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P. SAYAN, J. ULRICH*

Istanbul Technical University, Faculty of Chemical and Metallurgical Engineering, Chemical Engineering Department, Istanbul, Turkey

*Martin-Luther-Universität Halle-Wittenberg, FB Ingenieurwissenschaften, Institut für Verfahrenstechnik/ Thermische Verfahrenstechnik, Halle, Germany

Effect of Various Impurities on the Metastable Zone Width of Boric Acid

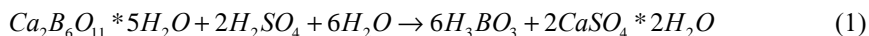
The metastable zone width of boric acid in aqueous solutions was measured in the presence of Ca^{+2} , Mg^{+2} , Cr^{+3} , Fe^{+2} ions. For the measurements of metastable zone width, the polythermal method was used. The impurity concentration is varied from 0 to 1000 ppm in each aqueous solution. It was found that the range of metastable zone width of boric acid in aqueous solutions is considerably affected by impurities. The width of metastable zone of aqueous solution of boric acid is reduced with increasing impurity concentration. In the presence of Ca^{+2} and Cr^{+3} , the equilibrium saturation concentration is changing.

Keywords: boric acid, metastable zone width, impurity, polythermal method

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1. Introduction

Boric acid is one of the most important boron compounds and it is usually manufactured from Colemanite ore. The Colemanite is ground to a very fine powder and added in portions to dilute mother liquor and sulphuric acid mixture at about 90 °C as shown in the following equation:



Gypsum crystals, which have a low solubility, are removed by filtration and clear solution is cooled to crystallize the boric acid. Generally, such saturated clear solution carries a wide variety of impurities like e.g. Ca^{+2} , Mg^{+2} , Cr^{+3} , Fe^{+2} and SO_4^{2-} . Most of these impurities originate from the ore, the others from crystallizer materials or from excess sulphuric acid in the process. All these impurities change the nucleation and growth mechanism of the main compound. During a crystallization process, two kinetic processes proceed simultaneously; nucleation and crystal growth. The crystal size distribution (CSD) of a product obtained in a crystallizer is mainly influenced by the rates and the controlling mechanisms of nucleation and crystal growth, both processes being strongly dependent on the supersaturation. Therefore, supersaturation control is often the most powerful tool for optimizing crystallization processes and must be known with some precision. The boundary of supersaturation can be characterized by measuring metastable zone width. The knowledge of the metastable zone width and effect of the parameters influencing it could give a lot of information in the design of the crystallization processes and help to improve the reproducibility of the process. The metastable zone width is mainly determined by the purity

of the material. There are several reports in literature e.g. (USHASREE; YOSHIOKA; KAREL; NYVLT and ULRICH) on the effect of some impurities on the metastable zone width of various salts and crystal growth process. Recently several workers (KARAKAYA; TEODOSSIEV) have also investigated the effect of Fe^{+3} and SO_4^{+2} ions on the crystallization kinetics of boric acid in MSMPR and fluidized bed crystallizer. Their results indicated that in the presence of SO_4^{+2} ions, the saturation temperature of boric acid solution is increased and the metastable zone width of boric acid is reduced. They also showed that in the presence of Fe^{+3} ions there is a significant change in the nucleation rate of boric acid in a MSMPR crystallizer. On the other hand, there are only limited reports in literature, on the metastable zone width of boric acid in the presence of impurities. In general, the effect of impurities are not predictable in a process. Therefore, in order to produce a product with a required quality and quantity in industrial crystallizers, the relationship between impurity and metastable zone width must be known. The knowledge of metastable zone width gives therefore an advantage in designing crystallization processes. Based on the above arguments, the aim was to investigate the influence of Ca^{+2} , Mg^{+2} , Cr^{+3} , Fe^{+2} ions on the metastable zone width of boric acid.

2. Theoretical

The width of metastable zone in aqueous solutions can be measured by the isothermal or polythermal method (NYVLT 1968). In the polythermal method, the solution is cooled at a constant rate from saturation temperature down to the temperature of appearance of the first visible nuclei. The difference in these temperature is described as a maximal supercooling (ΔT_{max}). The maximal supercooling (ΔT_{max}) is related to the cooling rate ($-T'$) by following equation:

$$\log \Delta T_{\text{max}} = \frac{1-m}{m} \log \left(\frac{dw_{\text{eq}}}{dT} \right) - \frac{1}{m} \log k_N - \frac{1}{m} \log (-T') \quad (2)$$

According to Eq.2 the dependence of ΔT_{max} on $(-T')$ is linear on a logarithmic plot and corresponds to the equation of a straight line

$$Y = A + BX \quad (3)$$

where $X = \log (-T')$ and $Y = \log (\Delta T_{\text{max}})$

The values of nucleation parameters m and k_N are obtained from the fitted constant of the correlation equation.

$$m = \frac{1}{B} \quad (4)$$

$$k_N = (1-m) \log \left(\frac{dw_{\text{eq}}}{dT} \right) - Am \quad (5)$$

3. Experimental Procedure

The width of metastable region of boric acid was measured using various concentrations of Ca^{+2} , Mg^{+2} , Fe^{+2} and Cr^{+3} ions. All solutions were prepared using distilled water and analytical grade substances. Saturated boric acid was prepared at 30 °C according to the solubility data

(SEIDEL and LINKE) and known amounts of impurity were added to the solution. Then solution was heated above saturation temperature, filtered using a membrane filter (Millipore 0.45 μm pore size) and 100 ml was taken to the nucleation cell. Measurement were carried out in a 0.25 l jacketed nucleation cell. The temperature of solution in nucleation cell was accompanied by a thermostatic bath and kept covered at all times to prevent evaporation. The solution is left undersaturated about 8°C above the saturation temperature for half an hour and mixed vigorously using a magnetic stirrer. The saturated solutions were cooled down at constant rates of 4.8, 10.2, 12 and 19.8 K/h with a programmer. The temperature of prepared solution was measured using the digital thermometer with a precision of ± 0.01 °C. The difference between the saturation temperature and the temperature at which the first precipitated nuclei are visually observed was recorded. The exact saturation temperature was checked using chemical analysis (SCOTT).

4. Results and discussion

The experimental data were treated using Eq. (2). The result of measurements of the metastable zone width of boric acid in the presence of Ca^{+2} , Mg^{+2} , Fe^{+2} and Cr^{+3} ions are summarized in Table.1 and the variation of maximum allowable undercooling with cooling rate are also presented graphically in Figs.1 to 4.

Table 1: Metastable region width of boric acid in the presence of various impurities

Impurity	Impurity Concentration (ppm)	Maximal Undercooling (K) at different cooling rate				Nucleation Order
		4.8 K/h	10.2 K/h	12 K/h	19.8 K/h	
Pure	-	2.75	2.95	3.04	3.29	8.01
Mg^{+2}	250	2.75	3.05	3.15	3.26	8.10
	500	2.40	2.61	2.67	2.90	7.59
	1000	2.15	2.32	2.36	2.59	7.81
Fe^{+2}	250	2.50	2.67	2.80	3.0	7.77
	500	1.90	2.13	2.25	2.38	6.16
	1000	1.67	1.97	2.02	2.14	5.60
Ca^{+2}	100	2.48	2.61	2.65	2.77	12.91
	250	1.97	2.01	2.05	2.13	18.51
	500	1.91	1.94	2.01	2.21	9.81
	1000	1.52	1.71	1.72	2.02	5.27
Cr^{+3}	10	2.40	2.49	2.54	2.65	14.45
	100	2.16	2.29	2.35	2.52	9.34
	250	2.02	2.20	2.30	2.43	7.57
	1000	1.70	1.84	1.88	2.04	7.90

In the presence of all examined impurities, a decrease on the metastable zone width of boric acid was observed. As it can be seen from Table 1 and Fig.1, the effect of Mg^{+2} ions on the metastable zone of boric acid is not a large effect in the investigated impurity concentration range. In the presence of 250 ppm Fe^{+2} ions, there is a noticeable decrease in the metastable zone and the nucleation order of system. By addition more than 250 ppm of Fe^{+2} ions to the solution, there is a gradual decreasing in the metastable zone width of boric acid (see Fig.2). Similar results were found also for Ca^{+2} and Cr^{+3} ions (see Figs.3 and 4). It is widely known

that, the certain polyvalent cations such as Cr^{+3} , are very active cations and have a strong effect on the crystallization. They can change drastically the properties of solution and/or equilibrium saturation concentration or the crystal habit (MULLIN).

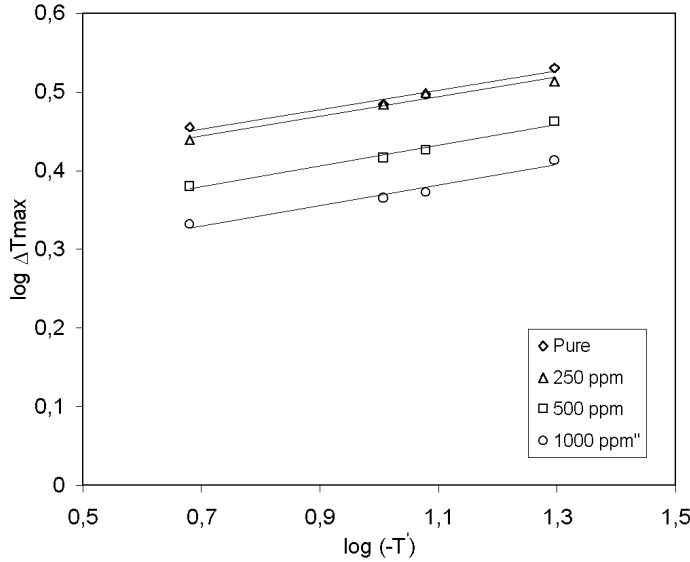


Fig. 1: The variation of maximum allowable undercooling with cooling rate in the presence of Mg^{+2} ions.

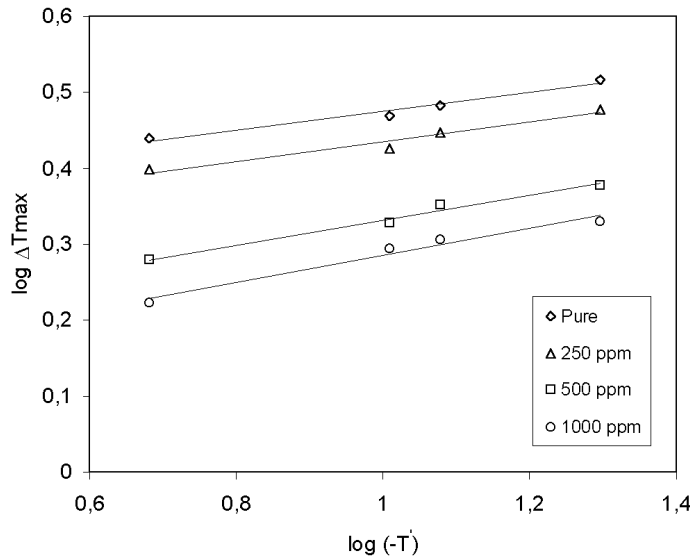


Fig. 2: The variation of maximum allowable undercooling with cooling rate in the presence of Fe^{+2} ions.

In the presence of Cr^{+3} ions saturation temperature slightly decreased with increasing the Cr^{+3} concentration. On the other hand, in the presence of Ca^{+2} ions, the homogeneous nucleation was started at concentrations higher than the saturation temperature. It means, equilibrium saturation concentration is changed by adding the Ca^{+2} ions to the solution. The change of equilibrium saturation temperature as a function of impurity concentration was given in

Fig.5. As it can be seen from Fig 5, in the presence of Ca^{+2} ions there is a significant change in the equilibrium saturation temperature of the solution. Similar results have been reported by KUBOTA et al. and ULRICH and STEPANSKI for potassium sulphate in the presence of Cr^{+3} ions. They showed that minute traces (<100 ppm) of Cr^{+3} in solution can prevent the dissolution of potassium sulphate crystals. The solubility of potassium sulphate in the presence of Cr^{+3} are always lower than the true equilibrium solubility.

Fig. 3: The variation of maximum allowable undercooling with cooling rate in the presence of Ca^{+2} ions.

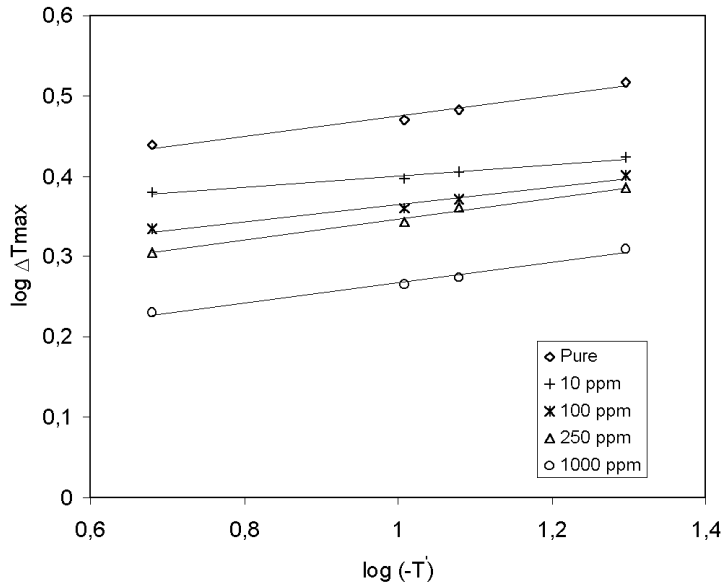
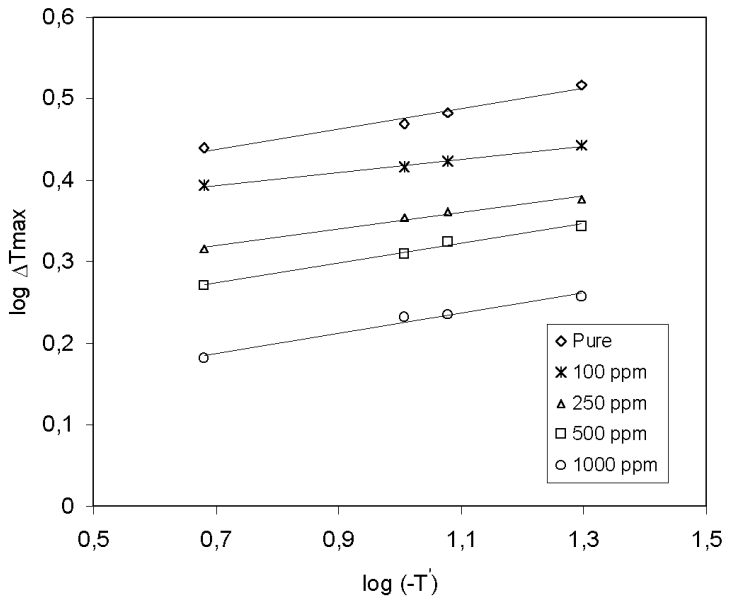


Fig. 4: The variation of maximum allowable undercooling with cooling rate in the presence of Cr^{+3} ions.



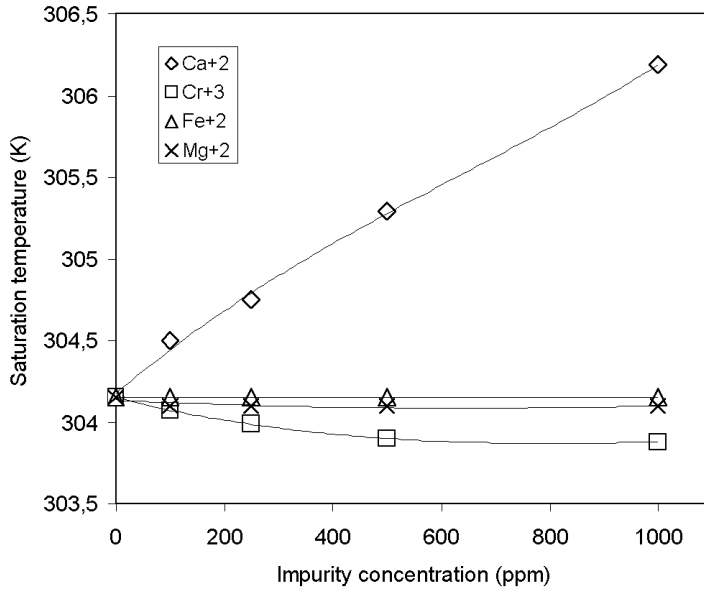


Fig. 5: The effect of impurity concentration on saturation temperature of boric acid.

In general, the impurities affect the width of metastable zone by different mechanisms. This effect also changes depending on the nature of solution, pH, impurities concentration, etc. A possible mechanism for the action of impurities on the metastable zone can be used to explain adsorption of impurities on the nuclei or heteronuclei of macrocompounds. The presence of impurities enhances the formation of clustering in the solution. This phenomenon causes a promotion of nucleation and tends to narrow the metastable zone width. The impurities also can suppress the primary nucleation and can enhance the secondary nucleation. These phenomena affect the growth rate of the crystals and the crystal size distribution of the product. The pure boric acid solutions have a narrow metastable zone (see Table 1). On the other hand, the boric acid is crystallized from pure solution only in dendrite form and the dendrites can be easily broken due to hydrodynamic conditions of the crystallizer (KELES et al.). This small fragment of crystals also contributes to the secondary nucleation in the crystallizer. In the presence of impurities, this situation becomes more complex. Because, in the presence of impurities, the width of the metastable zone of boric acid becomes even narrower, secondary nucleation arises and the control of the process stability becomes more difficult. Based on the above argument, it is clear that the impurities investigated may influence the whole crystallization process of boric acid. If the impurity concentration is not reduced in the solution, the product may show a very broad range in crystal size distribution, poor washing characteristics, caking tendency, high mother liquor content in centrifuged product and an effective dust problem in the dryer. These problems can only be reduced by controlling the concentration of the impurities during the crystallization process.

5. Conclusion

The width of the metastable zone of boric acid in aqueous solutions was measured in the presence of Ca^{+2} , Mg^{+2} , Cr^{+3} , Fe^{+2} ions. In the presence of all examined impurities, the metastable zone width of boric acid was reduced. In the presence of Ca^{+2} and Cr^{+3} ions, the equilibrium saturation concentration was also changed. The solubility of boric acid is much more influenced by the presence of Ca^{+2} ions in the solution. Results also show that in order

to produce boric acid with a required quality and quantity in industrial crystallizers, it is necessary to control the Ca^{+2} and Cr^{+3} concentration in the used solution.

Acknowledgement

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Notations

k_N	nucleation rate constant (-)
m	apparent nucleation order (-)
ΔT_{\max}	maximal undercooling (K)
T	Temperature (K)
$-T'$	cooling rate (K/h)
w_{eq}	solubility (kg/kg ₀)

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Contact information:

Perviz SAYAN, Dr.
Istanbul Technical University
Faculty of Chemical and Metallurgical Engineering
TR-80626, Maslak
Istanbul
Turkey

Joachim ULRICH*, Prof., Dr.
Martin-Luther-Universität Halle-Wittenberg
FB Ingenieurwissenschaften
Institut für Verfahrenstechnik, TVT
06099 Halle
Germany

*corresponding author; e-mail: Joachim.Ulrich@iw.uni-halle.de