EFFECT OF SODIUM DODECYLBENZENESULFONIC ACID (SDBS) ON THE GROWTH RATE AND MORPHOLOGY OF BORAX CRYSTAL

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ABSTRACT

An investigation of the effect of sodium dodecylbenzenesulfonic acid (SDBS) on both growth rate and morphology of borax crystal has been carried out. This experiment was carried out at temperature of 25 °C and relative supersaturation of 0.21 and 0.74 under in situ cell optical microscopy method. The result shows that SDBS inhibits the growth rate and changes the morphology of borax crystal.

Keywords: *Borax; growth rate; crystallization, SDBS*

INTRODUCTION

Fundamental studies of borax crystallization are very important for borax industry to improve the quality of product. In borax industry, borax from tincal is produced by a batch process. From this process, borax loss is about 45000 tons per year [1,2]. One of the fundamental studies to solve this problem is investigation of the effect of additive on the growth rate or on the morphology of borax crystal.

The effect of additive on crystallization processes has long been known as a matter of practical importance. Additives are succesfully applied to retard crystallization processes, to improve the size and shape of the crystals, or to alter their bulk properties. To diminish mineral scaling nucleation and growth, inhibitors are employed, while to improve filterability of the crystals habit modifiers are usually used. To enhance the precipitation rate of the crystals by aggregation all kinds of flocculating agents have been developed. Also, incorporation of additives to improve specific crystal qualities has found numerous applications [3].

Previous studies on the effect of additives on the crystallization of borax crystal have been carried out by several researchers. Garret and Rosenbaum examined a number of chemical additives with borax solutions to test their effectiveness in improving crystallizing conditions. Some of the additives for comparatively large quantities of the reagents altered the crystal habit or growth rate [4].

Garrett found that a pH of about 9.7 is required to form the most nearly cubical crystals, and may be obtained by the addition of any basic compound. The addition of small quantities of oleic acid helps to avoid the formation of clusters and dendrites, and favours the growth of larger crystals. Other additives such as Fe^{++}, Mg, Zn, Al, various dyes, etc., also have a beneficial effect upon the crystallization, but only when added in comparatively large concentrations. None of the common anions appears to have any direct effect (other than its pH influence), with the possible slightly detrimental effect of sulphate in medium to large concentrations [5].

Randolph and Puri [6] studied 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 results of this work are the presence of certain organic additives (at the 3 to 30 ppm) inhibits nucleation rate. Nucleation rate was totally inhibited with 6.4 ppm sodium dodecylbenzene sulfonate and 6 ppm sodium oleate. However, inorganic impurities (sodium and magnesium chloride) increased nucleation rate.

For this research, it was used sodium dodecylbenzenesulfonic acid (SDBS) as additive. This additive was used because it is a group of surfactant. The surfactant is well additive to inhibit the growth rate and to improve the morphology of crystal especially a borax crystal.

EXPERIMENTAL SECTION

Material

The material and instrument used in this work were AR grade Borax ($Na_2B_4O_710H_2O$), milli-Q water, 0,45 μm filter membrane, transparency film, and AR grade sodium dodecylbenzenesulfonic acid, a Nixon Optiphot-2 Microscope with automated video image capture, a Grant W14 (Grant Instruments Ltd.) circulating water bath, Pulnix TM-9701 Camera

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(Progressive Scanning Full Frame Shutter Camera), a Pentium II Computer, a digital thermometer (HANNA Intruments, HI 8424), Optimas Software Version 6.2 (Optimas Corporation, Bothell, Wa, USA), plastic bottle 250 mL, a peristaltic pump (Watson-Marlow model 505S/RL, manual control, and variable speed), a *in situ* growth cell, and rubber tubing.

Procedure

Solubility of borax in water

The driving force of crystallization is usually expressed as a supersaturation ratio, defined as [7]:

$$S = \frac{A}{A^*}$$

Where A and A^* are the initial and the equilibrium solute concentrations. The solubility of borax in water used has been reported by Nies and Hulbert [8].

Seed Preparation

The seed solution was prepared by dissolving of 30 gram of Univar AR grade borax in 100 mL of Milli-Q water by heating up to 60 °C and filtering through a 0.45 μm filter membrane. The solution was transferred into a petri dish that was lined with a transparency film, producing 40-200 μm well formed crystals. The transparency film was employed to avoid crystals sticking on the glass. These seed crystals were used to investigate the effect of additive on morphology of borax crystals. The form of borax crystal under microscope can be seen in Fig. 1.

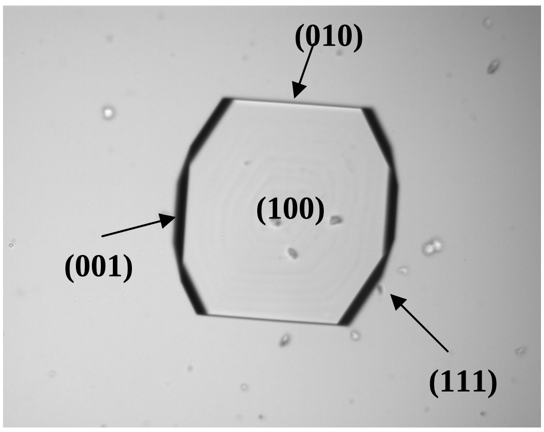

Fig 1. The form of borax crystal under in situ cell microscope

Preparation of Growth Solutions

The growth solution was prepared by dissolving and stirring the required amount of borax in 200 mL of Milli-Q water by heating up to 60 °C and filtering through a 0.45 μm filter membrane. The filtered solutions were transferred to a sealed plastic bottle and placed into a waterbath at temperature of 25 °C for 3 hours before use. To transfer solutions into the sample solution compartment, the growth solution was pumped by peristaltic pump *via* rubber tubing.

The growth *in situ* experiments [9-13] were carried out at 25 °C and at relative supersaturation of 0.21 and 0.74. The amount of additive ranged from 0 to 50 ppm at relative supersaturation of 0.21 and 0 to 150 ppm at relative supersaturation of 0.74.

RESULT AND DISCUSSION

Effects of SDBS on the growth rate of borax crystals

The effect of sodium dodecylbenzenesulfonic acid (SDBS) on the growth rate of single crystals of borax was investigated at temperature 25 °C and at relative supersaturation of 0.21 using *in situ* cell optical microscopy. The ranges of amount of additive added are 0 to 30 ppm. The result of this experiment is shown in Table 1 and the effect of various amounts of additives on the average growth rates of the (010), (001) and (111) faces of borax crystals is displayed in Fig 2.

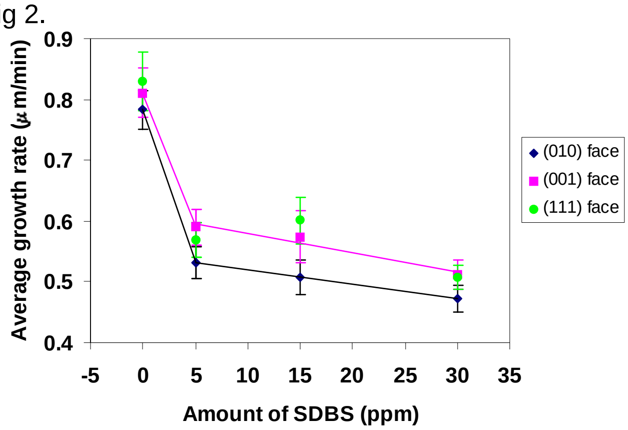

Fig 2. Effect of various amount of SDBS on the growth rate of the (010), (001) and (111) faces of borax crystal at relative supersaturation of 0.21 and temperature of 25 °C

Table 1. Effect of SDBS on the seed single crystal growth rate of borax at relative supersaturation of 0.21 and temperature of 25 °C

Additive	ppm	Average growth rate (μm/min)		
		(010) face	(001) face	(111) face
Sodium dodecylbenzenesulfonic acid (SDBS)	0	0.783±0.032	0.811±0.041	0.830±0.048
	5	0.531±0.026	0.590±0.029	0.569±0.029
	15	0.508±0.028	0.574±0.043	0.601±0.039
	30	0.473±0.022	0.512±0.024	0.508±0.020

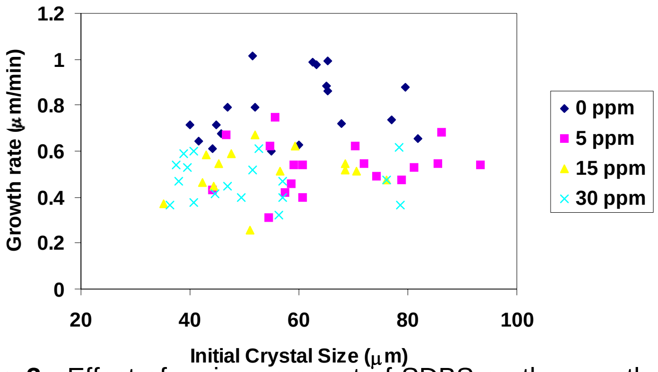

Fig 3. Effect of various amount of SDBS on the growth rates of the (010) face of borax crystal at (s-1) of 0.21 and temperature of 25 °C

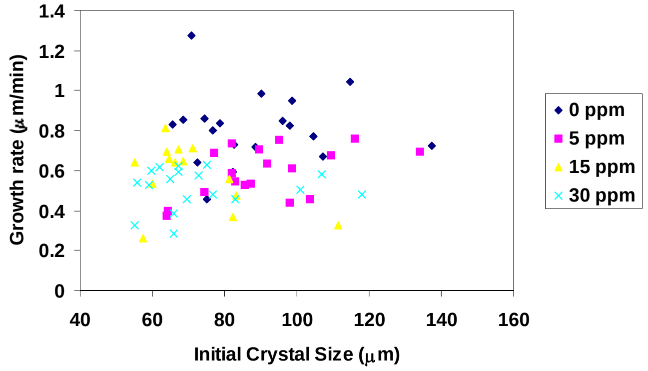

Fig 4. Effect of various amount of SDBS on the growth rates of the (001) face of borax crystal at (s-1) of 0.21 and temperature of 25 °C

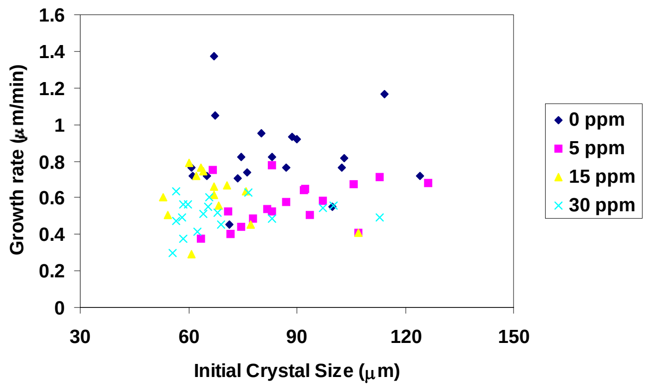

Fig 5. Effect of various amount of SDBS on the growth rates of the (111) face of borax crystal at (s-1) of 0.21 and temperature of 25 °C

This additive studied decreases the average of growth rate of seed single crystals of borax. As can be seen in Table 1, at the ranges of the amounts of impurity in a crystallizing solution from 0 to 30 ppm, increasing amount of impurity decreases the growth rate of borax crystals. SDBS inhibits growth rate of the (010), (001), and (111) faces and improves the crystal shape of borax.

The addition of sodium dodecylbenzenesulfonic acid (SDBS) on the crystallization of borax crystals can be seen in Fig 3, 4, and 5 for all faces. The addition of this additive from 5 to 30 ppm inhibits the growth rate of borax crystals for all faces. Figures 3, 4, and 5 show that the comparison of spreading of growth rate at the addition of SDBS from 5 to 30 ppm is not significant different. However, the average of growth rate showed Table 1 indicates that increasing the amount of SDBS decreases the average growth rate of borax crystals for all faces. The addition of this additive is very effective to reduce the average growth rate of borax crystals at level of 5 ppm or below for all major faces (see Fig 2).

Effects of SDBS on the morphology of borax crystals

In the absence of additives and at relative supersaturation of 0.21, the growth rate of the (010), (001), and (111) faces are nearly similar. Based on the data in Table 1, the growth rates of the (010), (001), and (111) face are 0.78, 0.81, and 0.83 μm/min, respectively. Fig 6 shows an *in situ* growth sequence of seed borax crystals at relative supersaturation of 0.21. From this figure, it can be seen that the shape of the crystal growth is a nearly square platelet shape.

Low concentrations of SDBS (30 ppm and less) had nearly no effect on the habit of borax crystals, but it inhibited the growth rate of borax crystals at relative supersaturation of 0.21 and temperature of 25 °C. Based on Table 1, the growth rate of the (010), (001) and (111) faces of borax crystals in pure solution of borax are 0.78, 0.81, and 0.83 μm/min, respectively. In the same condition, when 30 ppm of SDBS added, the growth rate of the (010), (001), and (111) faces decrease to be 0.47, 0.51, and 0.51 μm/min, respectively. Thus at this level of additive, SDBS decreases the growth rate of borax, but does not change the habit of borax.

Increasing the concentration of SDBS up to 90 ppm at relative supersaturation of 0.21 and temperature of 25 °C, the growth rate decreases and the habit of borax crystal changes to that of an elongated crystal. At these conditions, the growth rate of the (010) face will be slower than that of the (001) and (111) faces. This can be seen in Fig 7.

In the absence of additives and at relative supersaturation of 0.74, the growth rate of (010) face is faster than (001) and (111) face. An *in situ* growth sequence and the resulting habit of borax crystals under these conditions can be seen in Fig 8.

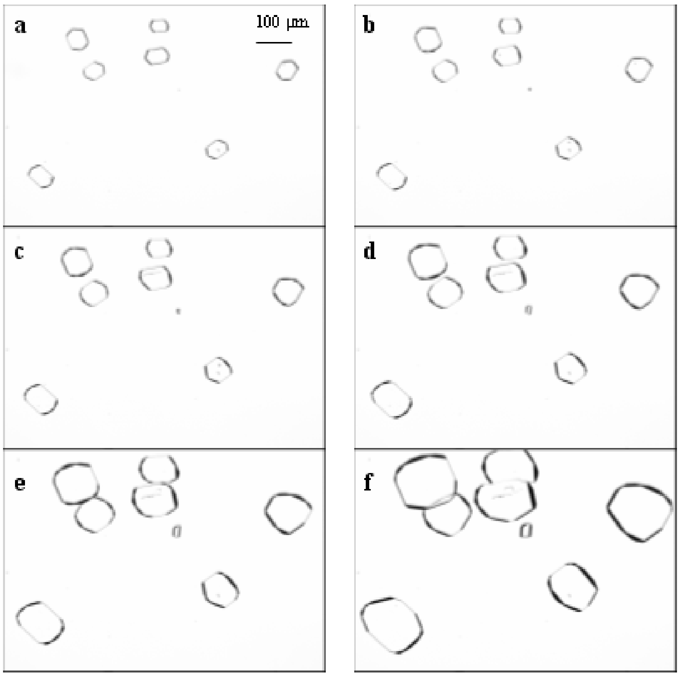

Fig 6. (a-f) In situ crystal growth experiment at 25 °C and relative supersaturation of 0.21 without additive after (a) 0, (b) 20, (c) 40, (d) 60, (e) 100 and (f) 220 minutes

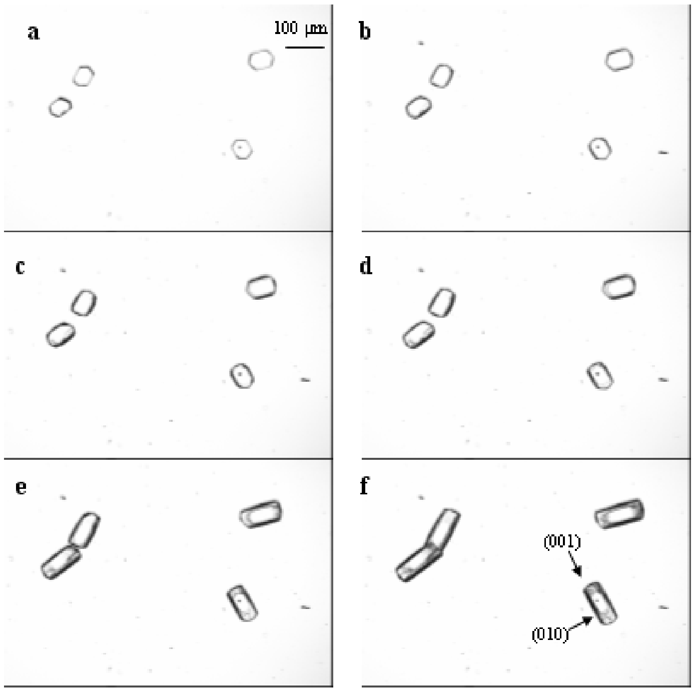

Fig 7. (a-f) In situ crystal growth experiment at 25 °C and relative supersaturation of 0.21 with 90 ppm of SDBS after (a) 0, (b) 20, (c) 40, (d) 60, (e) 120 and (f) 180 minutes

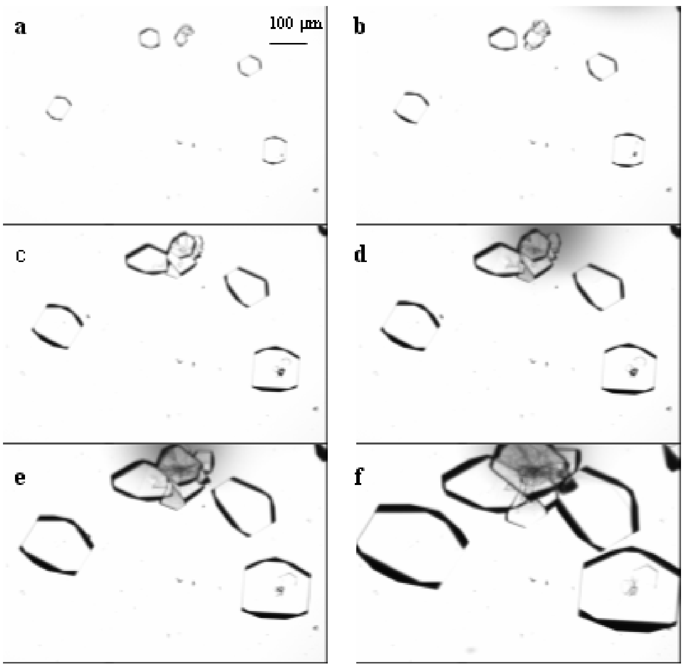

Fig 8. (a-f) In situ crystal growth experiment at 25 °C and relative supersaturation of 0.74 without additive after (a) 0, (b) 5, (c) 10, (d) 15, (e) 30 and (f) 55 minutes

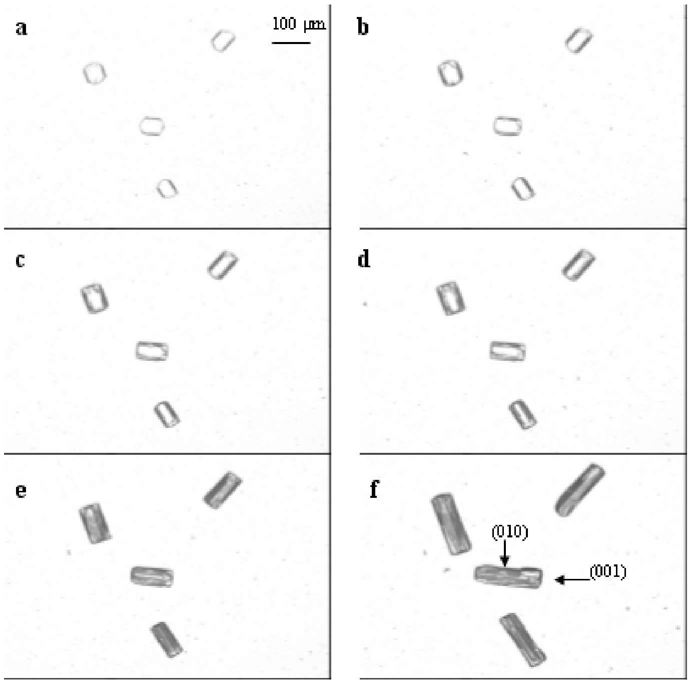

Fig 9. (a-f) In situ crystal growth experiment at 25 °C and relative supersaturation of 0.74 with 200 ppm of SDBS after (a) 0, (b) 2.5, (c) 5, (d) 7.5, (e) 12.5 and (f) 30 minutes

When the addition of 200 ppm of SDBS, this additive changes the habit of borax crystals. The habit modification of borax at these conditions is persistent to the habit obtained at supersaturation of 0.21 with 90 ppm of SDBS (Fig 7), resulting in elongated crystal. Fig 9 describes this habit modification of borax.

CONCLUSION

The effects of SDBS on the growth rate of borax crystals at relative supersaturation of 0.21 are strongly dependent on additive concentration. SDBS influences the growth rate of borax crystal with decreasing the average growth rates of seed single crystals of borax for all faces. Addition of 90 and 200 ppm SDBS in the crystallization solution (s-1 = 0.74, *in situ* cell seeded experiment) gives significant effect on morphology of borax crystal.

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