Mechanisms of Initiation of Incrustation

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Initiaton of incrustation by crystallization mechanisms is studied. An experimental technique was developed by which nucleation of a crystalline phase on a solid surface is investigated at controlled local supersaturation without the interference of particle deposition. Experiments were carried out with different substances and surface materials. The results show that the solid surface may catalyze primary nucleation and hence promote the initiation of incrustation, but this was recorded only at quite high supersaturation. Collision of crystals with the solid surface in a supersaturated solution may initiate incrustation at a reasonably low supersaturation and can be of substantial industrial importance.

Introduction

The performance of crystallization processes is occasionally reduced substantially by the deposition of the crystallizing substance onto the surface of the equipment. This deposition may take place on the inner surface of the crystallizer, on the stirrer, or on the sensors used to control the process. Incrustation of industrial crystallizers results in production loss, increased energy consumption, mechanical damage, reduced product quality, and safety problems (Jancic and Grootscholten, 1984). The fundamental mechanisms of incrustation relate to mechanisms of crystallization and particle deposition. Incrustation is a type of fouling, but as opposed to many other fouling situations, in crystallization processes conditions are deliberately generated that promote fouling, that is, supersaturation and particles.

There is only a limited number of studies published on incrustation, and, as is the case for fouling research in general, the work tends to be rather applied. Fundamental work on the underlying mechanisms is scarce. Duncan and Phillips (1979) and Shock (1983) determined the range of supersaturation, within which crusts are unlikely to form (the metastable zone width for crust formation), to be the same as the metastable zone width for nucleation in the bulk. The time before crusts are initiated (the induction period) has been shown to decrease with increasing supersaturation (Chandler, 1964; Hasson and Zahavi, 1970; Ritter, 1981), and the time is shorter in a mixed flow system than in a plug-flow system (Steinberg and Hasson, 1979). Duncan and Phillips (1979) found the wall surface material has no significant catalyzing effect on surface nucleation. However, Chandler (1964) and Heffels et al. (1984) claim that the surface wall material may influence the induction time and detachment rate, but not the deposition rate. It is suggested that hard deposits are due to crystallization onto the surface, and loose deposits result from particle deposition (Andritsos and Karabelas, 1991b; Duncan and Phillips, 1979).

Particle deposition, crystal nucleation, and crystal growth may occur simultaneously in the studies referred to above. In addition, the solid surface is usually used for indirect cooling or heating, by which the actual local supersaturation at the surface becomes uncertain and dependent on flow conditions. The supersaturation strongly influences the rate of crystal growth and, in particular, on nucleation rates. Hence, a detailed analysis of the importance of different mechanisms and conclusions concerning acceptable levels of supersaturation, become uncertain. Chandler (1964) expressed the need for isothermal experiments, but was unable to overcome the experimental difficulties. Isothermal experimental techniques have been developed by Smith (1965) and Andritsos and Karabelas (1991a).

Based on previous work and general reasoning, a structure of the underlying mechanisms of crust formation in cooling crystallizers below the liquid surface can be depicted (Figure 1). The formation of crusts comprises an initiation step followed by the growth of the deposition, and sometimes detachment. Initiation is either by deposition of particles or by crystal nucleation onto the solid surface. If the surface is used for cooling or acts as a "cold spot" because of heat transfer to the environment, nucleation may take place as a result of high local supersaturation. On the other hand, if the surface material in itself is able to catalyze spontaneous nucleation, crusts may form at local supersaturation below the bulk solution metastable limit. The present study focuses on initiation

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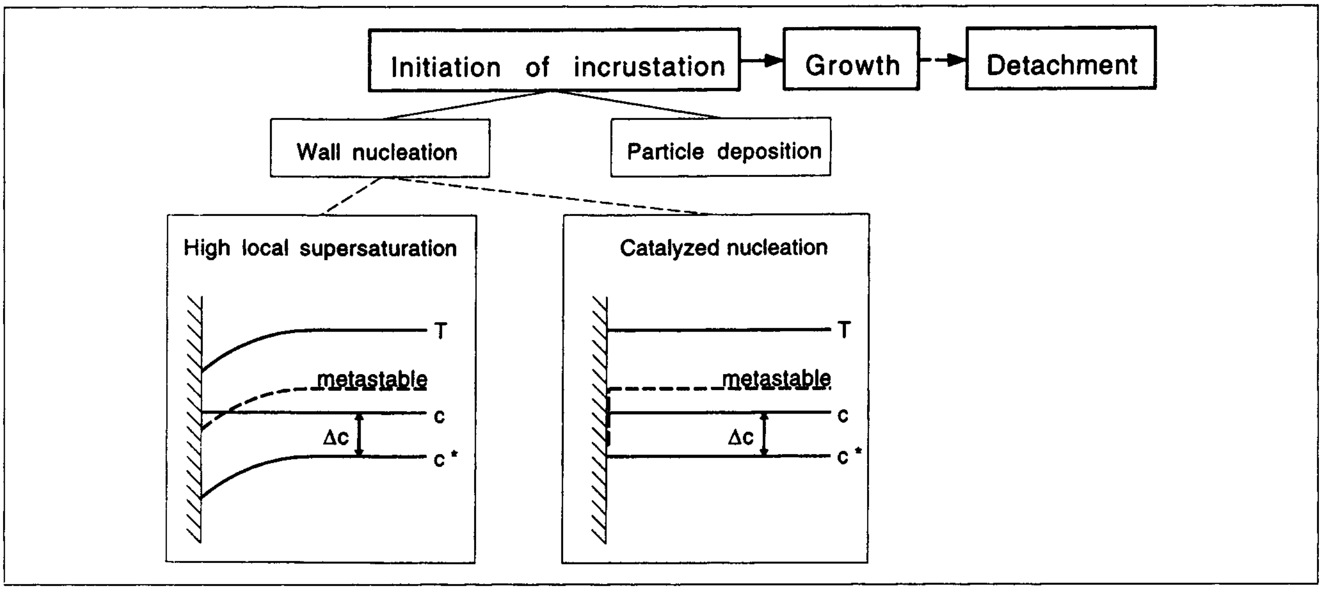

Figure 1. Problem structuring.

by crystallization mechanisms. Experiments are designed to distinguish crystal nucleation on the surface from crystal deposition in order to investigate the catalyzing effect of the surface material. The experimental work reveals that one additional crystallization initiation mechanism, referred to below as collision initiation, must be recognized. Collision initiation is also investigated in this study. In the experiments, the solid surface is not used for heat transfer, and hence the supersaturation becomes accurately known.

Experimental Work

Experiments have been performed on the catalytic effect of the solid surface on primary crystal nucleation, and on the importance of crystals colliding with the surface for a generation of surface attached crystal nuclei. Organic and inorganic compounds are investigated. Supersaturation is generated by gently decreasing the temperature of the solution. In the development of the experimental technique, two main difficulties were dealt with: (i) The air/liquid interface of a supersaturated solution can promote nucleation; (ii) in agitated solutions, crystals may form and deposit before they reach detectable size, when it becomes difficult to distinguish between particle deposition and crystal nucleation. The first problem is solved by keeping the interface unsaturated. However, a few experiments have been carried out to investigate the influence of the air/liquid interface on primary nucleation. The second problem is solved by keeping the solution nonagitated. However, during the introductory work the solid surface was kept rotating on an agitator shaft. It was discovered that crystals originally formed as nuclei on the surface could detach and create a trail of new nuclei on the solid surface when sliding off. This observation led to the experiments on the importance of crystals colliding with the surface and the discovery of the collision initiation mechanism.

Apparatus

A 0.5-L glass cylinder (Ø 49 mm, length 330 mm) is up to about 2/3 of its height submerged into a water bath. The top 1/3 of the glass cylinder is insulated. A small heating coil is placed in the top 1/3 of the cylinder to keep the temperature of the top fraction of the solution constant (5°C above the saturation temperature). The temperature of the water bath determines the supersaturation of the lower fraction of the solution. Three different designs of the apparatus have been made. On the left side of Figure 2, a plate of the investigated solid surface material (25×70 mm) is hanging close to the bottom of the cylinder. The catalytic effect of spontaneous wall nucleation of the solid surface is investigated. To be able to study spontaneous nucleation at a gas-liquid interface without any influence of heat and mass transfer over the interface, an air trap was designed. The air trap is illustrated in Figure 2. It is a glass test tube (Ø 10 mm) held upside down in the bottom attached to the end of a glass rod. To the right in Figure 2, a sole-shaped plate (48×99 mm), used to investigate the influence on crust initiation of collisions between

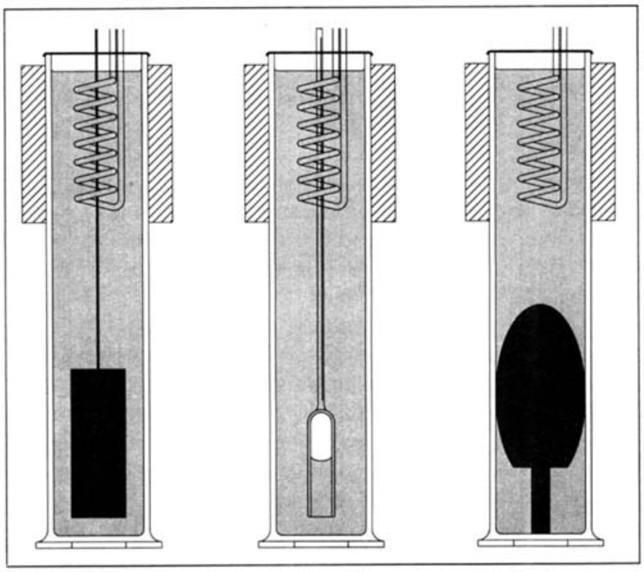

Figure 2. Rectangular test plate (left); air trap (center); and sole shaped test plate (right).

Table 1. Substances Briefly Tested and Excluded from the Study

Substance	Comment
Aluminum ammonium sulfate	Wide metastable zone
Ammonium chloride	Small crystals
Ammonium phosphate	No secondary nuclei generated, viscous
Ammonium sulfate	Wide metastable zone, no secondary nuclei generated
Benzoic acid	Small crystals
D-lactose	Small crystals
Ferrous sulfate	Oxidizes
Magnesium sulfate	No secondary nuclei generated, viscous
Paracetamol	Decomposes
Pentaerythritol	Small crystals
Potash alum	Wide metastable zone
Potassium nitrate	Needle shaped crystals
Sodium formate	No secondary nuclei generated, needle shaped crystals
Urea	Wide metastable zone, needle shaped crystals

crystals and a solid surface, is illustrated. The plate has an angle of about 65° to the horizontal plane. Please note that neither the plates nor the air-liquid interface of the air trap are used for heat transfer. The temperature in the center of the cylinder, 0.01 m above the plate, has been checked and found to differ by about 0.10°C from that of the water bath at a cooling rate of 0.010°C per min. A video equipment is utilized for registration of the events at the investigated surfaces. A video camera (Hitachi VM-S83E) connected to two video recorders (Panasonic JV-45) are used to record each experiment. The system allows for 20 h of unsupervised continuous recording.

Materials

The following six substances have been used in the experiments: adipic acid $(CH_2)_4(COOH)_2$ (Merck, > 99.6%), citric acid monohydrate $C_3H_4OH(COOH)_3 \cdot H_2O$ (Merck, >99.5%), glycine CH_2NH_2COOH (Merck, > 99.7%), succinic acid $(CH_2COOH)_2$ (Astra Sweden, > 99.5%), potassium bromide KBr (Merck, 99%), and sodium sulfate Na_2SO_4 (Merck, 99%). The chemicals are used as purchased without further purification. For practical reasons, the growth rate should not be too low, the solubility should increase with temperature, crystal shape should be compact, and the metastable region should be not too narrow and not exceedingly wide. A significant number of additional substances have been briefly examined, but found unsuitable for different reasons (Table 1). In all experiments, deionized water is used as solvent.

Stainless steel and Teflon (du Pont registered trademark) have been used as solid surface materials. The Teflon plate is used without additional polishing, while the steel plate is grinded with a fine grade emery paper. Plates are cleaned by washing in ethanol (96%) and in deionized water before each experiment. Contact angles of a resting drop of distilled water have been determined as advancing angles using a Ramè-Hart A100 contact angle goniometer (Mountain Lake, NJ, USA). On the prepared Teflon plate the angle is about 92°, and on the prepared steel plate about 56°.

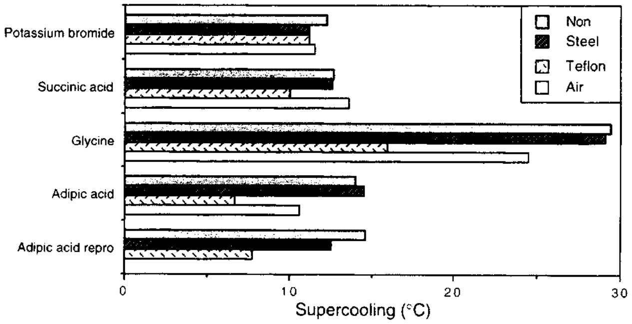

Figure 3. Catalyzed primary nucleation on steel, Teflon, and at the air/liquid interface.

Procedures

Catalytic effect experiment

All equipment is washed, first in ethanol and then in deionized water, prior to each experiment. The solution is prepared by mixing deionized water with excess of crystals. This suspension is allowed to equilibrate for several days under agitation at the desired temperature (the saturation temperature) in an accurately controlled water bath. The agitation is turned off and crystals are allowed to settle before the supernatant solution is withdrawn, filtered through a medium fast filter paper and heated up. The glass cylinder is almost completely filled with this still superheated solution and is placed in the water bath and kept at 5°C above the saturation temperature of the solution. The plate or the air trap is introduced into the solution. The cooling of the solution is generated by linearly decreasing the temperature of the water bath at 0.01°C per min. Any nucleation on the investigated surface or elsewhere in the cylinder is detected by means of the video camera. The position of the first crystal formed and the time of nucleation is registered. From the time of nucleation, the temperature and thereby the level of supersaturation may be calculated. It takes between one to two days to perform each experiment.

The nucleation rates are always very low in these experiments. Even at the highest supersaturation, one or a few crystals may continue to grow for hours without any new crystals appearing. This makes it possible to detect the first crystal generated. Highly supersaturated solutions are difficult to work with, and minor differences in dust particle content or impurities may influence the results considerably. Reproducibility is depicted in Figure 3 by the results of two identical sets of experiments for adipic acid. The difference between duplicated experiments is about 2°C or less.

Collision experiment

The procedures of preparation of the collision experiments are the same as for the catalyzed effect experiments. The collision experiment also starts at 5°C above the saturation temperature. The water bath is then cooled at a rate of 0.010°C per min, down to a desired operation temperature. The solution properties are stabilized for about 2 h at the chosen level of supersaturation. Two parent crystals are then dropped directly after one another into the supersaturated solution, falling free towards the bottom. (The terminal falling velocity is about 0.1 m/s for all substances except for citric

Table 2. Results of Catalytic Effect Experiments

Compound	Catalytic Effect: Steel	Teflon	Air/Liquid Interface
Potassium bromide	None	None	None
Sodium sulfate	*	*	*
Adipic acid	None	Strong	Weak
Citric acid	*	*	*
Glycine	None	Strong	Weak**
Succinic acid	None	Weak	None

*No crystals detected within the experimental temperature range, wide metastable zones (sodium sulfate $\Delta T > 18°C$, citric acid $\Delta T > 33°C$).
**First crystal not detected at the interface.

acid for which it is about 0.02 m/s). On their way down, they collide and slide along the sole shaped plate. Eventually they pass the lower edge, and fall to the bottom of the cylinder. The video camera records the path of each falling crystal, as well as any crystals gradually appearing on the plate or elsewhere. The new crystals formed are allowed to grow for 1 to 4 h, before the experiment is terminated.

The parent crystals are prepared by an uncontrolled cooling crystallization. The crystals are taken directly from the preparation solution (at room temperature) into the experimental solution and are neither dried nor washed. The size of the parent crystals is about 2 mm×2 mm×3 mm. The shape and size of the crystals of each substance do however vary and different substances produce crystals of different shapes. A scatter in the results can be due to differences in crystal size and shape, and differences in the descending movement of each crystal. Different faces and edges may contact the surface. It has been shown (Elwenspoek and Bennema, 1984) that slow growing faces are much more effective for contact nucleation than fast growing faces. The impacting conditions in these collision experiments are believed to be mild compared to those found in an agitated crystallizer.

Results

Catalytic effect experiments

The catalytic effect of steel, Teflon, and the liquid/air interface is investigated for nucleation of potassium bromide, sodium sulfate decahydrate, succinic acid, adipic acid, citric acid monohydrate, and glycine. The saturation temperature is 30°C for succinic acid, adipic acid, potassium bromide, and sodium sulfate decahydrate and 40°C for citric acid monohydrate and glycine.

Results are summarized in Table 2. For sodium sulfate and citric acid, no crystals are detected within the experimental temperature range. Sodium sulfate is supercooled 18°C below saturation and citric acid 33°C, with nucleation nowhere in the system. Nucleation is observed for the remaining four substances, and detailed results are presented in Figure 3. Each bar represents the degree of supercooling at which the first crystal is detected. For each substance, the upper bar is for an experiment "without" a surface, the second bar is for an experiment with a steel plate, the third bar is for an experiment with a Teflon plate, and the lower bar is for an air/liquid interface present in the solution.

For potassium bromide, if no surface is present, nucleation takes place at a supercooling of about 12°C, which accordingly is a measure of the metastable region under these particular conditions. In the case of a plate present, nucleation takes place at approximately the same supercooling, regardless of surface properties. For succinic acid, the results are almost the same with the Teflon surface possibly having a weak catalyzing effect. For adipic acid and glycine, the results indicate that Teflon catalyzes primary nucleation, even though the required supersaturation is still quite high. In the experiments with succinic acid, adipic acid and glycine, and a Teflon plate, the first crystal is observed on the plate. In all other experiments with a solid surface or without any plate, the first crystal appears on the bottom of the cylinder. Crystals are never observed on the walls of the cylinder before they appear elsewhere. For adipic acid and glycine, the results indicate a catalytic effect of the air/liquid interface. However, only for adipic acid is the first crystal observed at this interface. In all other air/liquid interface experiments, the first crystal is observed at the bottom of the cylinder.

Besides the test surface, a glass cylinder surface and the surface of dust particles are also present. If the test surface is found to induce primary nucleation, it means that the test surface has a stronger catalyzing effect than other surfaces present. If nucleation is not promoted by the test surface, the conclusion is that other surfaces are more active than the test surface. This means that if the solutions are more carefully filtered, higher supersaturations can be studied and perhaps also the steel plate can be found to promote nucleation.

Collision experiments

Collision initiation of potassium bromide, sodium sulfate decahydrate, succinic acid, adipic acid, citric acid monohydrate, and glycine on steel and Teflon is investigated. The saturation temperature is 30°C in all experiments. Results are summarized in Table 3. For all six substances, nucleation is

Table 3. Results of Collision Experiments

Compound	Steel Plate*	Teflon Plate*
Potassium bromide	Slide off at ΔT 3.0–5.0°C (2)	At bottom at ΔT 4.0°C (1)
Sodium sulfate	Slide off at ΔT 1.0–3.0°C (2)	At bottom at ΔT 1.5°C (1)
Adipic acid	Crust initiation at ΔT 4.0°C (1)	Crust initiation at ΔT 4.0°C (1)
Citric acid	Slide off at ΔT 8.0–15.0°C (5) No nucleation at ΔT 4.0–7.0°C (2)	Crust initiation at ΔT 9.0–15.0°C (4) No nucleation at ΔT 4.0–8.0°C (3)
Glycine	Slide off at ΔT 8.0°C (1) No nucleation at ΔT 5.0–6.0°C (2)	Crust initiation at ΔT 6.0°C (1)
Succinic acid	Crust initiation at ΔT 0.5–5.0°C (8)	Crust initiation at ΔT 2.0–5.0°C (6) No nucleation at ΔT 1.0°C (1)

*The number of experiments performed within the supercooling range are given within parentheses.

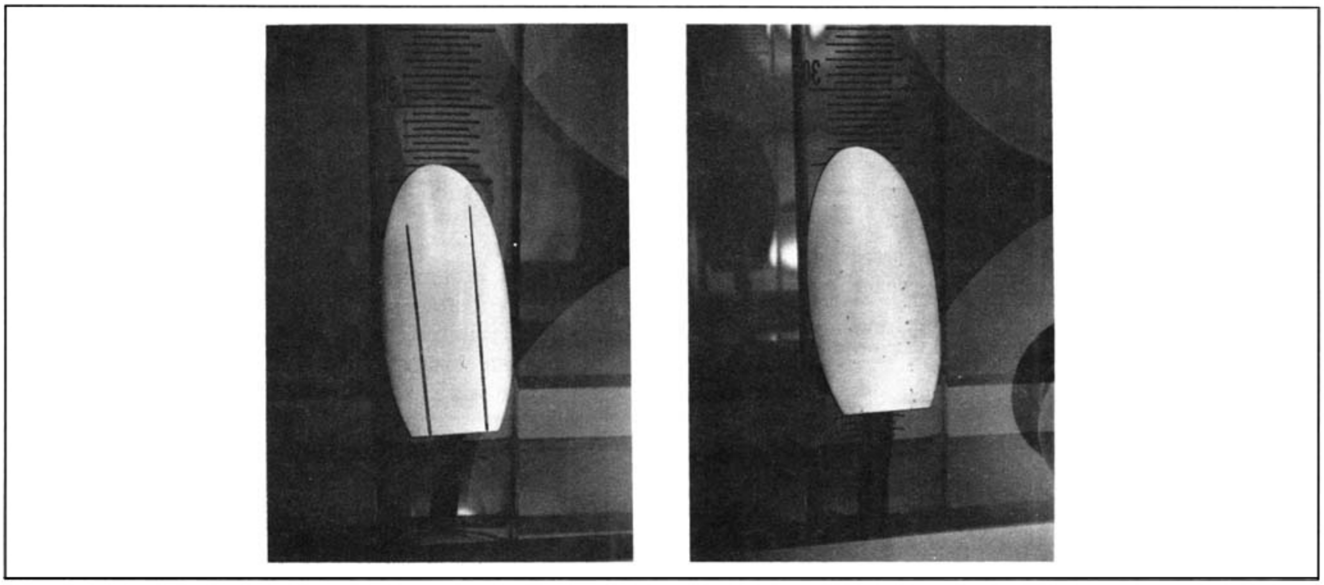

Figure 4. Sliding paths and nucleation strikes.

recorded and four different types of nucleation behavior are observed: (1) No nucleation found, denoted "no nucleation"; (2) crystals are nucleated by only found at the bottom of the cylinder, denoted "at bottom" in the table; (3) new crystals appear on the plate, but they detach and slide off the plate, denoted "slide off" in the table; (4) crystals nucleate on the plate where they stay and continue to grow, denoted "crust initiation." The range of supercooling and the number of experiments performed are given in the table. For potassium bromide and a steel plate, crystals are formed along the sliding path of the parent crystals, but they tend to slide off. In the case of the Teflon plate, new crystals are only found at the bottom. For sodium sulfate decahydrate, the behavior is similar. For succinic acid and adipic acid, nucleated crystals appear along the sliding path on both steel and Teflon at the termination of each experiment. For citric acid monohydrate and glycine, the crystals tend to slide off from the steel surface, while they stick to the Teflon surface. Figure 4 shows photographs of the sole shaped plate. The photograph to the left depicts the sliding paths of two parent crystals in a typical experiment for succinic acid/steel. The photograph to the right shows the nucleated crystals that can be observed after about two hours.

Series of collision experiments at various supercoolings have been performed with succinic acid and citric acid monohydrate. Results for succinic acid are shown in Figure 5. The diagram presents the number of nuclei generated per mm sliding path vs. supercooling. The total number of nuclei that can be observed on the plate in each experiment (two parent crystals) is counted and divided by the sum of the sliding path length of both particles, as measured from the video film. In the case of the steel plate the number of crystals per unit length sliding path increases linearly with supercooling. This straight line tends to deviate from the origin, indicating the possibility of a narrow metastable zone for collision initiation of crusts. In the case of the Teflon plate, no crystals are found on the plate at 1°C supercooling, a few at 2 and 2.5°C, a significant number at 3 and 3.5°C, and rather few again at 5°C supercooling. A few crystals are usually found outside the paths of the descending parent crystals (see discussion), but this is about the same in all experiments. A low number of crystals on the plate along the paths is hence not compen-

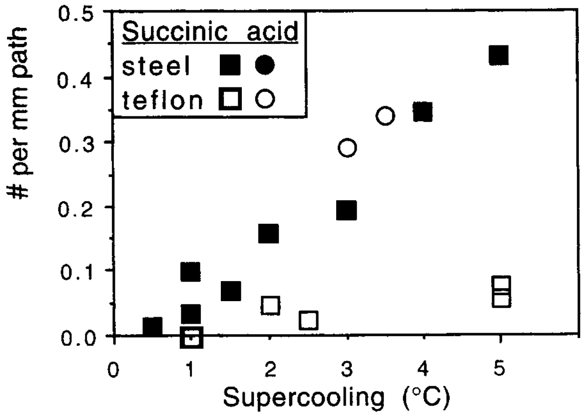

Figure 5. Collision initiation of succinic acid.

Rings denote sliding and squares tumbling motion.

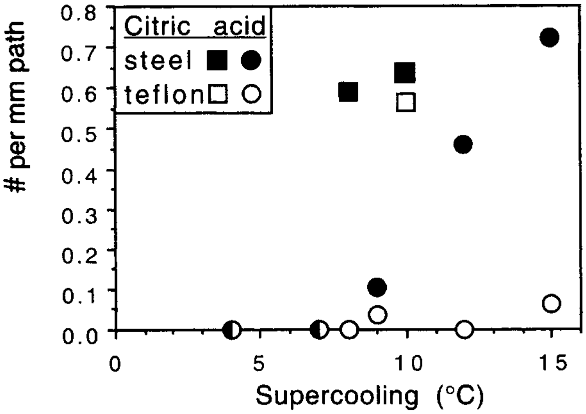

Figure 6. Collision initiation of citric acid monohydrate.

Rings denote sliding and squares tumbling motion.

sated for by a higher number elsewhere in these experiments. Even though the results are more scattered, the number of nuclei formed tends to be less on the Teflon plate than on the steel plate. Also on the Teflon plate, a narrow metastable zone is indicated. Results for citric acid monohydrate are shown in Figure 6. In the case of a steel plate the crystals tend to slide off as they reach a size of about 0.001 m. In the results the crystals have been counted before they slide off. For both plates, data are rather scattered but the overall picture is that the existence of a metastable zone is more pronounced than for succinic acid. Citric acid monohydrate does not nucleate on the plate until the supercooling exceeds 7°C. Again, it seems that the number of nuclei on the steel plate tends to be much higher than the number on the Teflon plate, at equal supercooling. For the sake of clarity, the low number on the Teflon plate is not compensated for by a higher number elsewhere.

The specific parent crystal motion down the plate can actually be observed on the video recordings. Mainly two different types of movement down the plates can be identified. Either the crystal is tumbling down the plate resulting in repeated contacts between crystal edges and the plate, or the crystal is sliding gently down the plate keeping the same face of the crystal more or less in contact with the plate throughout the descent. An analysis reveals that the actual motion of the parent crystal along the plate has significant influence on the number of crystals formed on the plate. For succinic acid, the tumbling motion is usually found. However, the sliding motion is observed in the experiments: succinic acid/Teflon at 3.0 and 3.5°C supercooling, where particularly high nucleation is found. Hence on Teflon, a sliding movement produces more nuclei than a tumbling motion. A tumbling motion on Teflon produces much less nuclei than a tumbling motion on steel at equal supercooling. A sliding motion on Teflon produces about the same number of nuclei as a tumbling motion on steel, but this is perhaps just a coincidence. A sliding motion was never observed for succinic acid/steel. For citric acid monohydrate, the parent crystals usually slide down the plate. However, the high nucleation rates observed at 8°C and 10°C supercooling on steel and at 10°C supercooling on Teflon are all a result of the tumbling type of motion down the plates. In all other citric acid experiments, the movement is of the sliding type. Hence for citric acid monohydrate, a sliding movement results in less crystals generated on the plate, which is the opposite of the results found for succinic acid.

The driving force for nucleation is more adequately represented by the supersaturation than by the supercooling. At 5°C supercooling the relative supersaturation is about 0.19 for succinic acid and about 0.11 for citric acid monohydrate. In spite of significant differences in the experimental conditions (such as supersaturation and particle size and shape) and in the physical properties (such as particle density and fluid viscosity), the number of nuclei formed per unit length of sliding path only differs by a factor of two for succinic acid and citric acid monohydrate.

Discussion

In the experiments, the local supersaturation is accurately known and particle deposition can be excluded as a possible mechanism. The results show that catalyzed surface nucleation may result in crust initiation (by which we denote the case when nuclei are formed at and stick to the surface) for succinic acid, glycine, and adipic acid. In the case of citric acid monohydrate, no nuclei are generated even at very high supercooling. It is also shown that collision nucleation may result in crust initiation for all four organic compounds. For the two inorganic compounds, no crusts are initiated by any of the mechanisms. In Table 4, the results of collision experiments are compared with those of the catalyzed effect experiments. The table shows that collision initiation occurs at a significantly lower supersaturation than initiation by catalyzed primary nucleation. In addition, collision initiation occurs on both steel and Teflon surfaces, while only the Teflon surface catalyzes initiation by primary nucleation. The catalytic effect of the air-liquid interface is shown to be quite weak (adipic acid and glycine) or negligible. Hence if nuclei appear at the air-liquid interface, this is likely to be mainly due to a local high supersaturation generated by evaporation, rather than due to a catalytic influence of the interface.

Table 4. Comparison of Collision and Catalytic Initiation

	Lowest Supercooling Demand	
	Collision Initiation	Catalytic Initiation
Adipic acid	< 4°C* (Teflon) < 4°C* (Steel)	7°C (Teflon) † (Steel) 11°C (air)
Citric acid	9°C (Teflon) 8°C (Steel)	> 33°C** (Teflon) > 33°C** (Steel) > 33°C** (Air)
Glycine	< 6°C* (Teflon) † (Steel)	16°C (Teflon) † (Steel) 24°C (Air)
Succinic acid	2°C (Teflon) 0.5°C (Steel)	10°C (Teflon) † (Steel) † (Air)

*No experiments are performed at less supercooling.
**No nucleation was detected, not even at the highest supercooling = 33°C.
†No initiation was detected.

Mechanisms of catalyzed surface nucleation

In the classical theory (Mullin, 1993), heterogeneous nucleation is regarded as a catalyzed homogeneous nucleation. The catalyzing effect is related to the conditions at the interface between the solution, the crystalline solid, and the surface of the catalyzing material, and is normally described as a reduction ϕ of the overall excess Gibbs free energy between the smallest stable solid particle of the solute and the solute in solution ΔG_{crit}

$$\Delta G'_{\text{crit}} = \phi \cdot \Delta G_{\text{crit}} \tag{1}$$

ΔG_{crit} (J) is the free energy change, homogeneous nucleation, and $\Delta G'_{\text{crit}}$ (J) is the free energy change, heterogeneous nucleation. ϕ increases (Mullin, 1993) from zero to unity with increasing contact angle θ between the crystalline deposit and the surface of the catalyzing material (Figure 7). The contact angle (θ) is a measure of the affinity of the crystalline deposit to the solid surface. When $\theta = 180°$, there is no affinity at all and from a primary nucleation point of view, the solid surface is nonexistent. At lower angles, there is a certain de-

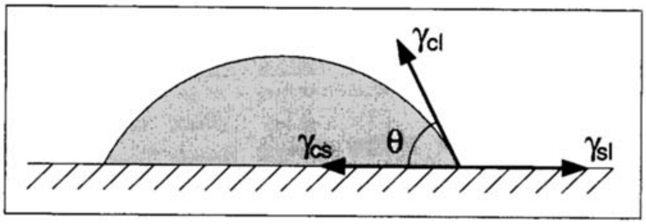

Figure 7. Definition of contact angle and interfacial tensions between the three phases.

gree of affinity and the supersaturation requirement for nucleation decreases with decreasing θ. θ depends on the interfacial tension between the solid surface and the liquid γ_{sl} (mN/m) between the deposit and the solid surface γ_{cs} (mN/m), and between the deposit and the liquid γ_{cl} (mN/m)

$$\cos\theta = \frac{\gamma_{sl} - \gamma_{cs}}{\gamma_{cl}} \tag{2}$$

Table 5 presents an attempt to make a rough comparison of interfacial tensions. The contact angle measurements in pure water reveal that the Teflon surface, as expected, is less hydrophilic than the steel plate. We expect that also in supersaturated aqueous solutions of the solutes, the solid-liquid interfacial tension γ_{sl} is relatively high for Teflon and significantly lower for steel. If the crystalline phase is reasonably hydrophobic, the crystal-solid interfacial tension γ_{cs} will be lower for Teflon and higher for steel. The crystal-liquid interfacial tension γ_{cl} is assumed to be independent of the solid surface material, as a first approximation. The comparison hence results in that the Teflon surface may have a lower contact angle to a hydrophobic crystal and will promote nucleation more strongly than the steel surface, as is found in the experiments. However, it should be recognized that this analysis is greatly simplified. A crystal is composed by different faces having different surface chemistry and hence different properties. Depending on the properties of the surface, the crystal may turn different faces towards it, and the properties of the faces exposed to the solution can be different from those of the face that is in contact with the surface. Hence, the crystal-liquid interfacial tension may also differ depending on the plate material. The solid surface may influence the habit of the attached growing crystal and may even promote the appearance of faces that would normally not be present.

On the molecular level, the solute tends to orient the hydrophobic part of the molecule towards a hydrophobic surface and the hydrophilic part into the aqueous solution. This may lead to a pre-ordering and perhaps to an increased local concentration that promotes nucleation. The shape and orientation of crystals nucleated on the surface has been visually examined, but no pattern in the orientation can be detected. However, at the scale of the size of a primary crystal nuclei, the solid surfaces are rough. Nuclei may possess a certain orientation to the surface microscopically that cannot be recognized in the orientation of the outgrown large crystals to the macroscopic plane.

Table 5. Analysis of Interfacial Tensions

	Steel	Teflon
Interfacial Tension		
Solid-liquid, γ_{sl}	Low	High
Crystal-solid, γ_{cs}	High	Low
Crystal-liquid, γ_{cl}	Equivalent*	Equivalent*
$\cos\theta$	Low	High
Contact angle, θ	Large	Small
ϕ	High	Low

*γ_{cl} is independent of the solid surface material.

Adhesion

In order for nuclei to stick to the surface, the adhesion force has to be stronger than the gravity force. The work of adhesion for a crystal on a solid surface W_{csl} (mJ/m^2) may be given by (Israelachvili, 1985)

$$W_{csl} = \gamma_{cl} + \gamma_{sl} - \gamma_{cs} \tag{3}$$

W_{csl} is the work needed to separate the crystal from the solid surface and create the corresponding crystal-liquid and solid-liquid interfaces. Hence, the larger the work of adhesion the stronger is the adhesion of the crystalline deposit to the solid surface. By the same reasoning as for the catalyzed nucleation (Table 5), Eq. 3 predicts that the work of adhesion for a hydrophobic crystal on Teflon should be higher than for the same crystal on steel, and hence the crystal should adhere more strongly to Teflon. Adhesion forces between crystals and the plate have not been properly measured. However, when the organic crystals are removed, they are found to adhere more strongly to the Teflon surface than to the steel surface. Crystals of citric acid monohydrate detach due even to gravitational forces from the steel plate at a size of about 0.001 m, while on the Teflon plate they stick to the surface. Equation 3 shows that adhesion of crystals to a surface is governed by the same physical properties as the catalytic activity on primary nucleation. Hence, there should be a relation between these two phenomena which is in fact found in our results. In the cases where a catalytic effect is observed (except for glycine/air), the crystals always adhere to the catalyzing surface.

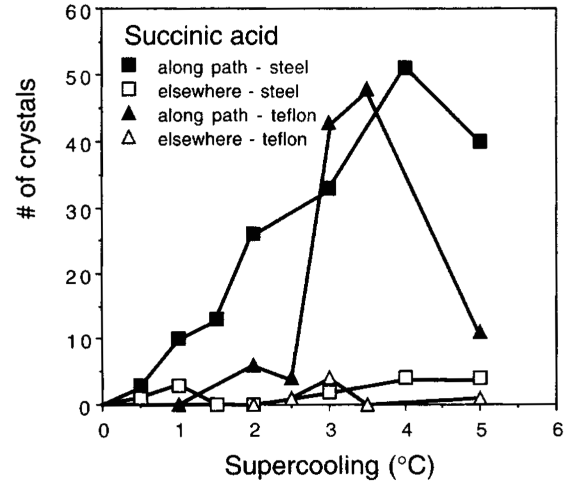

Figure 8. Comparison of crystal numbers along and outside sliding paths.

Mechanisms of collision initiation

The collision experiments show that a crystal gently colliding with a surface in a supersaturated solution may leave a trace of new crystals behind on the surface. In Figure 8, the number of nuclei formed along the sliding path is compared with the number found elsewhere. A very limited number of or no nuclei are found outside the sliding path or at the bottom of the cylinder. Obviously, the formation of crystals on the plate is closely related to the actual interaction of the descending parent crystal and the plate, which suggests a relation between collision initiation and secondary nucleation. In a separate experiment, two small (about 3 mm×4 mm×4 mm) glass pieces were dropped instead of crystals in a succinic acid solution at 4.0°C supercooling onto a steel plate. No crystals were generated, neither on the plate nor at the bottom within 3 h. This is similar to early results on the mechanisms of secondary nucleation (Clontz and McCabe, 1971). In our experiments the number of crystals found on the test surface is in general lower for the Teflon plate than for the steel plate. This corresponds to results on the rate of secondary nucleation (Shah et al., 1973) concerning the material of the agitator. For succinic acid and citric acid monohydrate, the number of new crystals formed on the plate increases with supersaturation, and for succinic acid on steel there is a linear relation (solubility data are given by Qiu and Rasmuson (1990)). This is a quite weak dependence for a phenomenon assumed to be related to secondary nucleation. Qiu and Rasmuson (1994) found the rate of secondary nucleation for succinic acid crystallized in aqueous solutions to depend on supersaturation to the order of 2.4, and in general the exponent ranges from 2 to 4 for different substances (Garside and Davey, 1980). According to the "survival theory" (Garabedian and Strickland-Constable, 1972a,b), a size distribution of pre-nuclei embryos are generated at the mechanical contact. The higher the supersaturation, the smaller is the critical size at which an embryo becomes a stable nucleus. The plate participates in the "contacting" of the parent crystal. However, the plate may also provide a surface at which the survival of embryos is enhanced. If so, it is likely that the mechanisms behind the enhanced survival of these embryos are similar to those of catalyzed primary nucleation. Hence, this may explain the finding in the present work that the four organic substances are all shown to initiate crust formation by both catalyzed surface nucleation and by collision initiation.

In a crystallizer, most secondary nuclei are believed to be due to collisions between crystals, and between crystals and the impeller (Ottens et al., 1972). In order for nuclei generated by crystal-crystal collisions to initiate incrustation, they have to reach the surface and attach. Transport of fine particles (< 1 μm) from the bulk to the wall through the viscous sublayer is regarded as a slow diffusion mechanism (Epstein, 1988). At increasing particle size, inertial forces increase but the particle also becomes increasingly exposed to detachment forces. Nuclei generated by collisions with the impeller are exposed to strong hydrodynamic forces which reduce the attachment to the impeller surface and especially the tendency to form larger crusts. Nuclei are also generated by collisions between crystals and the vessel wall. From a secondary nucleation point of view, the generation rate by this mechanism is many orders of magnitude lower than that resulting from crystal-crystal or crystal-impeller collisions. However, at crystal-wall collisions the conditions for crust formation are particularly favorable. Nuclei or small crystal fragments are generated at equipment surfaces where the hydrodynamics are moderate. They may attach properly before they reach a size where gravity and hydrodynamics become important. During outgrowth, surface roughness may be filled with crystalline phase, resulting in a particularly strong attachment of the deposit.

Duncan and Phillips (1979) circulated seeded supersaturated crystal slurries through an annulus, where the inner tube was cooled and used as the surface onto which crusts were formed, and the outer tube was transparent. They found the maximum allowable surface supercooling before incrustation occurs to be equal to the normal metastable zone width of the solution. Primary heterogeneous nucleation was assumed to be the initiation mechanism. No influence of the surface material was found. These results are in contradiction to the findings of the present work. Our results suggest that secondary nucleation mechanisms are of greater interest, and that we should refer rather to a relevant metastable limit for secondary nucleation. In addition, an influence of the surface material is found. However in the work of Duncan and Phillips (1979), the surface was used for cooling and seeded slurries were circulated, which makes the interpretation more complex. In addition, the slurry flow direction in their work is along the tube surface which significantly limits the frequency and energy of collisions between crystals and the surface.

Conclusions

Experimental techniques have been developed to study initiation of crusts in crystallization processes. Nucleation of a crystalline phase on a solid surface is investigated at controlled local supersaturation, and without the interference of particle deposition. Experimental results indicate that a foreign solid surface may catalyze primary nucleation. Nucleation of adipic acid, glycine, and succinic acid on a Teflon surface is shown to commence at a lower degree of supersaturation than spontaneous nucleation in the bulk solution. However, the required supersaturation is still quite substantial. Hence, the results do not reveal that this is an important mechanism for initiation of incrustation in industrial processes. On the other hand, the results suggest that crystals colliding with equipment surfaces in a crystallizer may play an important role for initiation of crusts. It is shown that crystals colliding with a foreign solid surface in a moderately supersaturated solution may nucleate new crystals that grow attached to the surface. This mechanism is called collision initiation, and is shown to be strongly related to secondary nucleation. Hence, the secondary nucleation properties of the system and the hydrodynamics in the crystallizer are of significant importance. The results indicate that catalyzed primary nucleation, crystal adhesion to the surface, and collision initiation are all partly governed by the same fundamental properties, namely the interfacial tensions between the phases involved. Increasing affinity of the crystallizing substance to the solid surface promotes catalyzed primary nucleation, collision initiation, and adhesion of the deposit.

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