Effect of Chemical Modifiers on Borax Crystal Growth, Nucleation and Habit

The effects on the fine-crystal CSD of various surface active and ionic additives were studied for the sodium tetraborate decahydrate (borax) system. The organic modifiers used were effective at the ppm level. Surface active agents inhibited nucleation rate, while ionic additives increased nucleation. A simultaneous reduction in both the linear-crystal growth rate and the degree of polycrystalline growth was observed in both cases. These effects correlated with modifier concentration in the liquor, but not with modifier/solids ratio. Borax exhibits classical magma and RPM-dependent secondary nucleation and the results were well-correlated with a conventional power-law kinetic model.

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SCOPE

Often a better control of crystallization can be achieved by the addition of selected impurities to the mother liquor in crystallization processes. These impurities adsorb on the crystal faces or change the supersaturation and thereby alter nucleation rate, growth rate or crystal habit. Typical examples of such industrial practice are the use of gelatine to produce boric acid flakes or sodium sulphate to improve growth rate of sodium carbonate monohydrate (Garret, 1959).

Extensive literature exists on the use of impurities for crystal habit and growth modification. Yet, little work has been reported on such impurities as they effect nucleation kinetics. Shor and Larson (1971), studied the effect of impurities on crystallization kinetics of potassium nitrate in a mixed suspension, mixed product removal crystallizer. Their results are specific to the potassium nitrate system.

This study examines the simultaneous effects of chemical modifiers on crystal nucleation, growth rate and habit to demonstrate the intimate relationship between secondary nucleation and surface growth. It also correlates nucleation and growth rate data in a design-useful, power-law kinetic model suitable for CSD predictions. The differences between inorganic and surface active organic modifiers were observed.

CONCLUSIONS AND SIGNIFICANCE

Borax exhibits collision breeding-type secondary nucleation which can be correlated with a power-law kinetic model in terms of agitator RPM, linear crystal growth rate, slurry density, and concentration of chemical modifiers. The RPM exponent of 3.05 indicates that secondary nucleation is proportional to agitation power per unit volume, while the respective growth rate and slurry density exponents of 1.48 and 0.84 indicate that nucleation is roughly proportional to rate and area of surface growth.

Surfactant-type modifiers inhibited growth rate in the same proportion as nucleation rate and could be incorporated into the power-law correlation with a negative exponential in terms of molar ppm of modifier. Nucleation was virtually stopped, when concentrations of sodium dodecyl benzene sulfonate or sodium oleate exceeded 6 ppm. Sodium or magnesium chloride additives were only effective at large concentrations (ca. 10^3 ppm) and increased the nucleation rate. Growth rate decreased slightly in the presence of inorganic additives. This study also demonstrated the utility of the mininucleator technique (Shadman and Randolph, 1978) for on-line measurement of crystallization parameters.

BACKGROUND

The presence of trace amount of impurities in the crystallizing solution sometimes has a spectacular effect on nucleation rate, growth rate, and crystal habit. Such additives can be organic or inorganic and are often used in crystallization practice to suppress nucleation of new crystals, to affect growth rate of existing crystals or to improve crystal habit. Examples are use of chromium and tin ions to affect elongation of ethylene diamine tetra acetate and ammonium dihydrogen phosphate crystals, and use of lead ions to initiate growth of sodium chloride crystals and sodium oleate to reduce multicrystal habit of borax crystals. Polycrystalline facets can be defined as the formation of new (h′k′l′) faces in addition to already existing (hkl) faces. In spite of the importance ascribed to the use of additives, very little is known about the actual mechanism of such modifiers.

Most published studies of secondary nucleation have been with pure systems. An exception was Shor and Larson (1971) who observed the effects of various surface active agents and ionic additives on the crystallization of potassium nitrate in a mixed suspension, mixed product removal (MSMPR) crystallizer. Inorganic impurities decreased the nucleation rate, while small amounts of surfactants increased the nucleation rate.

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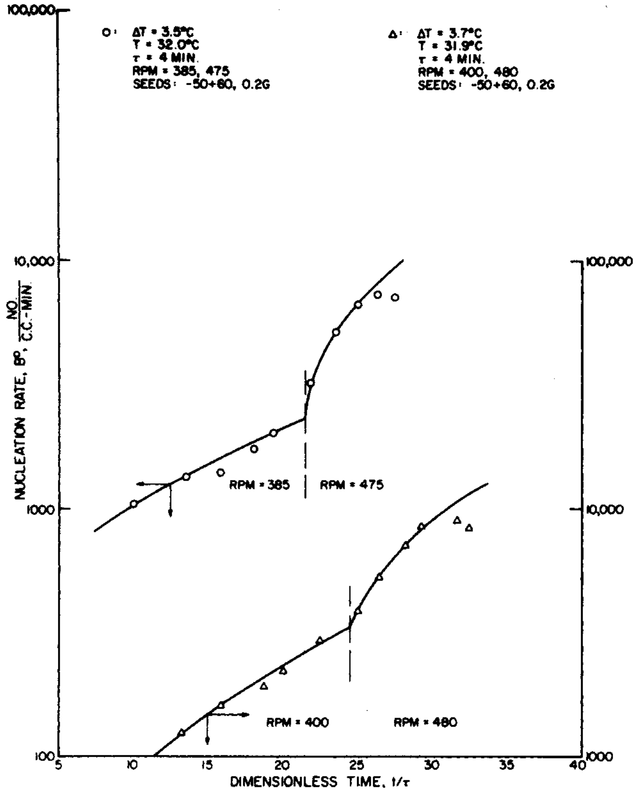

Figure 1. Effect of sudden increase of stirring RPM on nucleation rate.

The selection of an additive usually involves trial-and-error testing of specific compounds to observe those which favorably influence crystal properties and are compatible with the chemical process. No general theory has yet been stipulated which could predict the effect a particular additive would have on a given crystallizing system. Thus, finding a specific additive is still an art.

The present work describes the effect of organic and inorganic impurities on the nucleation rate, growth rate, and habit of borax crystals. The organic impurities used were sodium dodecylbenzene sulfonate, sodium oleate and sodium lauryl sulfate, whereas the inorganic impurities were sodium chloride and magnesium chloride. This work was carried out in a modified MSMPR crystallizer which operated with mixed discharge of the fine-crystal distribution and total retention of parent seeds. The borax system was chosen for the present study, because it readily crystallizes in polycrystalline habit at high supersaturation unless a modifier is present. Specific goals of this study were as follows.

- Evaluate the quantitative effects of surface active agents and ionic modifiers on the nucleation and growth rate of borax crystals.
- Determine the concentration effectiveness of such modifiers.
- Illustrate the intimate relationship between secondary nucleation and habit-determining crystal growth mechanisms, when both are affected by chemical modifiers.

Crystal nucleation has been shown to occur by three mechanisms: homogeneous, heterogeneous, and secondary. Homogeneous nucleation occurs from clear solutions as a result of supersaturation alone, while heterogeneous nucleation is stimulated by the presence of foreign substrates. Secondary nucleation occurs due to the presence of crystals of solute phase and commonly occurs at lower supersaturations than required for homogeneous or heterogeneous nucleation. Usually contact of the existing crystals (by impeller, walls, or other crystals) is required to produce nuclei.

Contact-type secondary nucleation has been identified as the nucleating mechanism for the borax-water system in this study.

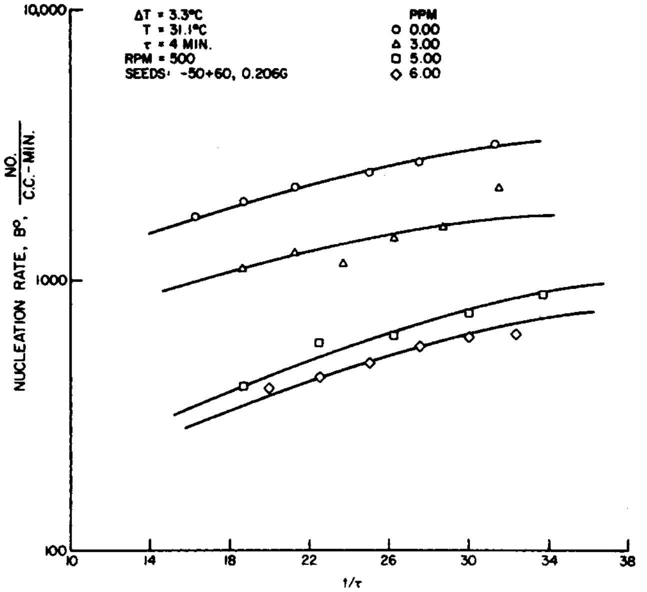

Figure 2. Nucleation rate for sodium oleate runs.

Typical correlations of the form:

$$B^o = k_N\,(T,\mathrm{RPM})\,s^b M_T{}^j \tag{1}$$

$$G = k_G s^a \tag{2}$$

have been extensively used in the literature to fit the data for secondary nucleation and growth rates (Larson, Timm, and Wolff, 1968; Randolph and Sikdar, 1976; Desai et al., 1974). Eqs. 1 and 2 can be combined to eliminate supersaturation to give:

$$B^o = k_N\,(T,\ \mathrm{RPM})\,G^i M_T{}^j \tag{3}$$

where k_N is redefined and the relative nucleation to growth sensitivity parameter is $i = b/a$. Eq. 3 is used to correlate the nucleation data of this study. Values of B^o and G were obtained by parameter fitting to the well-known MSMPR exponential population distribution. Thus,

$$n = [B^o/G]\,\exp\,\{-L/G\tau\} \tag{4}$$

EXPERIMENTAL

The apparatus used in this study has been described in detail by Randolph and Cise (1972). The crystallizer is of continuous mixed suspension type with the key feature of mixed removal of product fines coupled with total retention of larger seed crystals. This is accomplished by discharging the product stream through a 150-mesh stainless steel screen. Average retention time is typically 4 min. At this small retention time, secondary nuclei wash out of the system before any of them can grow to the size of the retaining screen (150 mesh). The size distribution of product fines leaving the crystallizer was determined using a zone-sensing electronic counter (Particle Data Counter). This instrument uses an associated PDP8A minicomputer which was programmed for on-line regression of particle data to Eq. 4 (Shadman and Randolph, 1978). Least-squares fit values of B^o and G could be obtained within a period of 3 min. after a particle count. A 190-micron aperture sampling probe allowed measurements in the size range of 7 to 60 micron.

Seed crystals were obtained by screening borax crystals. Typically, 0.20 g of $-50+60$ mesh size seed was used. Initial breeding was eliminated by ripening the seed crystals in slightly unsaturated solution before adding to the crystallizer. At the supersaturations used (ca. 2.5-4.0°C), no nuclei were observed until after the addition of the parent seed crystals.

Two types of nucleation experiments were performed in this study.

a) *Borax-Water Experiments.* The prime objective of these experiments was to study secondary nucleation in the pure borax system. These experiments were conducted at an average temperature of 31.4°C with a supersaturation range of 2.8 to 3.7°C. The agitator was varied between 380 to 550 RPM.

b) *Borax-Water-Impurity Experiments.* These experiments were

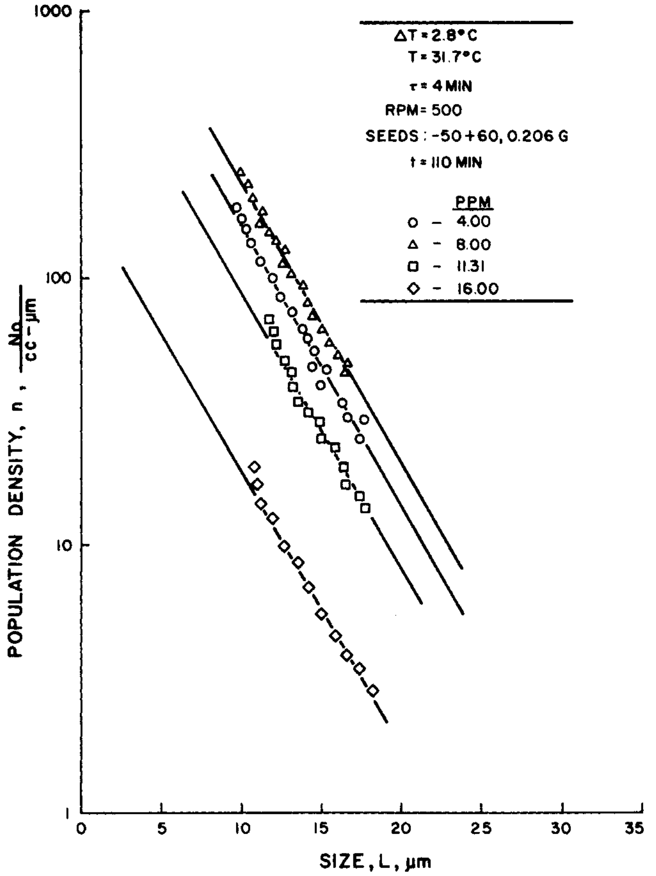

Figure 3. Influence of surfactant sodium dodecylbenzene sulphonate on densities of fine borax crystals.

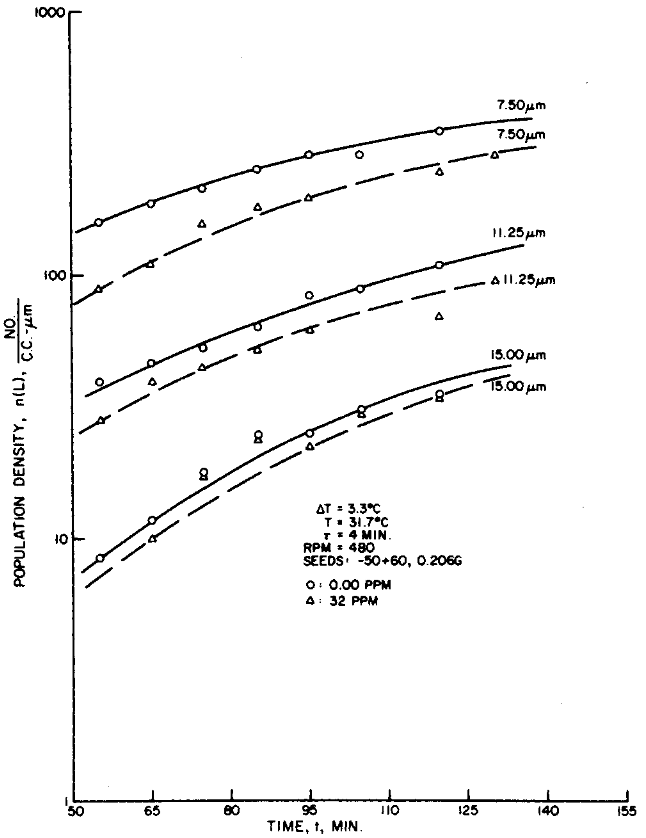

Figure 4. Effect of surfactant sodium lauryl sulphate on transient densities of fine borax crystals.

similar to the former except for the addition of a known amount of impurity. These experiments were conducted with these conditions: average temperature, 31.4°C; supersaturation, 3.1 to 3.7°C; RPM range, 470 to 500. The impurities studied were: $MgCl_2$, NaCl, sodium oleate, sodium lauryl sulfate, and Conoco C-560 (40% sodium dodecylbenzene sulfonate).

EXPERIMENTAL OBSERVATIONS

Borax-Water System

Figure 1 shows a plot of log-nucleation rate vs. dimensionless time. This figure also shows effect of stirrer RPM on nucleation rate. A sudden change in RPM at some point during a run caused an instantaneous increase in nucleation rate. These data suggest that secondary nucleation by impeller contacts results in direct nuclei formation. The effect of RPM convincingly demonstrates the importance of collision energy and collision frequency in such secondary nucleation. Higher agitation rates give rise to higher collision energy and more frequent collisions between seed crystals and impeller, resulting in higher nucleation rates. Nuclei generation continued to increase with time in all runs; pluggage of the retaining screen with excessive fines eventually caused each run to be discontinued.

TABLE 1. SEED CRYSTAL GROWTH RATE FOR ORGANIC ADDITIVES

Additive	ppm	Growth Rate μm/min
Conoco C 560 (containing 40% sodium dodecylbenzene sulfonate)	0	3.60
	4.00	3.303
	8.00	2.99
	11.31	2.88
	16.00	2.33
Sodium Oleate	0	3.41
	3.00	2.96
	4.00	2.45
	5.00	2.17
	6.00	2.02
Sodium Lauryl Sulfate	0	3.31
	4.00	3.05
	8.00	2.78
	16.00	2.71
	32.00	2.62

Borax-Water-Impurity System

Three levels of each impurity were studied. Organic impurities were effective at the ppm level. Moreover, organic impurities behaved differently from inorganic impurities. Thus, the effect of these two types of impurities is discussed separately.

Organic additives decreased nucleation rate. Nucleation rate was totally inhibited above 6.4 ppm concentration of sodium dodecylbenzene sulfonate and above 6 ppm concentration of sodium oleate, i.e. the fine-crystal population count decreased to a level that was not statistically greater than the background level. These observations agree with Randolph and Koontz (1976). Figure 2 shows this effect for sodium oleate.

Figure 3 shows the effect of sodium dodecylbenzene sulfonate on the quasisteady state population density distribution of fine borax crystals. The population density curves shift toward the left with the addition of additive except at 8 ppm concentration of Conoco C-560 and sodium lauryl sulphate.

Figure 4 shows a comparison between dynamic population densities at various sizes of pure borax vs. data when the system contained 32 ppm of sodium lauryl sulfate. The population densities decreased with additive, but not nearly to the extent observed with even lesser amounts of sodium oleate or sodium dodecylbenzene sulfonate. Organic additives decreased the average seed crystal growth rates which are listed for various runs in Table 1.

Changes in crystal habit are shown in the photomicrographs of Figures 5 and 6. The presence of an additive decreased both the extent of polycrystalline habit and the average crystal size of product crystals.

Unlike organics, *inorganic additives* gave a significant increase in nucleation rate. Figure 7 shows the effect of sodium chloride on borax nucleation rate. Figure 8 gives a comparison between transient population densities of fine crystals when the solution contained zero ppm or 400 ppm of magnesium chloride.

Parent seed crystal growth rates were slightly inhibited in the

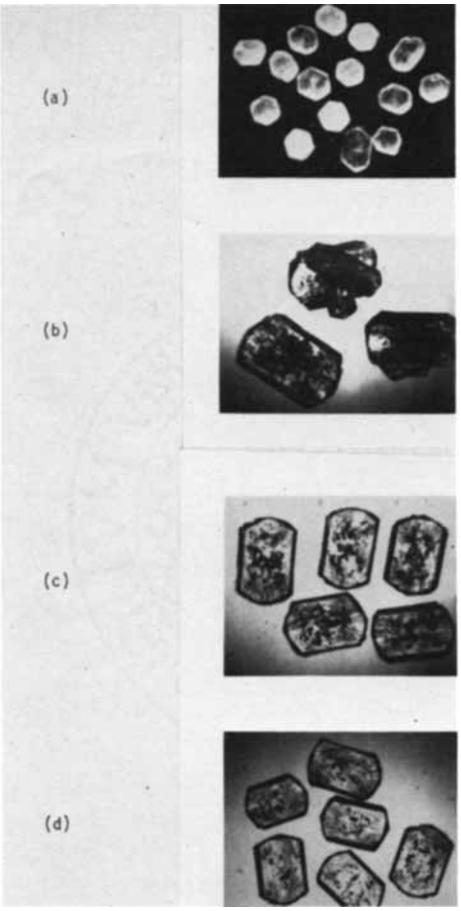

Figure 5. Borax crystals (40 times magnification). (a)−50+60 mesh seed crystals product crystals from (b) pure borax runs; (c) 3 ppm sodium oleate in solution; (d) 5 ppm sodium oleate in solution withdrawn after 150 min.

presence of ionic impurities even though nucleation rates were significantly increased. Table 2 shows the seed crystal growth rate data in the presence of inorganic additives. Figure 9 illustrates the habit changes of borax in the presence of ionic impurities. As with organics, these inorganic additives reduced the extent of polycrystalline growth.

GROWTH AND NUCLEATION KINETICS

Semilog plots of seed crystal growth rate vs. impurity concentration were made for each impurity, Figures 10 and 11. Reasonable straight lines were obtained. The slopes and intercepts of these plots were then calculated to fit the data to Eq. 5. Thus,

$$G_i = G(s) \exp \{bC_i\} \tag{5}$$

where G_i is the growth rate in the presence of impurity concentration C_i and $G(s)$ is the supersaturation-dependent growth rate in the pure system. The correlated values of G_i and C_i for a constant subcooling of 2.8 to 3.7°C are listed in Table 3. The different values of pure seed crystal growth rates in these correlations correspond to different supersaturations.

Figures 10 and 11 also plot nucleation rate vs. ppm organic additive at run times giving constant suspension density. Figure 10 shows an increase in nucleation rate at 3.2 ppm and 8 ppm

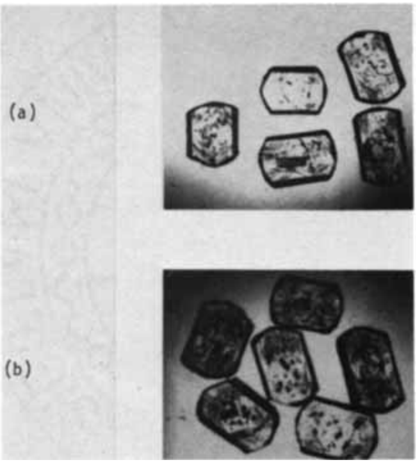

Figure 6. Borax crystals (40 times magnification). Product crystals from run containing (a) 6.4 ppm sodium dodecylbenzene sulphonate in solution; (b) 8 ppm sodium lauryl sulphate in solution withdrawn after 165 and 145 min., respectively.

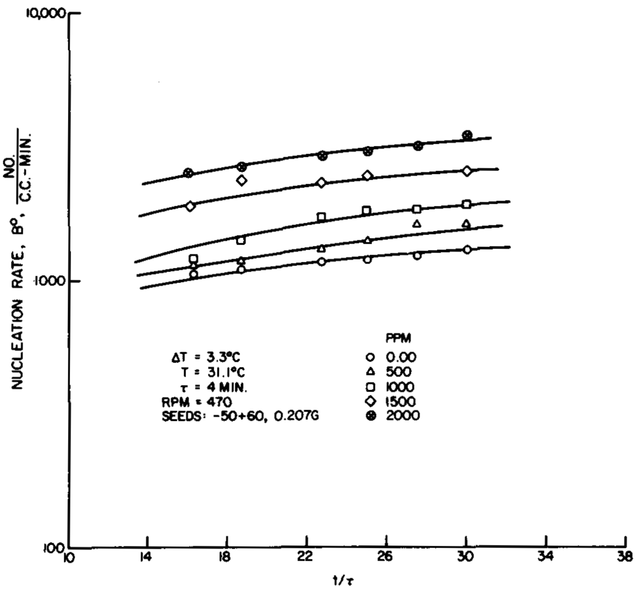

Figure 7. Nucleation rate for sodium chloride runs.

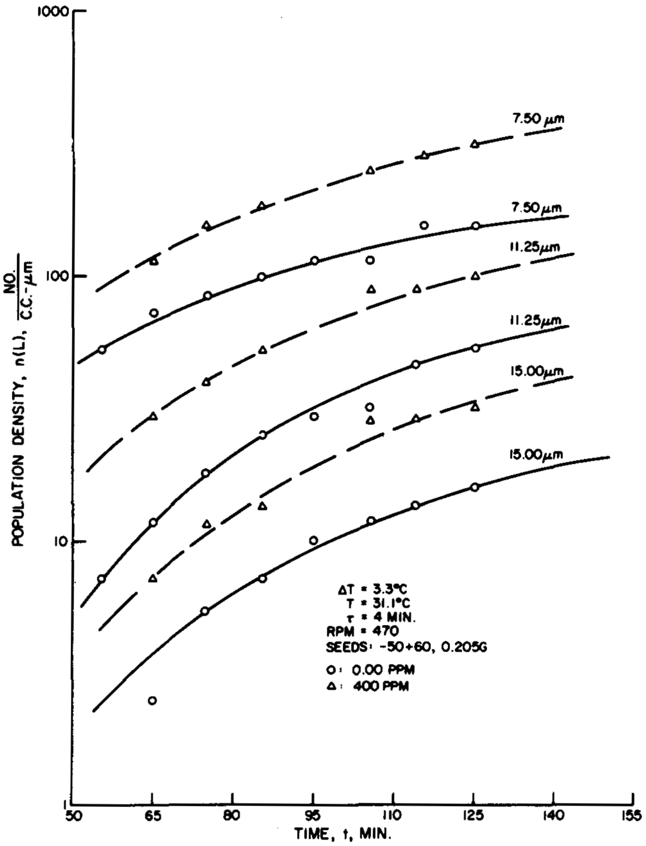

Figure 8. Influence of magnesium chloride on dynamic densities of fine borax crystals.

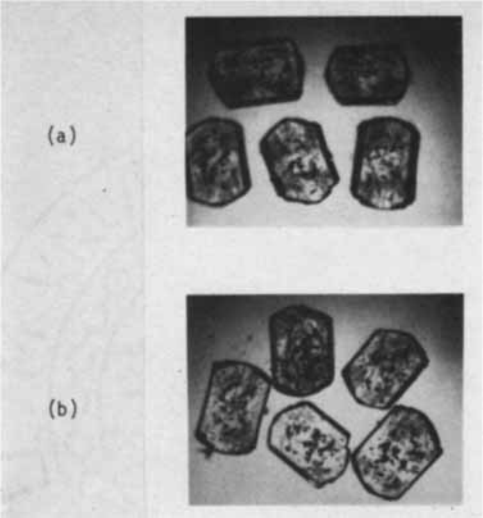

Figure 9. Borax crystals (40 times magnification). Product crystals from run containing (a) 200 ppm magnesium chloride in solution; (b) 1500 ppm sodium chloride in solution withdrawn after 150 min.

concentration of sodium dodecylbenzene sulfonate and sodium lauryl sulfate, respectively. Such an anomalous increase at small additive concentrations has not been explained.

These data were fit to a power-law nucleation model (Eq. 3, modified by an exponential additive concentration correction), using a library multilinear regression program available at the University of Arizona computer center. These nucleation kinetics relationships are listed in Table 3. The pure system RPM dependence on nucleation rate was fixed in these impurity nucleation kinetic relationships, as RPM was not varied during additive runs.

An overall nucleation correlation for the borax system, with or without active organic modifiers, was obtained. The effect of organic additives in this master correlation is expressed as a ratio of impurity concentration C_i to the molecular weight of the additive, i.e., molar ppm. Sodium lauryl sulfate data are not included in this correlation as only a limited nucleation inhibition response was observed. Thus, for the pure system or in the presence of sodium oleate or sodium dodecylbenzene sulfonate, nucleation rate can be correlated using Eq. 6.

$$B^o = 7.727\,(G_f)^{1.48}\,(M_T)^{0.84}\,(\mathrm{RPM})^{3.05} \exp\left(-\,0.0044 \times \frac{C_i}{M.W.}\right) R^2 = 0.904 \qquad (6)$$

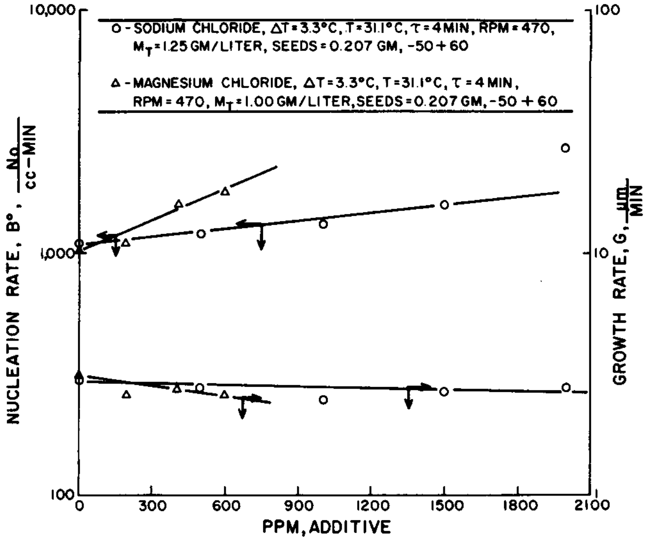

Figure 11. Effect of inorganic additive on nucleation and growth rate of sodium tetraborate system.

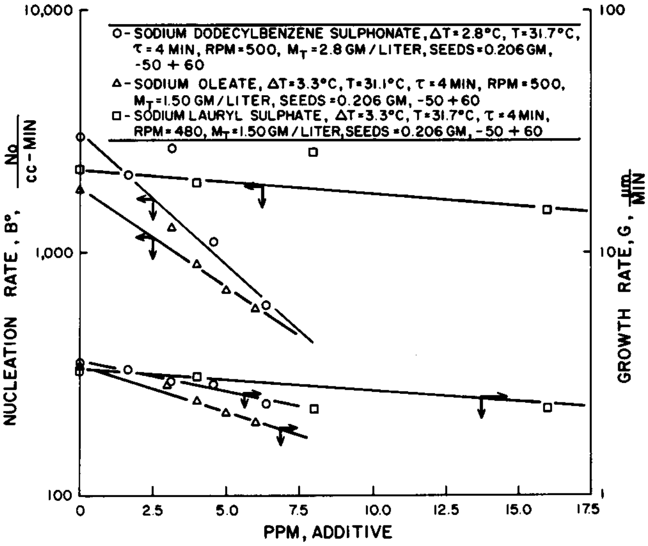

Figure 10. Effect of organic additives on nucleation and growth rate of sodium tetraborate system.

Table 2. Seed Crystal Growth Rate For Inorganic Additives

Additive	ppm	Growth Rate μm/min
Sodium Chloride	0	2.95
	500	2.71
	1000	2.52
	1500	2.68
	2000	2.85
Magnesium Chloride	0	3.10
	200	2.64
	400	2.83
	600	2.57

Figure 12 shows a comparison between experimental and calculated values obtained from Eq. 6. Eq. 6 gives a power-law nucleation correlation quite similar to the semitheoretical model developed by Ness and White (1974). Their model, fitted to the $MgSO_4 \cdot 7H_2O$ system, is given as:

$$B^o = k_N \cdot s^{2.5} N_T L_a^{4.0}\,(\mathrm{RPM})^{4.2} \qquad (7)$$

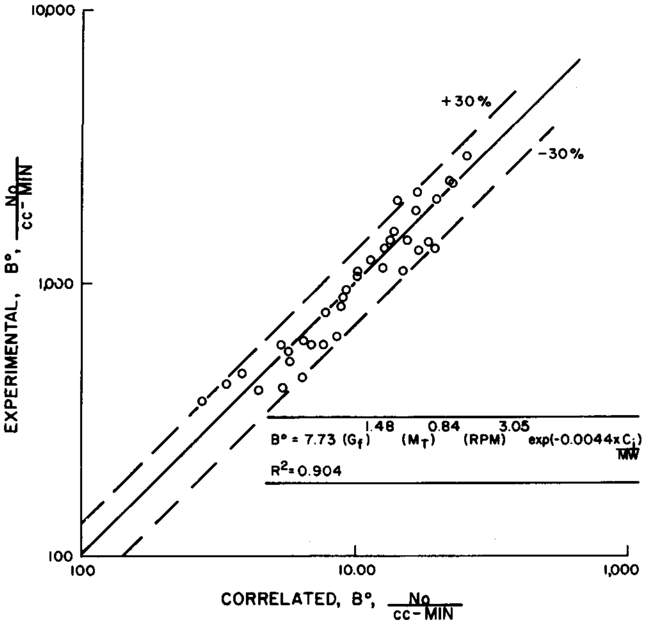

Figure 12. Experimental vs. correlated values of nucleation rates.

TABLE 3. NUCLEATION KINETICS RELATIONSHIPS

Additive	Growth Kinetics	Nucleation Kinetics	Correlation Coefficient for nucleation kinetics, R^2
Pure Borax		$B^o = 5.10 \times 10^{-1}(G_f)^{1.30}(M_T)^{0.46}(\text{RPM})^{3.25}$	0.743
Sodium Dodecylbenzene	$G_i = 3.60 \exp(-0.47 \times C_i)$	$B^o = 2.66 \times 10^{4}(G_f)^{1.50}(M_T)^{0.66}(\text{RPM})^{3.25}\exp(-0.197 \times C_i)$	0.710
Sodium Oleate	$G_i = 3.50 \exp(-0.092 \times C_i)$	$B^o = 2.60 \times 10^{-1}(G_f)^{1.50}(M_T)^{0.83}(\text{RPM})^{3.25}\exp(-0.171 \times C_i)$	0.949
Sodium Lauryl Sulfate	$G_i = 3.30 \exp(-0.0133 \times C_i)$	$B^o = 4.30 \times 10^{-1}(G_f)^{1.58}(M_T)^{0.38}(\text{RPM})^{3.25}\exp(-0.0093 \times C_i)$	0.780
Sodium Chloride	$G_i = 2.90 \exp(-0.000071 \times C_i)$	$B^o = 2.60 \times 10^{-1}(G_f)^{1.50}(M_T)^{0.40}(\text{RPM})^{3.25}\exp(0.00048 \times C_i)$	0.794
Magnesium Chloride	$G_i = 2.90 \exp(-0.00026 \times C_i)$	$B^o = 2.90 \times 10^{-1}(G_f)^{1.50}(M_T)^{0.43}(\text{RPM})^{3.25}\exp(0.0013 \times C_i)$	0.920

where L_a is the average size of (essentially) mono-sized parent seeds and N_T is the number of seeds. (Thus, $N_T L_a^{4.0}$ represents M_4, the 4'th moment of the seed distribution.) Assuming $G_f \alpha s^2$, a similar correlation for the borax data from the present study would be:

$$B^o = k_N s^{3.06} [N_T L_a^{3.0}]^{0.8} (\text{RPM})^{3.25} \tag{7'}$$

Agitation power per unit volume, ϵ, is roughly proportional to $(\text{RPM})^3$ in a baffled stirred tank. Thus, nucleation in the borax system might reasonably be scaled up in larger vessels using constant ϵ as a criterion.

DISCUSSION OF RESULTS

Seed crystal growth rates depend on impurity level in a negative exponential manner. These growth kinetics relationships for various impurities are listed in Table 3. Two important conclusions can be drawn from these relationships.

(i) Increased amounts of impurity in a crystallizing solution continually decreases the growth rate.

(ii) The relative effect of additives on growth rate varies with the type of impurity. Organic additives were found to be effective at a lower concentration level, typically 3 to 30 ppm, as opposed to 200 to 2000 ppm effectiveness level for inorganic additives.

Shor and Larson (1971) found that surface-active agents decreased the growth rate of potassium nitrate crystals, whereas inorganic additives increased the growth rate. However, their MSMPR results were constrained by an overall mass balance/yield relationship, whereas the present crystallizer acted as a differential reactor, i.e., had a negligible concentration drop between inlet and outlet. In Shor's crystallizer, if B^o increased, G had to decrease (and vice versa) to achieve an overall mass balance. Such a mass balance constraint does not apply to the differential reactor of the present study.

Nucleation rates were related to impurity concentration by a negative exponential argument as shown by the nucleation kinetics relationships for each impurity in Table 3. A comparison of these relationships indicates that although impurities considerably affect nucleation rate, the kinetic order of nucleation rate with respect to growth rate, suspension density, and RPM remains nearly the same irrespective of type and amount of impurity present. Shor and Larson (1971) and Liu and Botsaris (1973) arrived at the same conclusion from their work on crystallization in the presence of impurities. Shor and Larson found that surface active agents increased the nucleation rate, and ionic impurities decreased the nucleation rate. However, the present study showed exactly the opposite trend.

TABLE 4. EFFECT OF ORGANIC MODIFIERS

Impurity	$K_1(\text{m}^4/\text{kg} \cdot \text{s})$	$K_2(\text{m}^3/\text{kg})$
Sodium Dodecylbenzene Sulfonate	0.12×10^{-5}	0.2×10^{2}
Sodium Oleate	0.39×10^{-5}	0.68×10^{2}
Sodium Lauryl Sulfate	0.15×10^{-5}	0.27×10^{2}

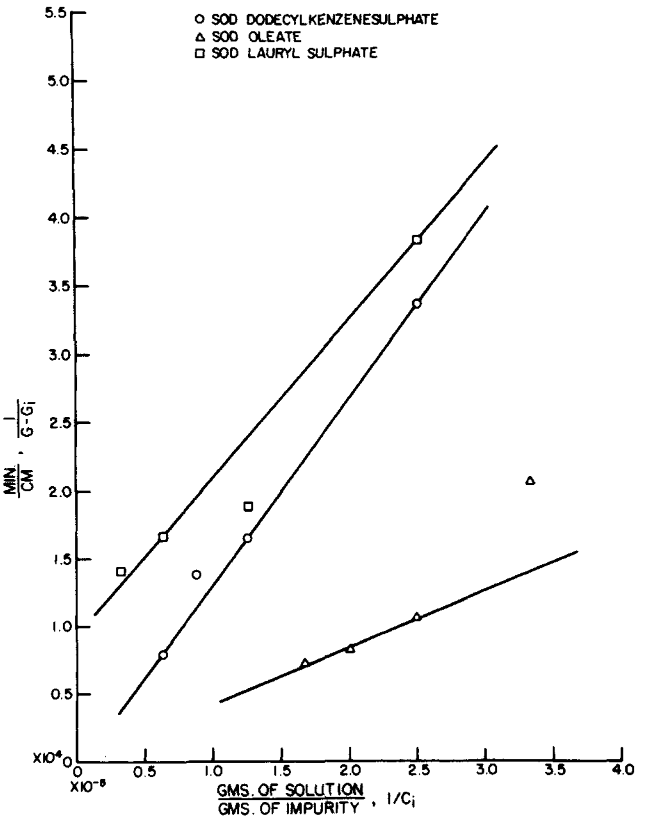

Figure 13. Langmuir's adsorption isotherm for organic additives.

Shor and Larson rationalized their surfactant results with classical heterogeneous nucleation theory. A decrease in contact angle between a protonucleus in the growth layer of a crystal and the crystal surface should result in an exponential increase in the heteronucleation rate. However, nucleation rate was inhibited in the presence of surfactants in this study of borax. The effects of ionic impurities were rationalized by Shor and Larson using an adsorption mechanism. They assumed that highly charged cations adsorb on nucleation sites on crystals in suspension, thus inhibiting solute nucleation by blocking the sites. However, in the present borax study, nucleation rate was significantly increased in the presence of ionic impurities. A direct comparison with Shor's work is not possible because of the different crystal systems and operation of the two types of MSMPR crystallizers.

Seed crystals grown under similar experimental conditions in this study were better formed, i.e., contained fewer polycrystals, when either organic or inorganic impurities were present. The effect of additives on crystal quality can possibly be explained by the mechanism of dendritic whisker growth. The rate of initiation of new growth layers increases with supersaturation to a power greater than unity, while the rate of advance of these growth layers across the crystal surface only increases directly with supersaturation (Michael and Tausch, 1961). Thus, with increasing levels of supersaturation, a point will eventually be reached at which the rate of initiation of new layers is faster than the rate of advance of these layers away from the point of initiation. Thus, a layer pile-up occurs which forms a growth protrusion on the surface.

Growth of these protrusions at angles different from the main crystal axes by definition result in polycrystalline habit. Because of the more favorable diffusion environment of such protrusions, they will become unstable and grow into solution faster than, and at the expense of, adjacent surface. This theory of dendritic growth explains the well-known phenomena of polycrystal growth at high supersaturations. Since additives were found to improve crystal quality, it appears that they must retard initiation of new layers relative to the advance of layers across the surface and/or reduce levels of supersaturation in the boundary layer adjacent to the crystal surface.

Several conflicting mechanisms have been proposed in the literature to explain the effect of impurities on the crystallization of pure substances. Recent developments in this field have postulated that an impurity must adsorb to some extent on the crystal surface to decrease growth rate. Davey and Mullin (1974) derived a model using Langmuir's adsorption isotherm. According to this model:

$$\frac{1}{G - G_i} = \frac{1}{K_1 C_1} + \frac{K_2}{K_1} \qquad (8)$$

Thus, a plot of $1/G - G_i$ vs. $1/C_i$ should be a straight line, if the adsorption mechanism prevails. For organic impurities, reasonably straight lines were obtained as shown in Figure 13. The values of K_1 and K_2 for various impurities are listed in Table 4.

These data indicate that organic impurities adsorb at the crystal surface and the adsorption on certain sites in a growing crystal result in reduction of growth rate. In this study, two active organic modifiers were studied, namely sodium oleate and sodium dodecylbenzene sulfonate. The effect of these two additives (on nucleation) was essentially identical as a function of additive concentration when the concentration was expressed on a molar basis. However, such a generalization did not correlate data from the much weaker crystal modifier sodium lauryl sulfonate. The idea of generalizing the concentration effects of crystal-specific additives using molar ppm is appealing. Such a basis could be easily rationalized assuming activity is a unique function of surface coverage and each surfactant molecule covers a single growth size.

The effect of organic modifiers correlated with solution concentration, not additive/solids ratio. Table 4 demonstrates this fact conclusively, when similar effects on nucleation rate were observed with a given additive level uniformly distributed in the circulating mother liquor vs. the same concentration ratio-metered to the entering feed and then adsorbed in an activated carbon bed before recycle of the mother liquor. In the former case, the solids/additive ratio would be thousands of times higher than the latter case due to recycle through the packed-bed saturator. Apparently, the presence of a large packed bed of borax had no effect on the nucleation inhibition properties of a few ppm organic modifiers in the circulating liquor.

The data for inorganic impurities does not fit Eq. 8. Furthermore, there is no reason to expect such simple inorganic molecules to adsorb on the surface. However, sodium tetraborate is a weak electrolyte. The presence of common Na^+ (added as sodium chloride) in a crystallizing sodium tetraborate solution will reduce the ionization of sodium tetraborate which will shift the ionic equilibria of sodium tetraborate to the left. The result will favor the formation of sodium tetraborate and hence result in more chemical driving force for nucleation. Mg^{++} ion could exert similar effects on the concentration of un-ionized borax through changes in total ionic concentration. Such an explanation for the effects of inorganic modifiers are more plausible in view of the high concentration of ions ($\sim 10^3$ ppm) needed to influence nucleation.

CONCLUSIONS

1. The borax system exhibits classical magma and RPM-dependent secondary nucleation.
2. The presence of certain organic additives (at the 3 to 30 ppm level) inhibits nucleation rate. Nucleation rate was totally inhibited with 6.4 ppm sodium dodecylbenzene sulfonate and 6.0 ppm sodium oleate. However, inorganic impurities (sodium and magnesium chloride) increased nucleation rate.
3. Growth rate of fine crystals and parent seeds was inhibited by organic and inorganic additives.
4. All of the additives studied improved crystal quality, i.e., fewer polycrystals were produced in the presence of additives.
5. The relative kinetic order of nucleation rate (in a generalized power-law kinetics correlation) with respect to growth rate, suspension density, and RPM remained nearly the same irrespective of the type and amount of impurity present.
6. Nucleation rate was modelled in an overall power-law kinetics correlation with growth rate, slurry density and RPM exponents of 1.50, 0.40, and 3.25, respectively. Such exponents are very near to those predicted in the semitheoretical secondary nucleation model of Ness and White (1974). The effect of active surfactants was modelled with a negative exponential argument proportional to molar concentration.

ACKNOWLEDGMENT

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NOTATION

a = kinetic order of supersaturation in growth-rate model
b = kinetic order of impurity concentration in growth-rate model
B^0 = nucleation rate, no/cc-min.
C_i = impurity concentration, ppm (molar)
G = growth rate of seed crystals, cm/min.
G_f = growth rate of fine crystals, cm/min.
G_i = growth rate of seed crystals in the presence of impurity, cm/min.
i = kinetic order of supersaturation in power-law model
j = kinetic order of suspension density in power-law model
k = kinetic order of RPM in power-law model
k_G = growth rate constant
k_N = nucleation rate constant
K_1, K_2 = constants in Langmuir's adsorption isotherm
l = kinetic order of impurity concentration in power-law model
L = crystal size, microns
M_T = suspension density, g/L
n = population density, no/cc-micron
n^0 = population density at zero size, no/cc-micron
s = supersaturation
T = temperature, °C
ϵ = agitator power per unit volume, erg/cc
τ = retention time, min.

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Drop Size and Continuous-Phase Mass Transfer in Agitated Vessels

Continuous-phase mass transfer coefficients and drop sizes in agitated vessels are correlated with operating variables and physical properties of liquid-liquid systems. In formulating mass transfer coefficients, a realistic mechanism has been developed, involving periodically varying rates of surface renewal associated with droplet circulation through varying degrees of turbulence around the vessel. Relationships are obtained for optimized design and scale-up.

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SCOPE

The rate of mass transfer between two immiscible liquids in mixing vessels depends on the concentration difference, the interfacial area, and the mass transfer coefficient. The comprehensive correlation of mass transfer coefficients and interfacial areas are therefore essential for the optimized design and scale-up of such equipment.

Schindler and Treybal (1968) and Keey and Glen (1969) studied liquid-liquid mass transfer rates in agitated vessels. Both investigations were confined to single systems, so that comprehensive correlations over a range of physical properties were not established.

The objects of this research are to measure and correlate such continuous-phase mass transfer coefficients and the corresponding drop sizes in the presence of mass transfer. Relationships for optimized design and scale-up will then be formulated.

CONCLUSIONS AND SIGNIFICANCE

The continuous-phase mass transfer coefficient has been correlated and separate correlations for high and low interfacial tension systems have also been attempted for a better fit of the data.

Comparison between our correlation for k_c and expressions derived from the penetration theory with Kolmogoroff's time scale and from turbulent boundary layer theory show significant differences between the exponents on any given variable, suggesting the need for a new model. Accordingly, a theory based on a periodically varying rate of surface renewal has been developed and the average rate of surface renewal s_a in this theory has been correlated.

Droplet size was determined from photographs of the dispersion taken through a plane glass water pocket. A correlation was obtained for the Sauter-mean drop diameter when about 50% of the possible mass transfer had occurred; this was chosen as an average value during batch operation.

These correlations have been used to develop relationships for optimized design and scale-up.

This study included five liquid-liquid systems, two sizes of six-flat-blade turbines, two vessel diameters, two principal liquid heights (T = H), impeller speeds between 3 and 8 rps, and dispersed-phase volume fractions between 0.03 and 0.09.

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