]), and

\[ f(S) = (S - 1)^{2/3} S^{1/3} \exp(-B_{2D}/3\ln S), \] (6)

for 2D nucleation-mediated growth, which is close to the \(f(S)\) dependence in ref.[12]. In the above equation
\[ B_{2D} = \beta_{2D} \kappa^2 \alpha / \delta (kT)^2, \]  
(7)

where \( \beta_{2D} \) is a numerical 2D shape factor (e.g. \( \pi \) for circles), \( \kappa (J \text{ m}^{-1}) \) is an effective edge free energy of the nucleus and \( \alpha \) is the molecular area.

The induction time \( t_s \) in seeded precipitation is defined as the time elapsing between the moment (\( t=0 \)) of seed addition to the supersaturated solution and the moment, when the start of precipitation can be detected. This time can be related to the formation of a minimum detectable volume \( V_{\text{min}} \) of the precipitate, and is thus dependent on the particular technique used for the determination of \( V_{\text{min}} \).

In accordance with the theory of Kolmogorov [13] and Avrami [14], under the assumptions mentioned above, the general relation between \( t_s \) and \( V_{\text{min}} \) is given by [7]

\[ V_{\text{min}} / V = 1 - \exp\left(\frac{-4\pi/3}{N[((r_s + Gt_s)^3 - r_s^3)]}\right), \]  
(8)

where \( N(\text{m}^{-3}) \) is the number density of the seeds. In view of eq.(3), from this equation the following general formula for \( t_s \) is obtained

\[ t_s(S) = A_s / f(S). \]  
(9)

where

\[ A_s = r_s [(1 + 3\alpha / 4\pi r_s^3 N)^{1/3} - 1] / K_G, \]  
(10)

and \( \alpha = V_{\text{min}} / V \) is the smallest experimentally detectable volume fraction of the newly formed phase. Two limiting cases concerning \( A_s \) can be recognized. In the first one the total volume fraction \((4\pi/3)r_s^3 N\) of the seeds is small compared to \( \alpha \), i.e.

\[ (4\pi/3)r_s^3 N << \alpha, \]  
(11)

and \( A_s \) is then given by

\[ A_s = (3\alpha / 4\pi N)^{1/3} / K_G. \]  
(12)

In the opposite limiting case of large seed volume fraction, i.e. when

\[ (4\pi/3)r_s^3 N >> \alpha, \]  
(13)

\( A_s \) is given by

\[ A_s = \alpha / 4\pi r_s^2 NK_G. \]  
(14)
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8.2.2. Unseeded precipitation

In this case progressive primary nucleation with a stationary nucleation rate \( J \, (m^{-3} \cdot s^{-1}) \) occurs and it can be shown that when statistically many nuclei are formed the induction time \( t_u \) is given by [7,15]

\[
t_u = (3 \alpha/\pi J G^3)^{1/4}.
\] (15)

To find the dependence of \( t_u \) on \( S \), we have to know the relation between \( J \) and \( S \), and to use \( G(S) \) from eq.(3). The classical formula for the steady state nucleation rate for three-dimensional (3D) nucleation reads (e.g.[16])

\[
J(S) = K_J S \exp(-B/\ln^2 S),
\] (16)

where \( K_J \) is a practically \( S \)-independent kinetic factor and

\[
B = \beta \sigma^3 \pi^2 / (kT)^3 \delta^2.
\] (17)

Here \( \beta \) is a numerical shape factor (e.g. \( 16\pi/3 \) for spheres), \( \Omega \) is the molecular volume, and \( \sigma (J \cdot m^{-2}) \) is an effective specific surface free energy. For homogeneous nucleation \( \sigma \) equals the specific surface free energy \( \sigma_{homo} \) of the nucleus/solution interface, but for heterogeneous nucleation \( \sigma < \sigma_{homo} \).

With eqs.(3), (15) and (16) the following general expression for \( t_u \) is found

\[
t_u(S) = A_u \left[ f(S) \right]^{-3/4} S^{-1/4} \exp(B/4\ln^2 S),
\] (18)

in which the nucleation and growth pre-factors \( K_J \) and \( K_G \) are coupled into the single \( S \)-independent kinetic factor

\[
A_u = (3 \alpha/\pi K_J K_G^3)^{1/4}.
\] (19)

8.3. Procedure to analyze experimental data

8.3.1. Seeded precipitation

In the case of seeded precipitation the experimentally obtained \( t_q(S) \) data can be used to distinguish between the growth mechanisms and for the
determination of $K_G$ and $G$. To analyze the $t_s(S)$ dependence it is convenient
to represent it in $\ln t_s$-vs-$\ln(S-1)$ coordinates. According to eqs.(4), (5) and (9),
a straight line should then result, its slope being $-1$ for normal and $-2$ for
spiral growth. A slope lower than $-2$ is an indication for 2D nucleation-
mediated growth. For this mechanism a different representation is required.
Eqs.(6) and (9) can be combined and rearranged into

$$ F_s(S) = \ln \left[ S^{1/3} (S-1)^{2/3} t_s \right] = \ln A_s + B_{2D}/3\ln S. \quad (20) $$

In this case a straight line is obtained when $F_s$ is plotted vs. $1/\ln S$. The slope
of this line is $B_{2D}/3$ and allows calculation of the edge energy $\kappa$ from eq.(7),
and the number $n^*_{2D}$ of molecules in the 2D nucleus by means of the known
formula (e.g. [10])

$$ n^*_{2D} = B_{2D}/\kappa \ln^2 S. \quad (21) $$

For all mechanisms, the intercept of the best-fit line is equal to $\ln A_s$.
When $A_s$ is known, $K_G$ can be computed from eq.(12) or (14) provided that
$\alpha$, $r_s$ and $N$ are known, too.

8.3.2. Unseeded precipitation

In this case, experimentally obtained $t_u(S)$ data can be used to determine
the operative growth mechanism and some physical parameters (e.g. the
effective specific surface energy $\kappa$ and the number $n^*$ of molecules in the 3D

For analysis of the experimental data, in view of eqs.(4) and (5), eq.(18)
can be rearranged into

$$ F_u(S) = \ln \left[ S^{1/4} (S-1)^{3/4} t_u \right] = \ln A_u + B/4\ln^2 S \quad (22) $$

for normal growth, and

$$ F_u(S) = \ln \left[ S^{1/4} (S-1)^{3/2} t_u \right] = \ln A_u + B/4\ln^2 S \quad (23) $$

for spiral growth. The plot of $F_u$ from eqs.(22) and (23) vs. $1/\ln^2 S$ has to be
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fitted by a straight line, whose intercept is \( \ln A_u \) and the slope is \( B/4 \). The quality of the fit, characterized by e.g. the squared correlation coefficient, may give information about the operating growth mechanism. It becomes thus possible to verify whether this mechanism is the same as in seeded precipitation.

Knowing \( B \) from the slope of the best-fit \( F_u \)-vs.-\( 1/\ln^2 S \) line allows calculation of \( \sigma \) from eq.(17) and evaluation of \( n^* \) from the known relation (e.g.[10])

\[
n^* = 2B/\delta \ln^2 S.
\]  

(24)

However, according to eq.(19) the intercept \( \ln A_u \) of the best-fit line only enables calculation of a combination of the nucleation and growth pre-factors \( K_J \) and \( K_G \). Thus, in the case of unseeded precipitation it is not possible to fully evaluate the nucleation and growth rates separately.

For 2D nucleation-mediated growth a different procedure has to be followed, due to the more complicated \( f(S) \) dependence in eq.(18). Combining eqs.(6) and (18) and rearranging lead to

\[
F_u(S) = \ln[(S-1)^{1/2}S^{1/2}t_u] = \ln A_u + (B_{2D}/4)(1/\ln S) + (B/4)(1/\ln S)^2. \tag{25}
\]

A plot of \( F_u \) vs. \( 1/\ln S \) should be fitted by a parabolic dependence. From the coefficients of the quadratic and the linear \( 1/\ln S \) terms in eq.(25), resulting from the best fit, \( \sigma \) and \( n^* \) along with \( \kappa \) and \( n^*_{2D} \) can be calculated. The first summand in eq.(25) yields the value of \( A_u \), so that again the separate calculation of \( K_J \) and \( K_G \) is not feasible.

8.3.3 Combined analysis of seeded and unseeded precipitation

The above analysis shows that in the case of unseeded precipitation \( G \) and \( J \) cannot be uncoupled, because the pre-factors \( K_G \) and \( K_J \) enter the \( t_u(S) \) dependence (18) through the single parameter \( A_u \). Thus, complete
determination of \( J \) from \( t_u(S) \) data can be done only if \( G \) is known independently. Since such a knowledge about \( G \) is obtainable from \( t_s(S) \) data, it is clear that a combined analysis of the induction times in both seeded and unseeded precipitation (preferably in the same \( S \)-range) can be very useful for the complete determination of \( J \).

For such an analysis it is convenient to use the ratio \( t_u^4 / t_s^3 \), since according to eqs.(3), (9), (12), (14)–(16) this ratio is determined by \( J \) only:

\[
t_u^4 / t_s^3 = K_c / J = (K_c / K_d) S^{-1} \exp(B/\ln^2 S),
\]

where for \( (4\pi/3)r_s^3N << \alpha \)

\[
K_c = 4N,
\]

and for \( (4\pi/3)r_s^3N >> \alpha \)

\[
K_c = 3(8\pi)^2\alpha^{-2} r_s^6N^3.
\]

Eq.(26) can be rearranged into

\[
F_c(S) = \ln(S t_u^4 / t_s^3) = \ln(K_c / K_d) + B/\ln^2 S,
\]

which shows that a plot of \( F_c \) vs. \( 1/\ln^2 S \) should give a straight line with slope \( B \) and intercept \( \ln(K_c / K_d) \). Thus, the slope yields directly the thermodynamic parameter \( B \) from which \( \sigma \) and \( n^* \) can be evaluated, and the intercept allows the separate calculation of the nucleation pre-factor \( K_d \).

In the case of precipitation in the presence of an additive it may be sufficient to know separately only the \( G_s/G \) and \( J_s/J \) ratios of the growth rates \( G_s \) and \( G \) and nucleation rates \( J_s \) and \( J \) in the presence and absence of the additive, respectively. Again, this information can be obtained by combining \( t_s \) and \( t_u \) and the corresponding induction times \( t_{s,u} \) for seeded and unseeded precipitation in the presence of the additive. Provided the growth dimensionality and the crystallite shape do not change in the presence of the additive, from eqs.(3), (9) and (26) it follows that

\[
G_s/G = t_s / t_{s,u},
\]

\[
J_s/J = (t_{s,u}/t_u)^3 (t_u / t_{u,u})^4.
\]
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These expressions show that it is possible to study the relative change of both the growth and the nucleation rates with S and/or the additive concentration by measuring independently the four induction times as functions of these two experimentally controllable parameters.

8.4. Experimental

Induction times were measured for seeded and unseeded precipitation of CaCO₃ in solutions of volume V = 1.4 dm³ and 1.3 dm³, respectively. In some experiments these times were measured in the presence of polyacrylic acid (PAA, MW=5000 D) or of a copolymer of polymaleic and polystyrene sulfonic acid (PMA-PSS, MW 13000 D). The general formula are shown in table 2.2 of chapter 2. The experiments were performed in a 1.5 dm³ double walled pyrex glass vessel thermostated at 25.00 ± 0.05 °C. The vessel was covered with a perspex lid with holes for the electrodes and for sampling. AR grade chemicals and doubly distilled water were used in all experiments.

The supersaturated solutions were made by mixing 0.65 dm³ of well-filtered (three times over 0.22 μm pore size filter) aqueous solutions of CaCl₂ and Na₂CO₃/NaHCO₃. The pH of both solutions was 10.0 ± 0.02. The supersaturation was changed by variation of the CaCl₂-concentration in the range from 3.00×10⁻⁴ to 10.00×10⁻⁴ M for unseeded and from 3.00×10⁻⁴ to 6.00×10⁻⁴ M for seeded precipitation. The composition of the other solution, consisting of 2.27×10⁻² M Na₂CO₃ and 3.39×10⁻² M NaHCO₃, was kept constant in all experiments.

The pH of the solution was measured by a pair of glass (Radiometer G202C) and saturated calomel (Radiometer K401) electrodes. A Ca ion-selective electrode (Radiometer F 2002) with a calomel electrode was used to monitor the Ca-ion activity. The induction times were determined from
recordings (Kipp BD-9) of the signal of the Ca ion-selective electrode versus time and were averaged from at least three separate experiments. During the experiments the development of the crystallite size distribution in time was followed by means of in-line measurements with a forward light scattering technique (Coulter LS 130). Samples were taken from the solution at the end of precipitation and analyzed by scanning electron microscopy (SEM, JEOL 35) and X-Ray diffraction (Philips PW 50). This last technique showed that the modification of the precipitate was vaterite.

Unseeded precipitation experiments with a $10.00 \times 10^{-4}$ M CaCl$_2$-solution were performed for the preparation of vaterite seeds. Suspension samples were taken at the moment when the signal of the Ca ion-selective electrode virtually stopped changing with time. In seeded precipitation experiments 0.1 dm$^3$ of a thus-prepared vaterite seed suspension was injected into the supersaturated solution at $t=0$. The added seed mass $M$ was 4.75 mg and the maximum radius of the seeds was about 1 $\mu$m (determined by SEM). We therefore expect the average seed radius $r_s$ to be from 0.01 to 1 $\mu$m, so that for further calculations we shall use the intermediate $r_s = 0.1$ $\mu$m. The seed number density $N = 3M/4\pi \rho r_s^3 V$ ($\rho = 2.54$ g cm$^{-3}$ is the density of vaterite) is thus estimated to be $N = 3 \times 10^{14}$ m$^{-3}$.

The supersaturation ratio $S$ was calculated from eq.(2) for the precipitation of vaterite by taking into account the formation of ionic complexes. The considered equilibria and the related values of the thermodynamic constants are summarized in table 8.1. Activity coefficients of the ions were calculated by the modified Debye-Hückel equation proposed by Davies (e.g.[17]). The formation of species in the solution was computed from the recorded pH-value and mass- and charge-balance equations by iterative approximations for the ionic strength [17].

- 169 -
### Table 8.1 Calcium carbonate equilibria and the corresponding equilibrium constants $K$ at 25°C.

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>$K$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^- $</td>
<td>$1.007 \times 10^{-14}$ mole$^2$ dm$^{-6}$</td>
<td>[18]</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{HCO}_3^- = \text{H}_2\text{CO}_3^+$</td>
<td>$2.249 \times 10^6$ dm$^3$ mole$^{-1}$</td>
<td>[19]</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$</td>
<td>$2.133 \times 10^{10}$ dm$^3$ mole$^{-1}$</td>
<td>[20]</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3^0$</td>
<td>$1412$ dm$^3$ mole$^{-1}$</td>
<td>[18]</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+$</td>
<td>$10.0$ dm$^3$ mole$^{-1}$</td>
<td>[18]</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{OH}^- = \text{CaOH}^+$</td>
<td>$19.95$ dm$^3$ mole$^{-1}$</td>
<td>[18]</td>
</tr>
<tr>
<td>$\text{CaCO}_3$ (solid) $\rightarrow$ $\text{Ca}^{2+} + \text{CO}_3^{2-}$</td>
<td>$1.2207 \times 10^{-8}$ mole$^2$ dm$^{-6}$</td>
<td>[21]</td>
</tr>
</tbody>
</table>

### Table 8.2 Total calcium concentration $T_{Ca}$ and corresponding values of the supersaturation ratio $S$ for seeded and unseeded precipitation of vaterite. The total carbonate concentration is always $2.83 \times 10^{-2}$ M.

<table>
<thead>
<tr>
<th>$T_{Ca}$ (M)</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unseeded</td>
</tr>
<tr>
<td>unseeded</td>
<td>seeded</td>
</tr>
<tr>
<td>1.50x10$^{-4}$</td>
<td>1.41x10$^{-4}$</td>
</tr>
<tr>
<td>2.00x10$^{-4}$</td>
<td>1.87x10$^{-4}$</td>
</tr>
<tr>
<td>2.50x10$^{-4}$</td>
<td>2.34x10$^{-4}$</td>
</tr>
<tr>
<td>2.75x10$^{-4}$</td>
<td>2.57x10$^{-4}$</td>
</tr>
<tr>
<td>3.00x10$^{-4}$</td>
<td>2.80x10$^{-4}$</td>
</tr>
<tr>
<td>3.50x10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>4.00x10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>4.50x10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>5.00x10$^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.2 gives the total Ca concentration $T_{Ca}$ and the calculated supersaturation ratio $S$ for the different types of experiments in which the total carbonate concentration was kept constant and equal to $2.83 \times 10^{-2}$ M. Depending on $S$, the $\text{CO}_3^{2-}/\text{Ca}^{2+}$ concentration ratio in the added solutions varied from 22 to 75.
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8.5. Results and discussion

8.5.1. General results

The assumption made in section 2.1 that the induction time $t_s$ (or $t_{s,a}$) for seeded precipitation is only controlled by growth of the added seeds requires this time to be sufficiently shorter than the corresponding induction time $t_u$ (or $t_{u,a}$) for unseeded precipitation. When this condition is not fulfilled, it is doubtful whether the effect of extra primary nucleation on the induction time in seeded precipitation is negligible. In that case we recommend to perform the seeded precipitation experiments with a higher seed number density $N$. This decreases $t_u$, as can be seen from eqs.(9), (12) and (14), and thus diminishes the effect of extra primary nucleation.

The determination of the induction times is illustrated in fig.8.1, which depicts the time evolution of the response of the Ca ion-selective electrode. Curves s, s,a and u refer to seeded, seeded additive-containing and unseeded solutions, respectively, at supersaturation ratio $S=3.55$ for the seeded and 3.67 for the unseeded solutions. In the following, precipitation experiments in the absence of an additive will be called blank experiments. As exemplified in fig.8.1, for all blank experiments $t_s$ was sufficiently smaller than $t_u$. The same effect, i.e. $t_{s,a} < < t_{u,a}$, was noticed in the precipitation experiments in the presence of the additives. These observations indicate that the impact of primary nucleation on $t_s$ and $t_{s,a}$ is negligible.

Another indication that extra primary nucleation plays virtually no role during seeded precipitation was obtained from in-line crystallite size distribution measurements with forward light scattering. The clear difference in the distributions obtained from seeded and unseeded precipitation is shown in fig.8.2.
Figure 8.1 *Time evolution of the response of the Ca ion-selective electrode during CaCO$_3$ precipitation in unseeded (u), seeded (s) and seeded 50 ppm PMA-PSS-containing (s,a) solutions.*

Figure 8.2 *Crystal size distributions in blank seeded (—) and unseeded (---) precipitation experiments.*
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If in the seeded precipitation experiments primary nucleation would be a dominating factor, a size distribution more or less similar to that of the unseeded precipitation experiments would have been observed. In principle, the crystallite growth rate can be determined from two consecutively measured size distributions. However, this was not possible to be done because during the precipitation from \( t = 0 \) to the induction time the solution contained too little solid phase for accurate measurements of the crystallite size distributions.

The possibility to neglect extra primary nucleation was also supported by SEM views of samples taken from seeded precipitation experiments, shown in fig.8.3B. These views showed much larger crystallites than in the unseeded precipitation experiments (fig.8.3A) at the same supersaturation, and almost no small crystallites. The SEM views shown in fig.8.3 also revealed the known [22] spherical shape of the vaterite crystallites, thus evidencing growth in three dimensions. This is a justification for the use of the formulae in sections 2 and 3 in the analysis to follow.

\[ -173- \]

Figure 8.3

SEM views of \( \text{CaCO}_3 \) crystals.

A unseeded precipitation without an additive
8.5.2. Seeded precipitation experiments

We now present the $t_s(S)$ and $t_{sa}(S)$ dependences for CaCO$_3$ precipitation, respectively in the absence and presence of additives. Fig.8.4 shows the plots of $\ln t_s$ and $\ln t_{sa}$ vs. $\ln(S-1)$. The two investigated additives and the applied concentrations are: PMA-PSS (13 ppm) and PAA (0.2 ppm). These concentrations were found to meet both the experimental and theoretical requirements. It can be seen from fig.8.4 that $t_s$ is smaller than $t_{sa}$ for both investigated additives, which implies that these additives retard the growth of vaterite under the given conditions.

From fig.8.1 it can be seen that the decrease of the signal of the Ca ion-selective electrode is less steep in the presence of PMA-PSS than in the
blank experiments. Because the same effect was also observed for PAA, the reliable determination of the induction times in the presence of this additive was impossible for S<3.

The drawn lines in fig.8.4 are the best fit lines obtained from linear regression of \( \ln t_s \) and \( \ln t_{s,a} \) vs. \( \ln (S-1) \). The slopes and the intercepts of these lines are given in table 8.3, together with the values of \( A_s \) calculated from the intercept.

The operating growth mechanism can be deduced from the slopes of the best-fit lines, given in table 8.3. As pointed out in section 8.3.1, the obtained value of the slope for the blank experiments is an indication for the spiral growth mechanism. This same mechanism for vaterite has been reported for S<3 on the basis of growth experiments [22]. For the experiments with the additives, here acting as growth inhibitors, significantly higher slopes are found, as has also been noticed e.g. when the growth of gypsum is retarded
by lanthanide ions [23]. It may be noted, however, that inhibition of growth is also possible without changing the slope, as e.g. in the case of SrF₂ growth in the presence of metal ions [24].

For the higher absolute values of the slope in the presence of the additives various explanations are possible. First, the growth of vaterite may then proceed via a mechanism different from the spiral growth mechanism in the blank experiments, namely via the 2D nucleation-mediated growth mechanism. A change in growth mechanism in the presence of additives has already been reported for other mineral salts [5]. Second, even for the same growth mechanism a higher slope can be found when the influence of the additive on the growth varies with the supersaturation, resulting in an extra S-dependent term in f(S) from eq.(5). In the third place, a combination of the first two explanations is possible, namely a change in growth mechanism together with a S-dependent effect of the additive on the growth.

In order to check the possibility of 2D nucleation-mediated growth in the presence of the additives Fₙₜ from eq.(20) was plotted vs. 1/lnS. The resulting plots are shown in fig.8.5. As described in section 3.1, the slope B₂D/3 allows calculation of the edge energy k by substitution of the 2D shape factor β₂D = π and the molecular area a = n²/3 = 1.575x10⁻¹⁹ m² into eq.(7). Furthermore the number n*₂D of molecules in the 2D nucleus can be computed from eq.(21). The results of the regression analysis of Fₙₜ vs. 1/lnS and the related calculated parameters are given in table 8.4.
Table 8.4  Results of regression analysis of $F_{s,a}$ (from eq.(20)) versus $1/\ln S$ and the related physical parameters $B_{2D}$, $\kappa$ and $n^*_{2D}$ for $S=3.55$ to 2.52. Additives: 13 ppm PMA-PSS or 0.2 ppm PAA.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Intercept</th>
<th>$A_s$ (s)</th>
<th>Slope</th>
<th>$B_{2D}$</th>
<th>$\kappa (J m^{-1})$</th>
<th>$n^*_{2D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA</td>
<td>1.2±0.1</td>
<td>3.3</td>
<td>8.9±0.1</td>
<td>26.6</td>
<td>4.3x10^{-11}</td>
<td>8.3 to 15.6</td>
</tr>
<tr>
<td>PMA-PSS</td>
<td>4.1±0.1</td>
<td>61</td>
<td>4.4±0.4</td>
<td>13</td>
<td>3.0x10^{-11}</td>
<td>4.1 to 7.7</td>
</tr>
</tbody>
</table>

From the $\kappa$-values in table 8.4 a specific surface free energy $\sigma$ can be estimated by means of the known relation $\sigma = \kappa/n^{1/3}$ [10]. With $n^{1/3} = 3.96 \times 10^{-10}$ m we thus find $\sigma = 76$ and 108 mJ m$^{-2}$ for vaterite in solutions containing PMA-PSS and PAA, respectively. These values compare with a theoretically computed specific surface free energy $\sigma_{\text{home}} = 90$ mJ m$^{-2}$ [22,25]. The analysis of seeded precipitation in the presence of additives
NUCLEATION AND GROWTH RATES OF CALCIUM CARBONATE

according to the 2D nucleation-mediated growth mechanism thus results in realistic physical parameters. We have, however, no possibility to check the other two explanations, because the necessary theoretical expressions for a S-dependent effect of additives on growth are not known. It is therefore impossible to reach a firm conclusion in favour of one of the three given explanations for the differing S-dependence of G in the presence of additives.

We will now calculate $K_G$ by using the $A_s$-values in tables 8.3 and 8.4. For the applied registration technique $V_{\text{min}}$ is estimated to be $6.5 \times 10^{-8}$ dm$^3$, which results in $\alpha = 5 \times 10^{-8}$. Also, $(4\pi/3) r_s^3 N = M/\rho V = 1.3 \times 10^{-6}$ so that inequality (13) is satisfied in our experiments. Accordingly, with the $r_s$- and $N$-values from section 8.4, eq.(14) gives values for $K_G$ which are summarized in table 8.5. The empirical $f(S)$ functions in this table are the result of the regression analysis of $\text{Int}_s$ and $\text{Int}_{s,a}$ versus $\ln(S-1)$ shown in table 8.3. Combination of the B$_{2D}$-values in table 8.4 with eq.(6) gives the f(S) functions for 2D nucleation-mediated growth.

Using the $K_G$-values and the empirical $f(S)$ functions from table 8.5 enables the $G(S)$ dependences to be calculated from eq.(3). From these dependences the $G_s/G$ ratios were computed, where $G_s$ and G correspond to the growth rate in the presence and absence of the additive, respectively.

Table 8.5  
Values for $K_G (m \text{ s}^{-1})$, computed by means of eq.(14) from $A_s$-values in tables 8.3 and 8.4, and the experimentally determined $f(S)$ functions from regression analysis of $\text{Int}_s$ and $\text{Int}_{s,a}$ vs. $\ln(S-1)$.

<table>
<thead>
<tr>
<th></th>
<th>$K_G$ (with $A_s$ from table 8.3)</th>
<th>f(S)</th>
<th>$K_G$ (with $A_s$ from table 8.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>$2.4 \times 10^{-12}$</td>
<td>$(S-1)^{1.8}$</td>
<td></td>
</tr>
<tr>
<td>PAA</td>
<td>$8.8 \times 10^{-15}$</td>
<td>$(S-1)^{6.1}$</td>
<td>$4.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>PMA-PSS</td>
<td>$8.1 \times 10^{-14}$</td>
<td>$(S-1)^{3.4}$</td>
<td>$2.2 \times 10^{-11}$</td>
</tr>
</tbody>
</table>
CHAPTER 8

These $G_a/G$ ratios are plotted in fig.8.6 as lines, while the points in this figure represent the $G_a/G$ values calculated from the experimentally determined $t_s$- and $t_{sa}$-data with the help of eq.(30). Fig.8.6 shows clearly the inhibiting effect of both PMA-PSS and PAA on vaterite growth. The effect of the additives on the growth becomes less pronounced with increasing supersaturation.

In ref.[22], $K_G=$5.6x10$^{-10}$ m s$^{-1}$ was experimentally determined for growth of vaterite. In that reference, on the basis of theoretical expressions derived in ref.[25], a $K_G$-value of 1.9x10$^{-10}$ m s$^{-1}$ was also calculated. The present $K_G$-value for the blank experiments is much lower than these values. This is probably due to the non-stoichiometry of the calcium and carbonate solutions, which normally leads to lower $K_G$-values [26].

![Graph](image)

**Figure 8.6** Relative change of the growth rate of vaterite with supersaturation in the presence of 13 ppm PMA-PSS (○) or 0.2 ppm PAA (■): lines - from eq.(3) with $K_G$ and $f(S)$ from table 8.5; points - from eq.(30) with measured $t_s$- and $t_{sa}$-data.
Concering the empirically obtained growth pre-factors $K_G$, table 8.5 shows that the presence of the additives leads to lower $K_G$-values than in their absence. This is expected for growth inhibitors, because $K_G$ is inter alia dependent on the density of the growth sites which is decreased when the inhibitor is adsorbed on the crystallite surface. PAA is a better growth inhibitor for vaterite than PMA-PSS, because higher $t_{s,a}$-values are measured despite the much lower concentration of PAA (see fig.8.4).

In addition to the above reported results, some experiments were performed at other additive concentrations. In fig.8.1 curve $s,a$ belongs to a seeded precipitation experiment in the presence of 50 ppm PMA-PSS. Examination by SEM revealed that abundant extra primary nucleation has occurred in this experiment (see fig.8.3C). For this reason this experiment could not be used for analysis of the effect of PMA-PSS on vaterite growth. Nevertheless, the position of the curve allows some qualitative information to be drawn. Namely, 50 ppm PMA-PSS seems to retard the growth, since $t_{s,a} > t_u$, and to stimulate the nucleation because $t_{s,a} < t_u$. Experiments in the presence of 5 ppm PAA showed no decrease in the signal of the Ca-ion selective electrode for a period of 8 hours. Apparently, the growth of vaterite at this PAA concentration is so strongly retarded that the system is able to remain for a rather long time in metastable equilibrium. Additives which exhibit such an effect are usually called threshold agents.

8.5.3. Unseeded precipitation experiments

In order to analyze the $t_u(S)$ and $t_{u,a}(S)$ data according to eq.(18), we have to use the $F_u(S)$ dependences, eqs.(22), (23) and (25), obtained by substitution of the theoretical $f(S)$ functions for normal, spiral and 2D nucleation-mediated growth. Since it was not possible to fit the $t_{u,a}$ data in $F_{u,a}$-vs.-$1/\ln S$
coordinates by a parabolic dependence (25) for 2D nucleation-mediated growth, alternatively we substituted in eq.(18) the empirical f(S) functions determined experimentally from the seeded precipitation data and given in table 8.5. The thus-obtained \( t_u(S) \) and \( t_{u,a}(S) \) dependences can be rearranged into the following \( F_u \) and \( F_{u,a} \) functions

\[
F_u(S) = \ln[t_u(S-1)^{1.35} S^{1/4}] = \ln A_u + B/4\ln^2 S, \tag{32}
\]

\[
F_{u,a}(S) = \ln[t_{u,a}(S-1)^{2.55} S^{1/4}] = \ln A_u + B/4\ln^2 S, \tag{33}
\]

\[
F_{u,a}(S) = \ln[t_{u,a}(S-1)^{3.823} S^{1/4}] = \ln A_u + B/4\ln^2 S, \tag{34}
\]

for precipitation in additive-free, PMA-PSS-containing and PAA-containing solutions, respectively. The corresponding \( F_u(S) \) and \( F_{u,a}(S) \) data along with the best-fit straight lines are plotted in \( F_u \)-vs.-\( 1/\ln^2 S \) coordinates in fig.8.7. The results of the regression analysis are given in table 8.6.

![Figure 8.7](image)

**Figure 8.7**

Plots of \( F_u \) and \( F_{u,a} \) from eqs.(32)-(34) versus \( 1/\ln^2 S \), for unseeded \( \text{CaCO}_3 \) precipitation in the absence (●), and in the presence of 13 ppm PMA-PSS (○) or 0.2 ppm PAA (■).
Table 8.6  Results of regression analysis of $F_u$ and $F_{u,a}$ (from eqs.(32)-(34)) versus $1/ln^2S$ and the related physical parameters $B$, $\sigma$ and $n^*$.

<table>
<thead>
<tr>
<th></th>
<th>Intercept</th>
<th>$A_u$ (s)</th>
<th>Slope</th>
<th>$B$</th>
<th>$\sigma$ (mJ m$^{-2}$)</th>
<th>$n^*$ (S = 4.73 to 2.60)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>5.5±0.1</td>
<td>2.4x10$^2$</td>
<td>3.0±0.1</td>
<td>12.2</td>
<td>37.3 ± 0.4</td>
<td>3.2 to 14.1</td>
</tr>
<tr>
<td>PAA</td>
<td>9.3±0.1</td>
<td>1.1x10$^4$</td>
<td>3.4±0.3</td>
<td>13.6</td>
<td>38.7 ± 1.0</td>
<td>3.6 to 15.7</td>
</tr>
<tr>
<td>PMA-PSS</td>
<td>8.1±0.2</td>
<td>3.3x10$^3$</td>
<td>2.9±0.4</td>
<td>11.5</td>
<td>36.6 ± 1.7</td>
<td>3.1 to 13.2</td>
</tr>
</tbody>
</table>

The thermodynamic constant $B$ can be calculated from the respective slopes which are equal to $B/4$. Knowing $B$, the specific surface energy $\sigma$ and the number $n^*$ of molecules in the 3D nucleus can be evaluated from eqs.(17) and (24), assuming spherical nuclei ($\beta = 16\pi/3$) and using $\Omega = 6.25x10^{-29}$ m$^3$ for the molecular volume of vaterite. The values of the so-obtained parameters are also reported in table 8.6.

For homogeneous vaterite nucleation, a theoretical specific surface free energy $\sigma_{\text{homo}} = 90$ mJ m$^{-2}$ has been computed on basis of a general relation between the specific surface free energy and the solubility [22,25]. The relatively low $\sigma$-value in table 8.6 for the blank experiments corresponds well to $\sigma = 34$ mJ m$^{-2}$ in [22], and, as suggested there, may be regarded as an indication for heterogeneous nucleation. Other $\sigma$-values reported in literature are mostly connected with heterogeneous nucleation of vaterite upon other substrates. For instance, it has been found that $\sigma = 11$ mJ m$^{-2}$ for vaterite upon cholesterol [27] and $\sigma = 76.8$ mJ m$^{-2}$ for impure vaterite upon heated metal surfaces [28].

In view of the standard deviation in the values of the slopes in table 8.6, no definite conclusion about the differences in the calculated $\sigma$-values for nucleation in the absence and presence of additives can be drawn. In general, when the effect of additives on nucleation is due to adsorption, theory [29,30] predicts lower $\sigma$-values. As seen from table 8.6, the 3D nuclei contain a
relatively low number \( n^* \) of molecules. This is often found in analysis of nucleation data and implies that the surface free energies obtained here have only a formal physical meaning.

The intercepts in table 8.6 and hence the \( A_u \)-values for additive-free and additive-containing solutions do differ significantly, but no separate information about \( K_J \) can be obtained from this parameter, as follows from eq.(19). Knowledge about \( K_J \) can be provided by a combined analysis of seeded and unseeded precipitation.

8.5.4. Combined analysis of seeded and unseeded precipitation experiments

We have now the necessary \( t_s(S) \), \( t_{s,a}(S) \), \( t_u(S) \) and \( t_{u,a}(S) \) data that can be used in eqs.(29) and (31) for a combined analysis of seeded and unseeded precipitation. The S-ranges for both types of precipitation overlap, but unfortunately the induction times in seeded and unseeded precipitation were not measured at exactly the same supersaturation. For calculating \( F_c(S) \) and \( F_{c,a}(S) \) from eq.(29) measured \( t_u \)- and \( t_{u,a} \)-data were combined with \( t_s \)- and \( t_{s,a} \)-values from the best fit for the \( \ln t_s(S) \) and \( \ln t_{s,a}(S) \) dependences in section 8.5.2. Also, combinations of measured \( t_s \)- and \( t_{s,a} \)-values with values for \( t_u \) and \( t_{u,a} \) obtained from the best fit of the \( F_u(S) \) and \( F_{u,a}(S) \) dependences (32)-(34) were formed. \( F_c(S) \) and \( F_{c,a}(S) \) functions were calculated using both types of combinations and plotted versus \( 1/\ln^2 S \) according to eq.(29), see fig.8.8. The slopes of the best-fit lines in fig.8.8 are equal to \( B \), and their values are presented in table 8.7. These values are comparable to those already determined from the \( F_u(S) \) and \( F_{u,a}(S) \) functions and given in table 8.6. This is understandable because for the calculations of \( F_u \) and \( F_{u,a} \) experimentally determined, and not theoretical \( f(S) \) functions, were used.
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![Graph](image)

Figure 8.8
Plots of $F_c$ and $F_{ca}$ from eq.(29) versus $1/\ln^2S$ for CaCO$_3$ precipitation in the absence (●), and in the presence of 13 ppm PMA-PSS (○) or 0.2 ppm PAA (■).

Table 8.7

<table>
<thead>
<tr>
<th></th>
<th>Slope (=B)</th>
<th>Intercept</th>
<th>$K_f$ (m$^{-3}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>12.8 ± 0.3</td>
<td>2.7 ± 0.2</td>
<td>1.4x10$^{18}$</td>
</tr>
<tr>
<td>PMA-PSS</td>
<td>11.5 ± 0.8</td>
<td>3.3 ± 0.6</td>
<td>7.9x10$^{17}$</td>
</tr>
<tr>
<td>PAA</td>
<td>13.7 ± 0.6</td>
<td>1.2 ± 0.2</td>
<td>5.9x10$^{18}$</td>
</tr>
</tbody>
</table>

The intercepts of the best-fit lines are equal to $\ln(K_f/K_p)$ and are given in table 8.7. These intercepts allow the evaluation of $K_f$ upon computing $K_c$ from eq.(28) with the help of the already used values of $\alpha$, $r_s$, and $N$. The so-calculated $K_f$-values are also given in table 8.7 and all of them are lower than the theoretically expected [10,16] $K_f \approx 10^{31}$ to $10^{36}$ m$^{-3}$s$^{-1}$ for homogeneous nucleation in solutions. This is again an indication for
heterogeneous nucleation in the system studied. The $K_J$-value in the presence of PMA-PSS is comparable to the one for the blank experiments, but in the presence of PAA a significantly different $K_J$-value is found.

With the $K_J$- and $B$-values from table 8.7, from eq.(16) the $J(S)$ dependences and the related $J_a/J$ ratios were computed. Here $J_a$ and $J$ correspond to the vaterite nucleation rate in the presence and absence of an additive, respectively. These ratios are depicted in fig.8.9 as lines, while the points in this figure represent the values of $J_a/J$ calculated from experimentally determined $t_u$, $t_a$, $t_{u,a}$, and $t_{a,a}$-data with the help of eq.(31). The large scatter of the points is due to the uncertainties in the measured induction times, enhanced by the powers in eq.(31). Despite the scatter, the points more or less follow the trend of the drawn lines.

![Figure 8.9](image)

**Figure 8.9** Relative change of the nucleation rate of vaterite with supersaturation in the presence of 13 ppm PMA-PSS (○) or 0.2 ppm PAA (■): lines - from eq.(16) with $K_J$ and $B$ from table 8.7, points - from eq.(31) with measured $t_u$, $t_{u,a}$, $t_a$ and $t_{a,a}$-data.
NUCLEATION AND GROWTH RATES OF CALCIUM CARBONATE

Fig. 8.9 shows that both additives seem to stimulate the nucleation of vaterite and that the nucleation rate increases or decreases with increasing S, in the presence of 0.2 ppm PAA or 13 ppm PMA-PSS, respectively. The relative change of the primary nucleation rate of vaterite in both cases is, however, rather small. A firm conclusion about the significance of the observed effect of PAA and PMA-PSS on J is therefore impossible.

8.6. Relation with incrustation experiments

The influence of PAA and PMA-PSS on the deposition of CaCO₃ on cotton in simple soda-based detergents, also called incrustation, has been determined in chapter 2. PAA increased the incrustation, while PMA-PSS diminished it. In chapter 4 it was concluded, on basis of their influence on the particle size distribution in batch precipitation experiments, that PAA inhibits the growth, and that PMA-PSS stimulates the nucleation of CaCO₃.

The present work only partially supports these conclusions. PAA is indeed a much better growth inhibitor for CaCO₃ than PMA-PSS. But it follows from the induction time measurements that PMA-PSS also inhibits the growth of CaCO₃, while this effect has not been noticed in the experiments, described in chapters 2 to 4. It must however be noted that the experimental conditions, a relatively low supersaturation and a relatively high PMA-PSS concentration, are expected to stimulate the inhibiting action of the additive.

The quantitative analysis of the induction time measurements revealed that both PAA and PMA-PSS seem to stimulate the primary nucleation rate of vaterite. The relative change of this parameter in the presence of the additives is, however, so small that no firm conclusion can be drawn about the significance of the observed effects. On the other hand, seeded
precipitation in the presence of 50 ppm PMA-PSS qualitatively pointed at a stimulation of CaCO$_3$ nucleation by this additive. It is unclear whether the absence of a significant stimulation of the nucleation by PMA-PSS in the quantitative analysis is caused by the changed experimental conditions compared to the incrustation experiments, or that the effect is obscured by the implicit uncertainty of the induction time measurements.

8.7. Conclusions

Theoretical expressions for the induction time are derived, applicable to the investigated seeded and unseeded precipitation of CaCO$_3$. An appropriate combination of these expressions allows separate determination of the nucleation and growth rates.

Precipitation experiments in both seeded and unseeded solutions show that the induction time changes with supersaturation, as well as in the presence of additives. A combined analysis of both types of precipitation, as proposed in this work, is used for evaluation of the experimentally measured induction times. This led to the conclusion that the proposed theory agrees with experiment.

Under the given experimental conditions CaCO$_3$ precipitates as vaterite. The analysis of the seeded precipitation experiments in the absence of additives points at the spiral growth mechanism for vaterite. In the presence of 13 ppm PMA-PSS or 0.2 ppm PAA other dependences of the growth rate $G$ on the supersaturation $S$ were observed. This can be explained either by a change of growth mechanism into 2D nucleation-mediated growth and/or a S-dependent influence of the additives on $G$. Both additives inhibit the growth of vaterite, but PAA is more effective than PMA-PSS. The growth inhibition is less pronounced with increasing supersaturation.
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The relatively low surface free energies $\sigma$ obtained from the analysis of
the unseeded precipitation experiments in both additive-free and additive-
containing solutions indicates primary heterogeneous nucleation of vaterite.

The combined analysis revealed that both PAA and PMA-PSS have no
significant influence on the nucleation rate of vaterite.

The results in this chapter only partially confirm the previously proposed
mechanisms for the influence of the here investigated additives on the
incrustation of cotton.

Acknowledgements

The authors are indebted to Dr. R.E. Herzog for suggesting an
experimental procedure for preparation of vaterite seeds. They are thankful
to J. Timmerman, M. Lentelink, G. Demian and V.M.J. Arkesteyn for
experimental assistance. Financial support from Household and Personal
Care Research, the Hague, is gratefully acknowledged.

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NUCLEATION AND GROWTH RATES OF CALCIUM CARBONATE


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CHAPTER 9

THE EFFECT OF ADDITION OF SEEDS ON THE DEPOSITION OF CALCIUM CARBONATE ON COTTON IN A SODA-BASED DETERGENT

Abstract

The effect of addition of foreign seeds on the deposition of calcium carbonate on cotton, also called incrustation, has been investigated. Two types of seeds were used, namely calcite and bentonite particles both with a relatively high specific surface area.

It is shown that the incrustation decreased markedly in the presence of calcium carbonate and bentonite seeds compared to the unseeded experiment. The underlying mechanism is that growth of the calcium carbonate seeds as well as heterogeneous nucleation and subsequent growth on the bentonite seeds compete successfully with the heterogeneous nucleation and growth of calcium carbonate on the textile surface, which is the main cause for incrustation in soda-based detergents.

Scanning electron micrographs showed differences in morphology between the particles formed in solution and those deposited on the cotton. This supports formerly findings that entrapment by the fibres of particles precipitated in solution seems to play only a minor role in the incrustation process.

The addition of seeds is a more promising method than the use of soluble polyelectrolytes as co-builders for obtaining an acceptable degree of incrustation in soda-based detergents.
THE EFFECT OF THE ADDITION OF SEEDS ON THE INCRUSTATION

9.1 Introduction

Sodium carbonate ($\text{Na}_2\text{CO}_3$) is an economically attractive and environmentally safe alternative for phosphates in detergents. The application of sodium carbonate as builder in detergents ensures an appropriate reduction of the free calcium ion concentration in the washing liquid. These ions originate from the tap water and have negative effects on the detergency. The $\text{Ca}^{2+}$ concentration is lowered by the precipitation of calcium carbonate (CaCO$_3$). This reaction, however, also leads to the major disadvantage of soda-based detergents, namely the deposition of part of the precipitated CaCO$_3$ on the textile surface. This phenomenon is also known as incrustation. Two potential causes for the observed high incrustation levels in soda-based detergents were proposed in chapter 2: (i) heterogeneous nucleation of CaCO$_3$ on textile and subsequent growth, and (ii) CaCO$_3$ particles formed in solution get entrapped by and adhered to the textile fibres.

Addition of low amounts of specific poly-electrolytes is claimed to diminish the incrustation [1-3]. It has been shown in chapter 2 that especially polystyrene sulfonic (PSS) acid or polyvinyl sulfonic (PVS) acid containing (co)polymers seem to be promising additives for reducing the incrustation in simple soda-based detergent formulations. Furthermore, scanning electron micrographs provided indications that incrustation is mainly caused by heterogeneous nucleation of CaCO$_3$ on the textile surface. The influence of the PSS containing polyelectrolytes on the development of the particle size distribution in batch precipitation experiments, leading to qualitative information about their effects on processes as nucleation, growth and agglomeration, has been treated in chapter 4. The adsorption behaviour of these polyelectrolytes on CaCO$_3$ and cotton and their impact on the zeta
potential of these substrates has been discussed in chapter 5. Induction time measurements, described in chapter 8, revealed the effect of a copolymer of polymaleic and polystyrene sulfonic acid on separately the nucleation and growth rate of vaterite. Considering and resuming all the results leads to the conclusion that stimulation of CaCO₃ nucleation in solution by the PSS and PVS containing polyelectrolytes, at the cost of heterogeneous nucleation on cotton, is a likely mechanism for explaining their effect on the incrustation.

The addition of seeds is a well-established method for the reduction of crystalline scaling on heater pipes in e.g. desalination of sea water [4]. Like incrustation on cotton, this type of scaling is often induced by heterogeneous nucleation on the heater walls. It is thus worthwhile to investigate the effect of the addition of seeds on the incrustation. Calcium carbonate and bentonite were selected as seeds in the present experiments. Bentonite is a mineral clay with montmorillonite as the major element. Montmorillonite is an aluminium-hydrosilicate build up of two layers of SiO₄ tetrahedra with in between an octahedron layer which mainly contains Al³⁺-ions. Isomorphous substitution of these ions with divalent positive ions leads to an overall negative charge, which can be compensated by ions as Na⁺, Ca²⁺ or Mg²⁺. These ions can be exchanged for other ions in the solution, as e.g. cationic surfactants. The potentials of applying bentonite in detergents has been the subject of various publications [5-8]. Claimed benefits of bentonite in detergents are: a decreased redeposition of soil, less calcium phosphate incrustation, a fabric softener action and prevention of the precipitation of cationic surfactants.

The selected bentonite and CaCO₃ seeds have a relatively high specific surface area, and can thus in principle provide many sites for heterogenous nucleation of CaCO₃ on bentonite or growth of the CaCO₃ seeds, respectively.
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The aim of the experiments is to find out whether the incrustation can be diminished by this kind of seeding, i.e. whether the named processes can compete with the heterogeneous nucleation of CaCO<sub>3</sub> on the rough textile surface.

9.2 Experimental

AR grade chemicals, doubly distilled water and standard cotton from TNO Delft for incrustation tests were used in all experiments. The equipment for the so-called incrustation experiments is shown in fig.2.1 of chapter 2. The experimental procedure is similar to that of the type 1 experiments in chapter 2. All incrustation experiments were started with a crystallization procedure by mixing 0.5 dm<sup>3</sup> 1.07x10<sup>-2</sup> M CaCl<sub>2</sub> with 0.5 dm<sup>3</sup> of a mixed solution of 2.27x10<sup>-2</sup> M Na<sub>2</sub>CO<sub>3</sub> and 3.39x10<sup>-2</sup> M NaHCO<sub>3</sub> in a thermostated reactor at 50°C. When necessary, the pH of the solutions was brought at a value of 10.0. Various amounts of dry seeds were added to the mixed soda solution, except for the blank experiment. The investigated seed densities in the soda solution were: 1.0, 2.0 and 3.0 g/dm<sup>3</sup>, corresponding with 0.5, 1.0 and 1.5 g/dm<sup>3</sup> in the reactor at the start of the crystallization procedure.

The CaCl<sub>2</sub>-solution simulates tap water resulting in an initial water hardness in the reactor of 535 ppm as CaCO<sub>3</sub>. The average hardness of European tap water is 250 ppm, but a higher value was chosen to include hardness arising from soil and fabrics. The mixed soda solution imitates a very simple soda-based detergent formulation. After mixing of the solutions the reactor contains a supersaturated CaCO<sub>3</sub> solution, in which almost instantaneously precipitation of CaCO<sub>3</sub> occurred. After 30 minutes the resulting suspension was removed and replaced by 1 dm<sup>3</sup> water. The aim of
this rinsing procedure, which also lasts 30 minutes, is to remove the CaCO$_3$
particles which are not tightly attached to the cotton. An experiment consists
of three alternating crystallization and rinsing procedures.

Small calcium carbonate seeds were prepared by the method described
in chapter 5. The bentonite was obtained from ECC International. The
specific surface areas of the seeds were determined by BET measurements
with Krypton gas and were found to be 13±2 and 11.53±0.02 m$^2$/g for CaCO$_3$
and bentonite, respectively.

At the end of each experiment the cotton was dried and weighed. The
deposited CaCO$_3$ was dissolved in a 6% HCl solution and the Ca$^{2+}$ concentra-
tion in this solution was measured with inductively coupled plasma (further
abbreviated as ICP, Perkin Elmer Plasma 2 Spectrometer). From this Ca$^{2+}$
concentration the incrustation was calculated, expressed as mg CaCO$_3$
deposited per g cotton. All experiments were performed in duplicate.

Residual Ca$^{2+}$ concentrations in the filtrate of the crystallization
procedures were measured with ICP. The modification of the filtered calcium
carbonate crystals was determined by means of X-ray diffraction (Philips).

Two other incrustation experiments were performed in which 2.0 g/dm$^3$
CaCO$_3$ or bentonite was added to the soda solution. These experiments
consisted of only one crystallization and one rinsing procedure and at the end
both the cotton and the crystals formed in solution were collected and dried
in air at 50°C. The morphology of the crystals collected from solution and
those deposited on the cotton was examined with a JEOL 35 scanning
electron microscope, further abbreviated as SEM.

9.3 Results and discussion

The precipitation of calcium carbonate in the crystallization procedures
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started immediately after mixing of the CaCl₂ and Na₂CO₃/NaHCO₃/seeds solutions. In solution both heterogeneous (on dust particles) and homogeneous nucleation, due to the high supersaturation, will take place. This supersaturation S is defined as \( [(Ca^{2+})(CO_3^{2-})/K_{sol}]^{1/2} \), where \( (Ca^{2+}) \) and \( (CO_3^{2-}) \) are the activities of the free ions and \( K_{sol} \) is the thermodynamic solubility product. The complexes formed in solution and the supersaturation \( S \) were calculated by mass-balance and charge-balance equations by successive approximations for the ionic strength [9]. The considered equilibria and the values of the thermodynamic constants were obtained from ref.[10]. With \( K_{sol} = 2.1806 \times 10^{-6} \) mole²dm⁻⁶ for calcite and \( 6.9597 \times 10^{-6} \) mole²dm⁻⁶ for vaterite [10], the supersaturation \( S \) at the start of a crystallization procedure was computed to be 25.8 and 14.4 for calcite and vaterite, respectively.

X-Ray diffraction showed that the added CaCO₃ seeds and the precipitate were in all cases calcite, independent of the seed material and the seed density. When the precipitation mainly proceeds by growth of the calcite seeds, it can be expected that the precipitate will also be calcite, but bentonite seeds apparently also promote the deposition of the most stable polymorph in a supersaturation region where sometimes vaterite is formed. In the presence of those polyelectrolytes which diminish the incrustation vaterite was even predominantly formed (see chapter 2).

The residual Ca²⁺ concentration in the filtrate of the crystallization procedures was independent of the seed material and density. In all cases the measured residual Ca²⁺ concentration was about 0.5 ppm, which is even lower than in the blank experiment or in the presence of polyelectrolytes where a minimal residual Ca²⁺ concentration of 1.5 ppm was found. A low Ca²⁺ concentration is expected to give benefits for the detergency of the system.
Figure 9.1 The effect of the addition of seeds on the incrustation. The results for the blank experiment and the best result with polyelectrolyte (50 ppm PSS) are also depicted in the figure.

The influence of the addition of various amounts of CaCO$_3$ and bentonite seeds on the incrustation of cotton is given in fig.9.1, which shows that the incrustation decreases markedly compared to the blank experiment, when CaCO$_3$ or bentonite seeds are added.

The incrustation in the presence of CaCO$_3$ seeds is comparable to the lowest incrustation level obtained in the presence of 50 ppm polyelectrolyte (see type 1 experiments, chapter 2). This result for PSS has been indicated by the horizontal dashed line in fig.9.1.

The incrustation is not significantly dependent on the seed density in case of CaCO$_3$, because the observed differences are within the experimental error. Contrary to the type 4 experiments described in chapter 2, CaCO$_3$
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particles and cotton are both present at the start of the crystallization procedure, when the supersaturation $S$ and thus the growth rate of CaCO$_3$ are maximal. When the incrustation would mainly originate from entrapped CaCO$_3$ particles which stick to the fabric during their further growth, a higher incrustation were awaited in the presence of CaCO$_3$ seeds than in the blank and an increase in the incrustation when more seeds were added. Since both effects were not noticed, the entrapment mechanism does not predominantly contribute to the incrustation.

Heterogeneous nucleation of CaCO$_3$ on the cotton surface followed by growth is the other proposed incrustation mechanism. Growth of the added CaCO$_3$ seeds will consume the supersaturation and lower its value more rapidly to a critical value below which heterogeneous nucleation on cotton will no longer occur. When more seeds are added, the number of available growth sites is increased and a faster decrease of the supersaturation was expected and an even lower incrustation. This effect, however, was not observed, maybe because the positive effect of a faster decrease of the supersaturation is now counterbalanced by a simultaneous increase of the entrapment of CaCO$_3$ particles at the higher seed density, although this process does not predominantly contribute to the incrustation.

The incrustation in the presence of bentonite seeds is lower than in the corresponding experiments with CaCO$_3$ seeds or with the polyelectrolytes. A potential mechanism is that heterogeneous nucleation of CaCO$_3$ on the bentonite particles competes successfully with the same process on the cotton surface. Secondly, it cannot be excluded that deposition of bentonite particles on the cotton screens part of the textile surface, which is then not longer available for heterogeneous nucleation of CaCO$_3$. Such an effect has been mentioned as a potential explanation for the reduction of the calcium phosphate incrustation [6]. In this second case CaCO$_3$ should not nucleate on
the deposited bentonite particles.

The decrease in incrustation obtained by increasing the bentonite density from 0.5 to 1.0 and 1.5 g/dm$^3$ is larger than the standard deviation in the measured values. Such an effect is in agreement with both explanations, but must be treated carefully due to the relatively low number of observations.

Fig.9.2 shows SEM pictures of the seed material before the experiment, the particles collected from solution, and those deposited on the cotton in the incrustation experiments consisting of one crystallization procedure with 1.0 g seeds per dm$^3$ in the reactor followed by a single rinsing procedure.

Micrographs 9.2 A and B show that the morphology of the CaCO$_3$ seeds, which seem to exist of very rough agglomerates, does not change during the crystallization procedure. The particles collected from solution seem to be much larger that those deposited on the cotton, but this could have happened during the filtration of the sample after the experiment, prior to the sample preparation for the SEM. Some particles on the cotton, shown in fig.9.2 C, have the same habit as those collected from solution, and are presumably entrapped seeds which stuck to the cotton during the crystallization procedure. Other crystals on the cotton, however, exhibit a different rhombohedral shape, which is characteristic for calcite. These particles are formed by heterogeneous nucleation on the cotton, since crystals with this shape are not observed in the batch collected from solution.

The shape of the bentonite seeds is shown in micrograph D. After the incrustation experiment the bentonite particles seem to be covered with a layer of CaCO$_3$ particles with a poorly developed shape, as can be observed in fig.9.2 E. The bentonite seeds thus indeed seem to act as a substrate for heterogeneous nucleation of CaCO$_3$. The material deposited on the cotton consisted of rhombohedrally shaped CaCO$_3$ crystals (see fig.9.2 F). This morphology was also observed in the experiment with CaCO$_3$ seeds. No bentonite particles could be observed on the cotton surface.
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Figure 9.2

A Calcium carbonate seed material before the experiment.

B Seeds after the experiment with 1.0 g calcium carbonate seeds per dm³.

C Cotton after the experiment with 1.0 g calcium carbonate seeds per dm³.
Figure 9.2

D Bentonite seed material before the experiment.

E Seeds after the experiment with 1.0 g bentonite seeds per dm³.

F Cotton after the experiment with 1.0 g bentonite seeds per dm³.
THE EFFECT OF THE ADDITION OF SEEDS ON THE INCrustATION

Much work has been published on heterogeneous precipitation of calcium carbonate on heated metal surfaces, because this is an important step in the formation of crystalline scaling. Furthermore, it has also been reported that pyrex glass seeds are a suitable substrate for heterogeneous nucleation of calcite [11]. The number of heteronucleated particles increased with the mass of the added pyrex seeds. But desupersaturation curves showed that the supersaturated CaCO₃ solution lost its metastability earlier in the presence of calcite seeds (specific surface area 10 m²/g) than with the pyrex seeds. Heterogeneous nucleation of calcium carbonate monohydrate was also observed on sulfonated polymeric substrates [12]. This CaCO₃ modification converted slowly into the thermodynamically stable calcite. The surface free energy of the growing phase was reported to be 29 mJ m⁻².

9.4 Conclusions

Heterogeneous nucleation of calcium carbonate on textile and subsequent growth seems to be the main cause for the high incrustation levels in soda-based detergents.

The addition of calcite and bentonite seeds results in a significantly lower incrustation. Growth of the CaCO₃ seeds and heterogeneous nucleation of calcium carbonate on the bentonite seeds compete successfully with the heterogeneous nucleation of CaCO₃ on cotton, leading to a decrease in the incrustation.

The addition of seeds is a more promising method than the use of soluble polyelectrolytes as co-builders for obtaining an acceptable degree of incrustation in soda-based detergents.
CHAPTER 9

Acknowledgements

The authors are indebted to Household and Personal Care Research B.V., The Hague, for financial support and to E.G.P. Cornelissens and J. Pronk for stimulating discussions. They are most grateful to V.M.J. Arkesteijn, E.J.A. van Dam and J.F. van Lent for practical assistance and analyses.

References

SUMMARY

Sodium carbonate (soda) is potentially a good, cheap and from environmental point of view safe alternative for the substitution of phosphates in laundry detergents. A major disadvantage of the application of soda in detergents is, however, that part of the precipitated calcium carbonate is deposited on the textile surface. The fact that this unwanted process, which is usually referred to by the term "incrustation", can be affected by small amounts of polymeric additives was already known from literature. This phenomenon was confirmed by the performed incrustation experiments in which a very simple detergent was simulated by a combination of soda with a polymeric additive. Incrustation experiments in which this simple detergent formulation was extended with other frequently used detergents ingredients revealed that the effects of the polymeric additives on the incrustation were in general preserved but the ingredients did on their own also influence the degree of the incrustation.

The various publications did not give a definite answer about the cause of the incrustation nor about the mechanisms by which the additives affect this phenomenon. The general aim of this thesis was thus to find satisfying answers on these two questions.

The incrustation has in principle two possible causes, namely

1) Calcium carbonate crystals are formed in the washing liquor after which they get entrapped in the textile fabric. The entrapped crystals can adhere to the textile during further outgrowth or by bridges formed by Ca\(^{2+}\) ions,

2) Incrustation is the consequence of heterogeneous nucleation of calcium carbonate on the textile followed by the outgrowth of these nuclei.

Colloid chemical aspects could play an important role during the entrapment between the textile fibres of crystals formed in the washing
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liquor and the adherence of the entrapped crystals to the textile. The degree of adsorption of additives on calcium carbonate crystals as well as on textile and their influence on the surface charge of these substrates gives an indication for the presence of sterical hindrance or electrostatic repulsion between both substrates. These two effects could determine the degree of entrapment and adherence of crystals. The experiments performed in this thesis did not show a correlation between the degree of adsorption of additives and their impact on the surface charge on the one side and their influence on the incrustation on the other side.

This observation and the results of the incrustation experiments provided a strong indication that heterogeneous nucleation of calcium carbonate on textile is the main cause of the incrustation. This also implies that the effects of the additives on the incrustation must be related to their influence on the nucleation behaviour of calcium carbonate in solution as well as on the textile or to their impact on the growth rate of the crystals. A qualitative analysis of the impact of the additives on the particle size distribution in batch precipitation experiments of calcium carbonate revealed that the stimulation of the nucleation of calcium carbonate in solution by additives is the most likely explanation for the observed decrease of the incrustation in the presence of these additives, while they do not seem to affect the growth rate of calcium carbonate. Furthermore growth inhibition of calcium carbonate by additives seems to result in an increased or hardly affected degree of incrustation.

Applying a combined analysis of induction time measurements in seeded and unseeded precipitation makes it possible to determine the separate influence of an additive on both the nucleation and growth rate of crystals. The assumed stimulation of the nucleation of calcium carbonate could not be definitely confirmed by applying this method on the precipitation of calcium
carbonate. On the basis of the other results it remains, however, acceptable that the incrustation is mainly caused by heterogeneous nucleation of calcium carbonate on textile and that the degree of incrustation can be diminished by additives which stimulate the nucleation of calcium carbonate in solution.

In order to sustain these assumptions some incrustation experiments were performed in which the polymeric additives were replaced by two types of seeds, namely calcium carbonate and bentonite seeds. Also in the presence of seeds a relative increase of the amount of solid calcium carbonate in solution can be expected. This will be caused by outgrowth of the CaCO$_3$ seeds or by heterogeneous nucleation on the bentonite seeds and consequences of these processes should be a decrease of the heterogeneous nucleation on the textile, and thus of the incrustation. These effects were indeed observed and when bentonite was used as seed material this even resulted in a lower degree of incrustation than was found in the presence of the most effective polymeric additive.
SAMENVATTING

Natrium carbonaat (soda) is in potentie een goed, goedkoop en uit milieutechnisch oogpunt veilig alternatief om fosfaten te vervangen in wasmiddelen. Het grote nadeel van het toepassen van soda in wasmiddelen is echter dat een gedeelte van het neergeslagen calcium carbonaat zich afzet op het textieloppervlak. Het feit dat dit ongewenste proces, wat veelal aangeduid wordt met de term "incrustatie", beïnvloed kan worden door kleine hoeveelheden polymere additieven was reeds bekend uit de literatuur. Dit verschijnsel werd ook teruggevonden in de uitgevoerde incrustatie experimenten, waarbij een heel eenvoudig wasmiddel gesimuleerd werd door een combinatie van soda en een polymeer additief. Uit incrustatie experimenten waarbij het eenvoudige wasmiddel verder werd uitgebreid met andere veelgebruikte ingrediënten blijkt dat de relatieve effecten van de polymere additieven in het algemeen behouden blijven maar dat de ingrediënten zelf ook een invloed hebben op de mate van incrustatie.

De diverse publikaties gaven in het algemeen geen eenduidig uitsluitend over de oorzaak van de incrustatie en over de manier waarop additieven dit verschijnsel kunnen beïnvloeden. Het algemene doel van dit proefschrift was dan ook om een bevredigend antwoord te vinden op deze twee vragen.

Incrustatie heeft in principe twee mogelijke oorzaken, namelijk

1) In de wasvloeistof ontstaan calcium carbonaat kristallen die hierna ingevangen kunnen raken in het textiel weefsel. Deze ingevangen kristallen kunnen hechten aan het textiel oppervlak gedurende hun verdere uitgroei of door brugvorming via $\text{Ca}^{2+}$ ionen,

2) Incrustatie ontstaat als gevolg van heterogene nucleatie van calcium carbonaat op het textiel, gevolgd door uitgroei van deze kiemen.

Colloid chemische aspecten zouden een belangrijke rol kunnen spelen bij de invang van in de wasvloeistof gevormde kristallen door het textiel.
SAMENVATTING

weefsel en bij de hechting van de ingevangen kristallen aan het textiel. De mate van adsorptie van additieven op zowel calcium carbonaat kristallen als op textiel en hun invloed op de oppervlaktelading van deze beide substraten geven een indicatie over de aanwezigheid van sterische hindering of electrostatische afstoting tussen beide substraten. Deze twee effecten zouden de mate van invang en hechting van de kristallen kunnen bepalen. De in dit proefschrift uitgevoerde experimenten gaven echter geen verband te zien tussen de mate van adsorptie van additieven en hun invloed op de oppervlaktelading enerzijds en hun effect op de incrustatie anderzijds.

Deze waarneming en resultaten van model incrustatie experimenten geven een sterke aanwijzing dat heterogene nucleatie op textiel de belangrijkste oorzaak is voor het ontstaan van incrustatie. Dit houdt tevens in dat de effecten van de additieven op de incrustatie gerelateerd moeten zijn aan hun invloed op het nucleatie gedrag van calcium carbonaat in zowel de vloeistof als op het textiel of aan hun effect op de groei snelheid van de kristallen. Uit een kwalitatieve analyse van de effecten van de additieven op de deeltjes grootte verdeling in batch precipitatie experimenten van calcium carbonaat blijkt dat het aannemelijk is dat additieven die de incrustatie verlagen dit hoogstwaarschijnlijk doen door de nucleatie van calcium carbonaat in de vloeistof te stimuleren, terwijl ze de groeisnelheid niet beïnvloeden. Verder lijken additieven die tot een remming van de groei van calcium carbonaat aanleiding geven een verhoogde mate van incrustatie te veroorzaken of de incrustatie nauwelijks te beïnvloeden.

Een gecombineerde analyse van induktietijd metingen in geënte en ongeënte precipitatie experimenten blijkt het mogelijk te maken om de afzonderlijke effecten van een additief op zowel de groei- als de nucleatiesnelheid van kristallen te bepalen. De veronderstelde stimulering van de nucleatie van calcium carbonaat kon niet definitief bevestigd worden door het
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toepassen van deze methode op de precipitatie van calcium carbonaat. Op grond van de overige resultaten blijft het echter waarschijnlijk dat de incrustatie veroorzaakt wordt door heterogene nucleatie van calcium carbonaat op textiel en dat de mate van incrustatie verlaagd kan worden door additieven die de nucleatie van calcium carbonaat in de vloeistof stimuleren.

Om deze veronderstellingen te bewijzen werden er ten slotte incrustatie experimenten uitgevoerd waarbij de additieven vervangen werden door twee soorten enten, namelijk calcium carbonaat en bentoniet enten. Ook in aanwezigheid van enten kan namelijk een relatieve toename van de hoeveelheid vast calcium carbonaat in de vloeistof worden verwacht. Dit zou dan een gevolg zijn van groei van de CaCO₃ enten of van heterogene nucleatie op de bentoniet enten, waardoor de heterogene nucleatie op textiel en dus de incrustatie af zouden moeten nemen. Deze effecten werden inderdaad gevonden en voor bentoniet als entmateriaal was de incrustatie zelfs lager dan in aanwezigheid van het best werkende polymere additief.
ACKNOWLEDGEMENTS

This thesis has been accomplished thanks to the work and the help of many other persons, which I want to thank here for their indispensable contributions. I am aware of the fact that it is impossible to mention everybody and I apologize to those who are unjustly not mentioned here.

I want to acknowledge Prof. Dr. Ir. G.M. van Rosmalen and Prof. Dr. D. Kashchiev for teaching me the principles of crystallization and for the stimulating and fruitful discussions.

I gratefully acknowledge Household and Personal Care Research B.V. for financially supporting this project. The personnel of the Research and Development group, and especially E.G.P. Cornelissens and J. Pronk, are thanked for their assistance and the helpful discussions.

Great support was received from V. Arkesteijn, W. Boeken, H. Bruggeman, G. Demian, M. de Jonge, M. Laldjising, M. Lentelink, L. Maass, R. Nijhuis, D. Stajcer and J. Timmerman, who contributed to this thesis with experimental work during their graduation period. I am indebted to Ing. R.C. van Landschoot and Ing. P.F.M. Durville for their experimental assistance and valuable suggestions.

The following persons are acknowledged for their help with the analyses: E.J.A. van Dam for the SEM micrographs, J.F. van Lent for the X-Ray diffraction analyses, H.L. Jansma for the Coulter Counter measurements and J. Tiggelman and M. van der Aa for the ICP analyses.

I wish to thank the supporting personnel of the Laboratory for General and Analytical Chemistry and the Laboratory for Process Equipment for their help.

Finally, I can look back at a very nice PhD period thanks to the pleasant and cooperating atmosphere created by all my colleagues, and especially by M.C. van der Leeden and C.H. de Vreugd.
CURRICULUM VITAE


De doctoraalfase van zijn studie bestond uit het hoofdvak Vaste Stof Chemie (Dr. D.J.W. IJdo) en de bijvakken Heterogene Katalyse (Prof. Dr. V. Ponec) en Inleiding Toepassingsgerichte Informatica (Dr. D. van Albeda). Het doctoraalexamen (oude stijl) werd behaald in oktober 1986.

Vanaf november 1986 was hij als A.I.O. werkzaam bij de groep Industriële Kristallisatie en Precipitatie binnen de Faculteit der Scheikundige Technologie en der Materiaalkunde van de Technische Universiteit Delft. In opdracht van Household and Personal Care Research werd daar een promotieonderzoek uitgevoerd, met als onderwerp: Het vormings- en aanhechtingsgedrag van calcium carbonaat in soda bevattende wasmiddelen. De resultaten van dit onderzoek zijn weergegeven in dit proefschrift.