Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 7 (10): 1390-1396, 2007
ISSN 1812-5654

Effect of Cetyltrimethylammonium Bromide (CTAB) on the Growth Rate and Morphology of Borax Crystals

[1]Suharso, [2]Gordon Parkinson and [2]Mark Ogden
[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Lampung University, Jl. Sumantri Brojonegoro No. 1 Gedong Meneng, Post Code 35145, Bandar Lampung, Indonesia
[2]School of Applied Chemistry, Curtin University of Technology, Perth-Western, Australia

Abstract: An investigation of the effect of cetyltrimethylammonium bromide (CTAB) 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 CTAB inhibits the growth rate and changes the morphology of borax crystal.

Key words: Borax, growth rate, crystallization, CTAB

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 (Boncukcuoglu *et al*., 1999, 2002). 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 additives in crystallization processes has long been known as a matter of practical importance. Additives are successfully 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 (Van der Leeden and Van Rosmalen, 1984).

Previous studies on the effect of additives on the crystallization of borax crystal have been carried out by several researchers. Garret and Rosenbaum (1958) 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.

Garrett (1959) 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.

Randolph and Puri (1981) 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 study 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.

MATERIALS AND METHODS

Solubility of borax in water: The driving force of crystallization is usually expressed as a supersaturation ratio, defined as (Mullin, 1993):

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

Corresponding Author: Suharso, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Lampung University, Jl. Sumantri Brojonegoro No. 1 Gedong Meneng, Post Code 35145, Bandar Lampung, Indonesia

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 (1967) and Sprague (1980) in Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry.

Experimental set-up: *In situ* cell optical microscopy method described by Lee and Parkinson (1999), Lowe *et al*. (2002) and Suharso (2005a) was used. Optical microscopy *in situ* growth experiments were conducted at Crystallization Laboratory of Curtin University of Technology using a set up that consists of a Nixon Optiphot-2 Microscope with automated video image capture, a Grant W14 (Grand Instruments Ltd.) circulating water bath with temperature controller, Pulnix TM-9701 Camera (Progresive Scanning Full Frame Shutter Camera) and a Pentium II Computer. The schematic diagram of the *in situ* growth cell is given in Fig. 1 (Lowe *et al*., 2002). The *in situ* growth cell has two compartments; water at desired temperature was circulated through the lower chamber of the cell to keep the temperature constant in the sample solution compartment (volume 5 mL). During the growth experiments, a digital thermometer (HANNA Instruments, HI 8424) monitored temperature of the sample solution compartment. The images of the growing seed crystals were recorded using the video camera and the change in length of the (001) face was measured using the Optimas Software, Version 6.2 (Optimas Corporation, Bothell, Wa, USA.) linked automatically with Microsoft Excel Program, 1997. The schematic of crystal measurement of the (001), (010) and (111) face in the *in situ* growth cell is shown in Fig. 2. Following measurement of crystal length, a linear regression was performed on the length data for each crystal. In order to obtain the growth rate of the (001) face, the slope of the plot was divided by two. The final growth rates are reported as μm min^{-1}.

Seed preparation: The seed solution was prepared by dissolving of 30 g 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.

Preparation of growth solutions: The growth solution was prepared by dissolving and stirring the required amount of sodium borate 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 water bath at temperature of 25°C for 3 h 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 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 200 ppm at relative supersaturation of 0.74.

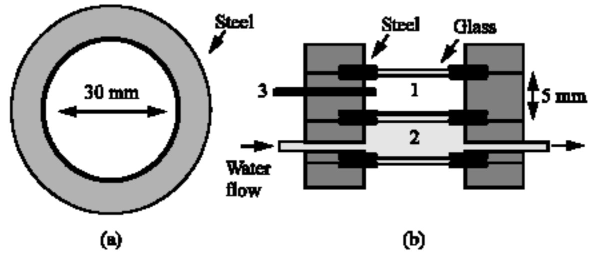

Fig. 1: The *in situ* cell used in the growth experiments, (1) sample solution compartment, (2) constant temperature water compartment and (3) thermocouple. (a) Top View and (b) side view

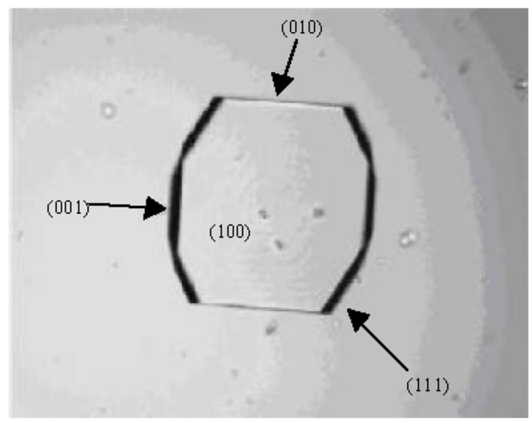

Fig. 2: The form of borax crystal under *in situ* cell microscope

RESULTS

The effect of cetyltrimethylammonium bromide (CTAB) 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 50 ppm. The result of this experiment is shown

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

		Average growth rate (μm min⁻¹)		
Additive	ppm	(010) face	(001) face	(111) face
Cetyltrimethylammonium bromide (CTAB)	0	0.783±0.032	0.811±0.041	0.830±0.048
	5	0.440±0.017	0.493±0.021	0.492±0.019
	30	0.362±0.011	0.482±0.011	0.475±0.010
	50	0.249±0.012	0.401±0.025	0.405±0.026

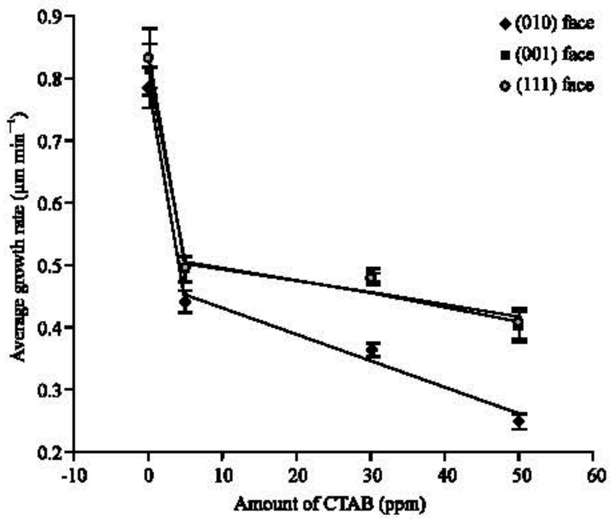

Fig. 3: Effect of various amount of CTAB on the growth rate of the (010), (001) and (111) faces of borax crystal at relative supersaturation of 0.21 and temperature of 25°C

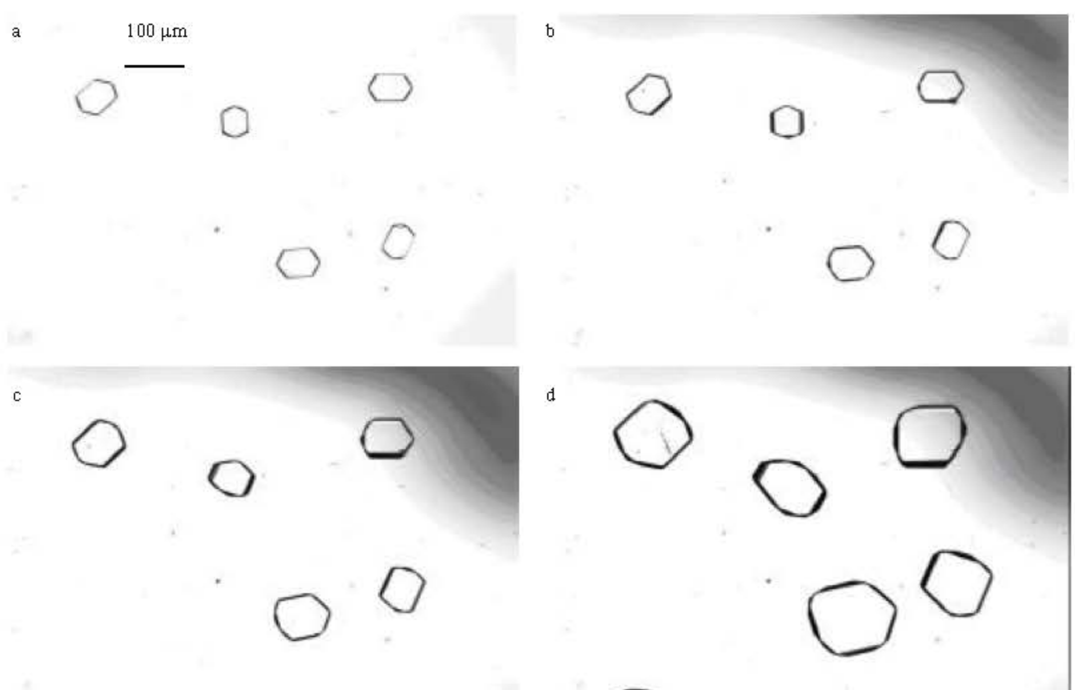

Fig. 4: (a-d) *In situ* crystal growth experiment at 25°C and relative supersaturation of 0.21 with 30 ppm of CTAB after (a) 0, (b) 20, (c) 80 and (d) 200 min

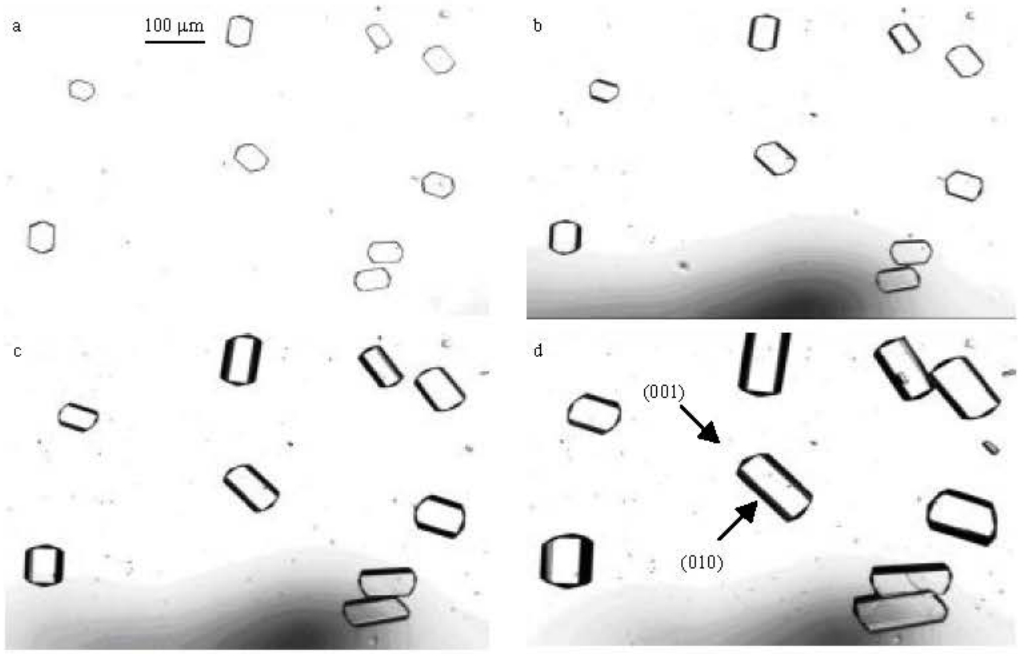

Fig. 5: *In situ* crystal growth experiment at 25°C and relative supersaturation of 0.21 with 50 ppm of CTAB after (a) 0, (b) 20, (c) 80 and (d) 210 min

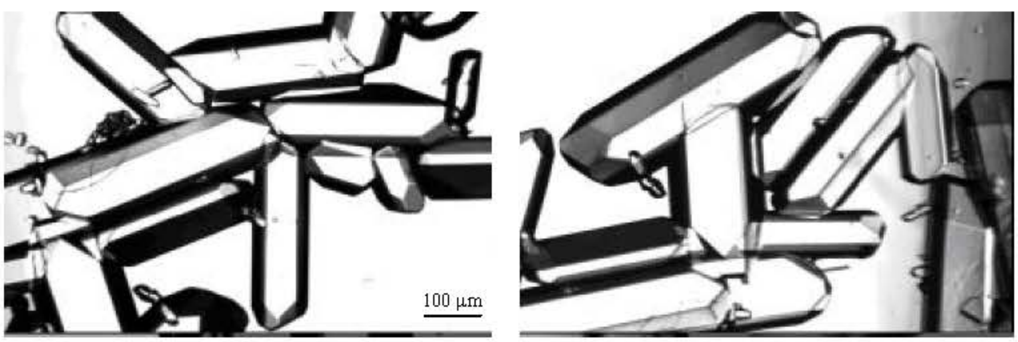

Fig. 6: Unseeded crystal growth experiment at 25°C and relative supersaturation of 0.21 with 50 ppm of CTAB after few days

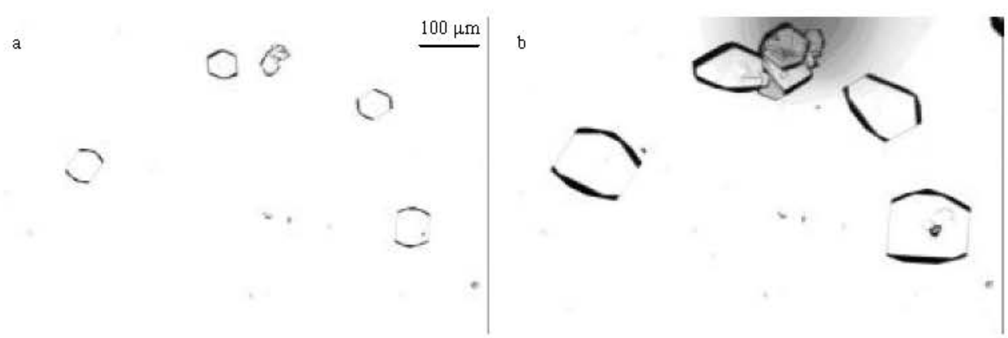

Fig. 7: *In situ* crystal growth experiment at 25°C and relative supersaturation of 0.74 without additive after (a) 0 and (b) 15 min

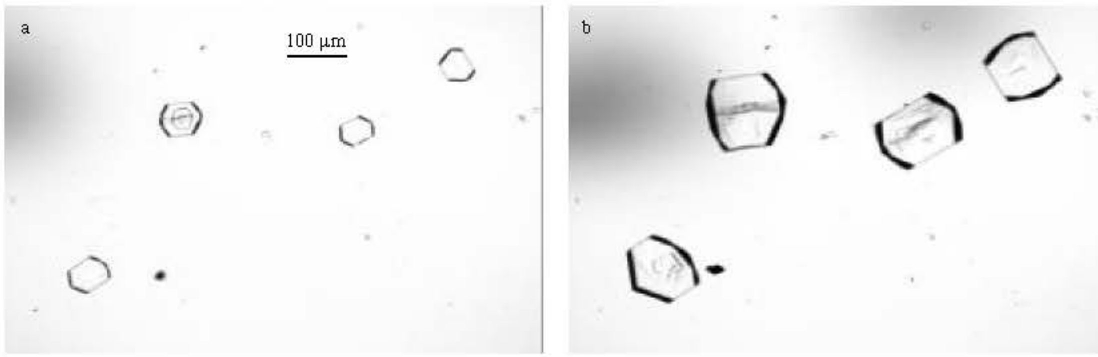

Fig. 8: *In situ* crystal growth experiment at 25°C and relative supersaturation of 0.74 with 150 ppm of CTAB after (a) 0 and (b) 15 min

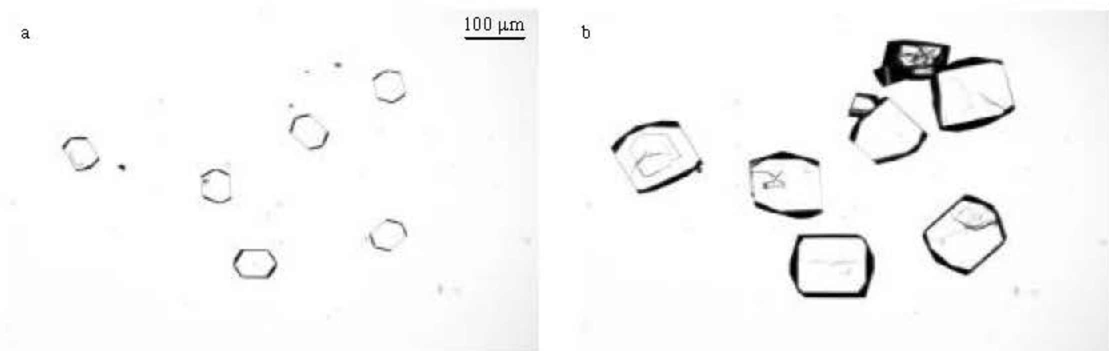

Fig. 9: *In situ* crystal growth experiment at 25°C and relative supersaturation of 0.74 with 200 ppm of CTAB after (a) 0 and (b) 15 min

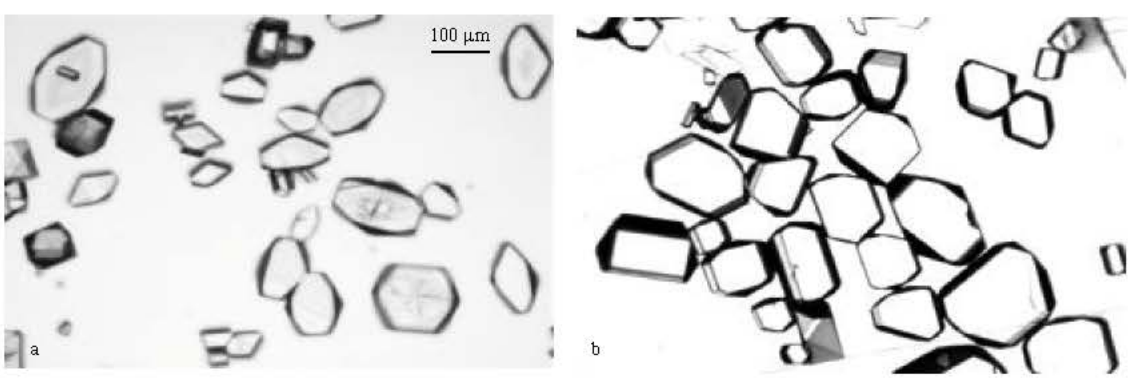

Fig. 10: Unseeded crystal growth experiment at 25°C and relative supersaturation of 0.74, (a) no additive (b) 150 ppm of CTAB after 1 days

in Table 1 and the effect of various amounts of additives on the average growth rates of the (010), (001) and (111) face of borax crystals is displayed in Fig. 3. The results of the morphology of borax crystal growth with additive and without additive are shown in Fig. 4-10.

DISCUSSION

Effects of CTAB on the growth rate of borax crystals: 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 5 to 50 ppm, increased amount of impurity decreases the growth rate of borax crystals. CTAB inhibits growth rate of the (010), (001) and (111) faces and improves the crystal shape of borax. With the addition of 5 ppm of CTAB, growth on the (001) and (111) faces is more rapid than on the (010) face.

Figure 11-13 describe the effect of initial crystal size under various amount of CTAB on the growth rate of (010), (001) and (111) faces, respectively. The presence of CTAB from 5 to 50 ppm decreases the growth rate of all faces of borax crystals. Figure 11-13 show that the growth rates of all faces vary with different initial crystal size and different amount of CTAB, but the growth rate is not dependent on the size. This additive was found to have a significant influence on the average growth rate of borax crystals (Fig. 3). The addition of 5 ppm of CTAB reduces the growth rate of the (010), (001) and (111) faces from 0.783, 0.811, 0.830 to 0.440, 0.493, 0.492 μm min^{-1}, respectively. The addition of 50 ppm of CTAB in the growth solution reduces the growth rate of (010), (001) and (111) face to 0.249, 0.401 and 0.405 μm min^{-1}, respectively. Therefore, the presence of 50 ppm of CTAB will dramatically change the form of borax crystal to elongated crystal.

Effects of CTAB on the morphology of borax crystals: A low concentration of CTAB (30 ppm) retards the growth rate on any face and improves the habit of borax crystals at relative supersaturation of 0.21 and temperature of 25°C. Increasing the concentration of CTAB up to 50 ppm causes drastic retardation on the (010) face and improves drastically the habit of borax crystal. The retardation and improvement are strongly dependent on CTAB concentration. Figure 4 and 5 explain the retardation of growth rate and improvement in habit of borax crystals. Using the *in situ* cell optical microscopy method, this additive was shown to have a stronger effect than lauric acid (LA), Sodium Lauryl Sulphate (SLS) and sodium dodecylbenzenesulfonic acid (SDBS) at these conditions (Suharso, 2002, 2005b).

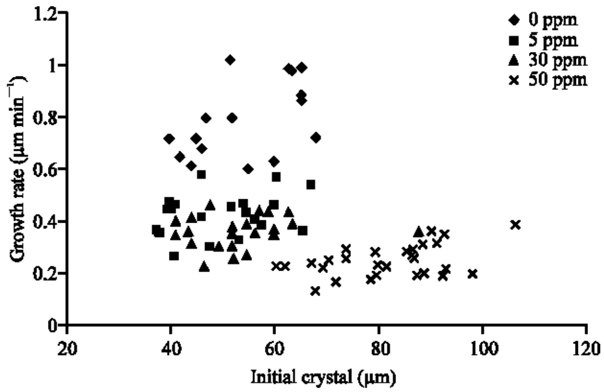

Fig. 11: Effect of various amount of CTAB on the growth rates of the (010) face of borax crystal at (s-1) of 0.21 and temperature of 25°C

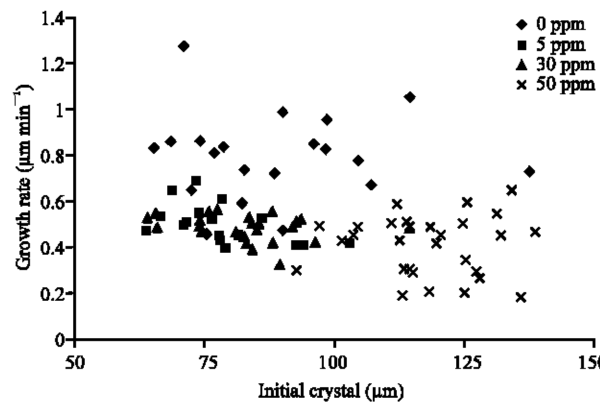

Fig. 12: Effect of various amount of CTAB on the growth rates of the (001) face of borax crystal at (s-1) of 0.21 and temperature of 25°C

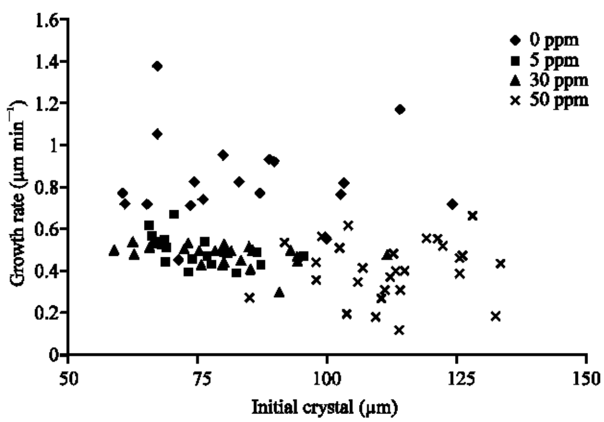

Fig. 13: Effect of various amount of CTAB on the growth rates of the (111) face of borax crystal at (s-1) of 0.21 and temperature of 25°C

Using an unseeded experiment, Fig. 6 illustrates the effect of CTAB (50 ppm) on the precipitation of borax crystal at relative supersaturation of 0.21 and temperature of 25°C. This image shows the morphology of borax crystal is improved dramatically under these conditions.

Investigation of CTAB addition on the growth rate and habit modification of borax crystal at the range of 150-200 ppm of CTAB at the relative supersaturation of 0.74 and temperature of 25°C shows that this additive inhibits the growth rate of seed borax crystals, but has a very little effect on the habit of borax crystal. Figure 7 shows the growth of borax crystal without additive and Fig. 8 and 9 describe the effect of CTAB on the growth rate and habit of borax crystals at the relative supersaturation of 0.74. These pictures show the morphology of borax crystal under these conditions is similar.

While addition of 150 ppm CTAB in the crystallization solution (s-1 = 0.74, *in situ* cell seeded experiment) gives little effect on morphology of borax crystal (Fig. 8), from unseeded experiments (s-1 = 0.74) the presence this additive at the same amount in the crystallization solution improves the morphology of borax crystal (Fig. 10b). The main difference between crystals grown in the presence of CTAB and blank is that more elongated crystals can be observed than in the blank (Fig. 10a and b).

CONCLUSIONS

The effects of CTAB on the growth rate of borax crystals at relative supersaturation of 0.21 are strongly dependent on additive concentration. CTAB influences the growth rate of borax crystal with decreasing the average growth rates of seed single crystals of borax for all faces.

Addition of 150 ppm CTAB in the crystallization solution (s-1 = 0.74, *in situ* cell seeded experiment) gives little effect on morphology of borax crystal and greatly modifies under the unseeded borax crystal experiment.

REFERENCES

Boncukcuoglu, R. and M.M. Kocakerim, 1999. Technical note upgrading of the reactor waste obtained during borax production from tincal. Mineral Eng., 10: 1275-1280.

Boncukcuoglu, R., M.T. Yilmaz, M.M. Kocakerim and V. Tosunoglu, 2002. Utilization of trommel sieve waste as and additive in Portland cement production. Cement Concrete Res., 32: 35-39.

Garret, D.E. and G.P. Rosenbaum, 1958. Crystallization of Borax. Ind. Eng. Chem., 50: 1681-1684.

Garret, D.E., 1959. Industrial crystallization: Influence of chemical environment. Br. Chem. Eng., 4: 673.

Lee, M. and G.M. Parkinson, 1999. Growth rates of gibbsite single crystals determined using *in situ* optical microscopy. J. Crystal Growth, 198/199: 270-274.

Lowe, J., M. Ogden, A. McKinon and G. Parkinson, 2002. Crystal growth of sodium oxalate from aqueous solution. J. Crystal Growth, 237-239: 408.

Mullin, J.W., 1993. Crystallization. 3rd Edn., Butterworth-Heinemann Ltd., Oxford.

Nies, N.P. and R.W. Hulbert, 1967. Solubility isotherm in the system sodium oxide-boric oxide-water. J. Chem. Eng. Data, 12: 303-313.

Randolph, A.D. and A.D. Puri, 1981. Effect of chemical modifiers on borax crystal growth, Nucleation and Habit. AlChE J., 27: 92-99.

Sprague, R.W., 1980. In Mellor's comprehensive treatise on inorganic and theoretical chemistry, London and New York, Longman, 5: 254.

Suharso, 2002. Effect of Additives on Borax Crystallization. 7th Annual Student Seminar Day, Nanochemistry Research Institute, Curtin University of Technology, Perth-WA.

Suharso, 2005a. Growth of the (001) face of borax crystals. Indonesian J. Chem., 5: 98-100.

Suharso, 2005b. Effect of lauric acid on borax crystallization. Prosiding Seminar Nasional Kimia, Jurusan Kimia FMIPA Unila, Bandar Lampung.

Van der Leeden, M.C. and G.M. Van Rosmalen, 1984. The role of additives in the agglomeration of barium sulfate. Industrial Crystallization, 84. Elsevier Science Publishers B.V., Amsterdam.