

Ö. SAHIN

Dept. of Chemistry, Harran University, S.Urfa, Turkey

Effect of Electrical Field and Temperature on the Crystal Growth Rates of Boric Acid

Growth rates of boric acid have been measured both in the absence and in the presence of electrical field at 1.00 DC voltage as a function of supersaturation in a laboratory-scale fluidized bed crystallizer at the temperature range of 20 °C to 52 °C. The values of overall rate coefficient (K_G), diffusion rate coefficient (k_d), reaction rate constant (k_r) and reaction order (r) were determined by trial and error method at different temperatures. In the absence of electrical field increasing the temperature causes to increase the values of K_G , k_d , k_r and r . Activation energies are also determined for K_G , k_r and k_d separately. The effect of electrical field on the crystallization steps were determined by similar route. It was observed that electrical field caused to decrease the values of kinetic parameters (K_G , k_d , k_r and r) by increasing temperature.

Keywords: crystallization, boric acid, electrical field, activation energy, mass transfer coefficient, surface reaction constant, reaction rate order

(Received September 25, 2001; Accepted January 17, 2002)

Introduction

Crystallisation is a very complex operation. The reason for this complexity is due to two main processes in series namely, bulk diffusion through the mass transfer boundary layer, i.e. diffusion step, and incorporation of growth units in the crystal lattice, i.e. integration step [GARSIDE, MERSMANN, NYVLT, 1990; BOMIO et al., 1975]. Each of these steps is governed by different mechanisms and influenced by external conditions. Changing of external conditions such as cooling and stirring rates, temperature, magnetic and electrical fields [SHÖNEL, MULLIN, 1988b; DALAS, KOUTSOUKOS, 1989b; SHUBNIKOV, 1956] cause to change the growth rate, morphology and nucleation rate of crystals, all are very important in industrial crystallization. Among these, data on the effect of electrical field are limited.

The effect of electrical field on the nucleation rate was studied by Shubnikov [SHUBNIKOV, 1956; SHUBNIKOV, PORVOV, 1961] and Kozlovskii [KOZLOVSKII, 1962; KOZLOVSKII, 1966]. Results obtained in these works showed that external electrical field has a deep effect on growth rates of ammonium chloride and ammonium bromide crystals whereas it has no effect on the growth rates of copper and nickel sulfate crystals.

The results obtained in earlier studies [SHUBNIKOV, 1956; SHUBNIKOV, PORVOV, 1961; KOZLOVSKII, 1962; KOZLOVSKII, 1966; SHABLA KH et al., 1983] proved that electrical field leads to increase the nucleation rate. The effect of electrical field on the nucleation rate was expressed by Kozlovskii as follow:

$$B^{\circ} = K(C - C^*) \cdot E^2 \quad (1)$$

The effect of electrical field on the crystallization rate of phenyl salicylate was investigated by Roulleau and Capus [ROULLEAU, CAPUS, 1967] at different temperatures. Under the influence of electrical field, crystal rates of phenyl salicylate increased, decreased and did not change at the temperature range of 32-20 °C, 20-12 °C and below 12 °C, respectively.

In this study, the crystal growth rate of boric acid were investigated in the absence and in the presence of external electrical field at the temperatures of 20 °C, 35 °C, 45 °C, 52 °C in order to achieve the effect of electrical field on the both diffusion and reaction steps of crystallization. Thus, from the experimental data, mass transfer coefficient (k_d) the surface reaction constant (k_r) and surface reaction order (r) are determined by trial and error method for each temperature in both conditions.

Theory

Diffusion and reaction steps in the crystal growth may be conveniently expressed as follow:

$$R_G = k_d (C - C_i) \quad (\text{diffusion step}) \quad (2)$$

$$R_G = k_r (C_i - C^*)^r \quad (\text{integration step}) \quad (3)$$

Since it is very difficult to measure the concentration at the boundary layer (C_i), this value is eliminated by the combination of Eq.2 and Eq.3. A general expression, which contains the diffusion and reaction constants, can be derived as follows:

$$R_G = k_r \left(\Delta C - \frac{R_G}{k_d} \right)^r \quad (4)$$

Because of the complexity of Eq.4, overall growth rate is generally expressed in a simpler form:

$$R_G = K_G (\Delta C)^g \quad (5)$$

In the literature, attempts were made to determine the mass transfer coefficient (k_d), the surface reaction constant (k_r) and the surface reaction rate order (r) used in Eq.4 under the assumption of $r=2$ [KARPINSKI, 1980; BUDZ et al., 1985; PHILLIPS, EPSTEIN, 1974; SOBCZAK, 1990] or by assuming that the equality of the mass transfer coefficient (k_d) of the crystal growth with the mass transfer coefficient of crystal dissolution [KARPINSKI, 1980, TANRIKULU et al., 1998]. The coefficients of eq.4 (k_r , k_d and r) may be estimated by genetic algorithm without any assumption [SAHİN et al., 2000]. Another approach was given by Sobczak [SOBCZAK, 1990] by linearizing the Eq.4 as follow:

$$\Delta C = \frac{R_G}{k_d} + \left(\frac{R_G}{k_r} \right)^{\frac{1}{r}} \quad (6)$$

$$\Delta C \cdot R_G^{-1} = k_d^{-1} + k_r^{-1/r} \cdot R_G^{1/r-1} \quad (7)$$

with introducing $a=k_d^{-1}$; $b=k_r^{-1/r}$; $y = \Delta C \cdot R_G^{-1}$; $x = R_G^{1/r-1}$

Eq.7 may be arranged in the form of a linear equation as follow:

$$y = a + bx \quad (8)$$

Furthermore, Sobczak [SOBCZAK, 1990] was determined the coefficients (k_r , k_d) of Eq.7 under the assumption of a reaction order of $r = 2$.

In this study, however we use Eq.7 in order to determine the rate constants (k_r , k_d , r) under variable r values. If r -value is known then a and b constants can be calculated easily by the intercept and slope of straight line. In order to obtain the best r value from Eq.(7), the following trial and error method was used.

- For any data series, r value was randomly selected between 0,6 to 2,5 and then $\Delta C.R_G^{-1}$ versus $R_g^{1/r-1}$ was plotted.
- The suitable straight-line equation was calculated by the least square method in excel software. The suitability of the line was observed by R^2 (the best values of R^2 is 1).
- After that, the increment of r value is taken as 0.1 and then the changes of R^2 is observed graphically. By this coarse approach r is compressed between two values. While r is selected, the straight line equation must appears in Eq.8, otherwise the selected r values lead to wrong kinetic constants (k_r , k_d , r).
- Then increment of r value was taken as 0,01 and the changes of R^2 is also observed, when the higher R^2 is obtained then the best r values are calculated for used series.

The relative standard deviations between $R_{G(4)}$ and experimental values $R_{G(5)}$, described by Eq. 5 can be calculated as

$$s = \sqrt{\frac{\sum_{i=1}^n ((R_G(5) - R_G(4)) / R_G(5))^2}{n-1}} \quad (9)$$

Where n is the number of data. Finally, the intercept and the slope of straight line were used to calculate k_r and k_d values, respectively.

Both the diffusion and integration coefficient (k_r , k_d) are temperature dependent and this can be characterised by activation energy. Thus, the overall mass transfer coefficient (K_G), diffusion coefficient (k_d) and integration rate constant (k_r) can be represented by the following equations, respectively;

$$K_G = K_{G_0} \exp\left(-\frac{E_G}{RT}\right) \quad (10)$$

$$k_d = k_{d_0} \cdot \exp\left(-\frac{E_d}{RT}\right) \quad (11)$$

$$k_r = k_{r_0} \cdot \exp\left(-\frac{E_r}{RT}\right) \quad (12)$$

Where the E_G , E_d and E_r are the corresponding activation energies. These values may be easily obtained from the data at different temperatures.

Experimental

In this study, the classical differential measurement method was used to calculate the growth rate of boric acid crystals in fluidized bed crystal growth cell. In this method, the weight of

crystals put into the crystallizer is m_1 and the weight of the same number of crystals taken out from the crystallizer is m_2 , the relation between the size and the weight of crystals can be shown as follows:

$$m_1 = \alpha \rho L_1^3 \tag{13}$$

$$m_2 = \alpha \rho L_2^3 \tag{14}$$

where L_1 and L_2 are characteristic sizes of the input and output crystals, respectively.

It is given that the overall linear growth rate, G (m/s) is defined by the following equation

$$G = \frac{\Delta L}{t} = \frac{L_2 - L_1}{t} \tag{15}$$

The overall linear growth rate can be calculated by combining of Eqs.13-15:

$$G = \frac{L_0}{t} \left[\left(\frac{m_2}{m_1} \right)^{1/3} - 1 \right] \tag{16}$$

The overall linear, G and the mass, R_G growth rates are interrelated to each other as follow;

$$R_G = \frac{3a}{b} r_c \cdot G \tag{17}$$

Herein, β/α can be taken as 6 since the used boric acid crystals are spherical.

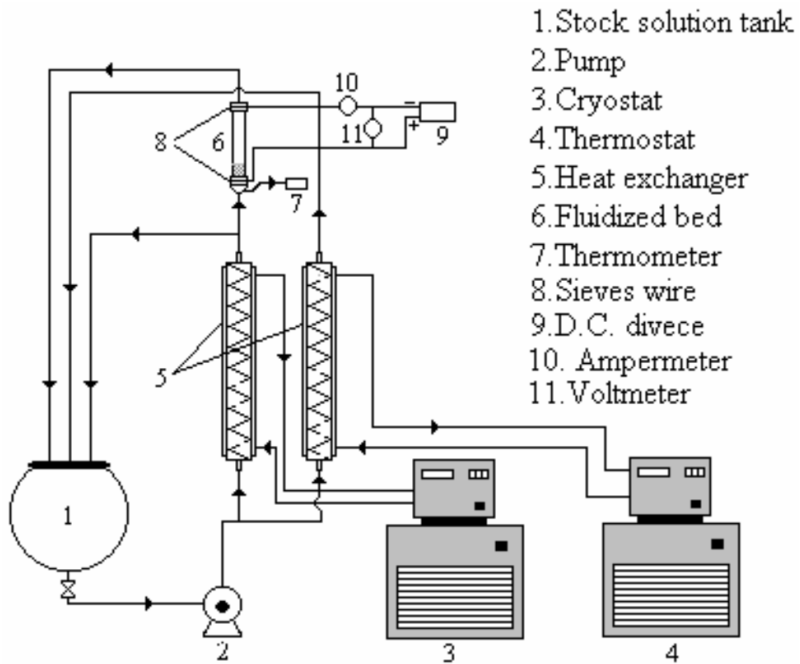


Fig. 1: Schematic diagram of laboratory-scale fluidized-bed crystallizer

Figure 1 shows the fluidized-bed measurement system with a solution capacity of 6 l. An amount of $2,5 \pm 0,0001$ g seed crystals with sieve fraction of $-600+500 \mu\text{m}$ was used in the experiments of crystals growth rate of boric acid both under normal conditions and in presence of electrical field. 1.00 volt D.C. voltage was applied between bottom and top of fluidized bed (6) in which a stainless steel sieves wire of $250 \mu\text{m}$ was used to obtain electrical field. The distance between two sieves wires is 20 cm. Experiments were performed at constant fluidization velocity determined by Karakaya [KARAKAYA, BULUTCU, ULRICH, 1992] for 12 min. When the system reached the desired operation temperature, seed crystal ($2,5 \pm 0,0001$ g) were put into the cell of fluidized bed. During the experiment the temperature of solution was recorded in 1 min. interval within $0,1 \text{ }^\circ\text{C}$ sensitivity, using a Pt-100 resistance thermometer placed at the inlet of the fluidized bed cell. At the end of the run the crystals were removed and then dried in air for 24 h. After drying, the crystals were weighed to calculated the linear and mass growth rate using Eqs.16 and 17.

Results and Discussion

Effect of temperature on crystal growth rate

Results of crystal growth rates of boric acid versus supersaturation at the temperature of 20°C , 35°C , 45°C , 52°C are shown in Figure 2.

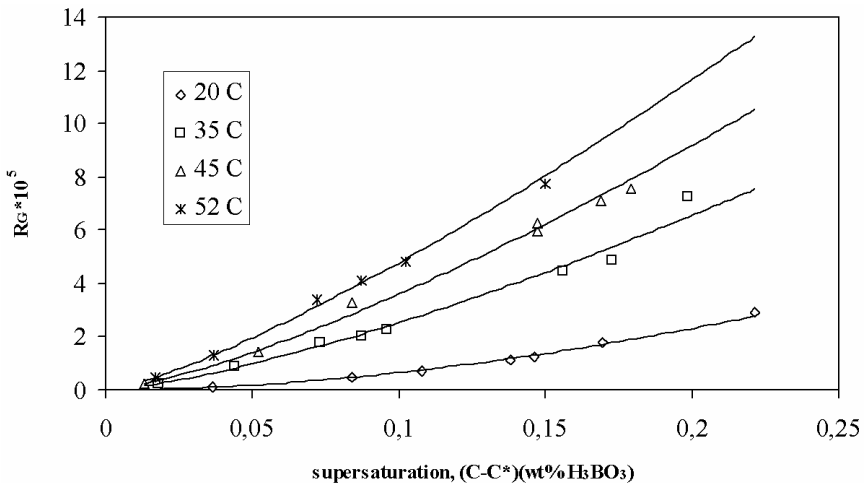


Fig. 2: Growth rates of $-0.600+0.500$ mm boric acid crystals as a function of supersaturation at different temperatures (In the absence of electrical field).

The increasing of growth rates with increasing temperature indicates the importance of diffusion step in the growth of process, the growth rate apparently tending to asymptotic values as the temperature is increased. The growth rate data are evaluated with respect to Eq.5 for calculating the overall rate coefficient (K_G) and the growth rate order (g) at each temperature. The methodology used for obtaining the best curve fit is the least square method. The obtained values are tabulated in Table 1. It can be observed from Table 1 that the growth rate order, g has a value of about 1.3-1.8. These values show that the crystal

growth of boric acid at the temperature range of 20-52 °C is controlled by both diffusion and reaction steps. The overall rate coefficients (K_G) obtained at different temperatures is applied through Eq.10 in order to calculate the activation energy for overall crystal growth rates. The plots $\ln(K_G)$ versus $1/T$ are illustrated in Figure 3. The Arrhenius equation line in Figure 3 leads to the following expression.

$$K_G = 1.12659 \exp (-2311.9/T) \tag{18}$$

According to this last equation, activation energy for overall crystal growth is found as 19.22 kJ/mol in the temperature range of 20°C to 52°C.

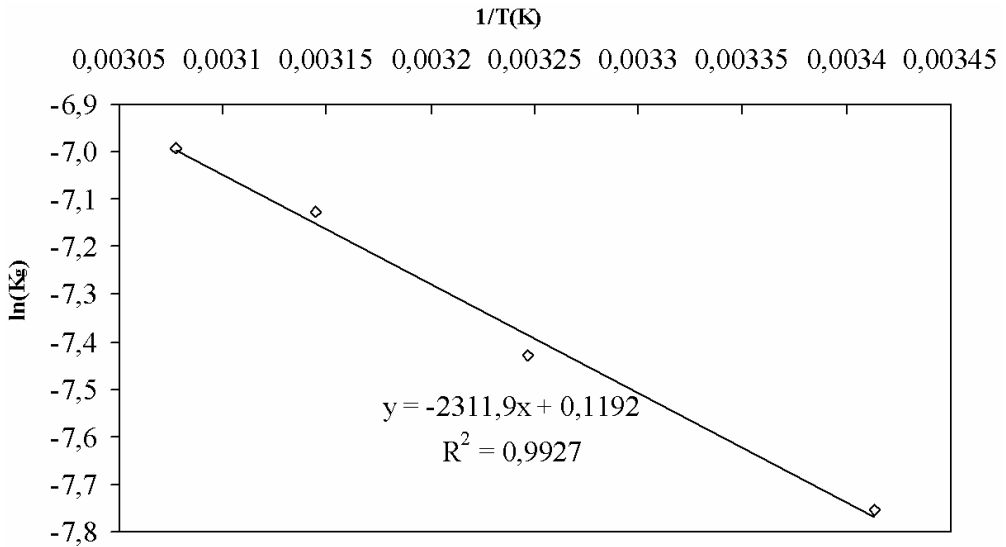


Fig. 3: Plot of Arrhenius Eq.10 for the overall growth rate constant

The values obtained from Eq.5 for each temperature are applied to Eq.7 to find the value of mass transfer coefficient, k_d surface reaction constant, k_r and reaction order, r using the proposed trial and error method. The calculated k_d , k_r and r values and their standard deviation values are evaluated according to Eq.9 and the results are presented in Table 1. The values at Eq.4 were computed by trial and error method for the values of $R_{G(5)}$ with respect to standard deviation, provided that convenient r values are chosen. This fact is also stated by Karpinski [KARPINSKI, 1980] that if the surface reaction order, r is properly chosen, the correlation error of Eq.4 is smaller than those of Eq.5. Also, Table 1 indicates that the values of k_d are much greater than the values of k_r , thus it can be said that the surface reaction completely controls the growth rate of boric acid. According to these results, the values of K_G tend to k_r and the values of g tend to r .

Furthermore, the plots $\ln(k_d)$ and $\ln(k_r)$ versus $1/T$ are shown in Figure 4. The activation energy for diffusion and integration steps are found to be 13.93 kJ/mol and 19.22 kJ/mol from the slopes of lines in Figure 4, respectively. According to the results of activation energy (E_d , E_r), it is possible to conclude that, the rate of integration process increases more rapidly with temperature than the rate of diffusion process and so crystal growth rate tend to diffusion controlled at high temperatures and integration controlled at low temperatures.

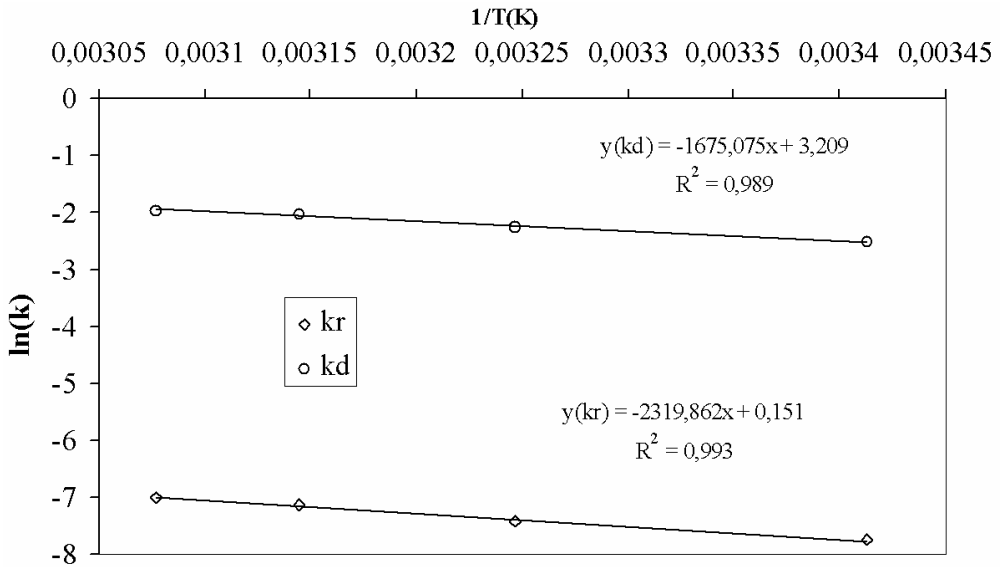


Fig. 4: Plot of Arrhenius Eqs.11,12 for both the reaction rate constant and diffusion coefficient

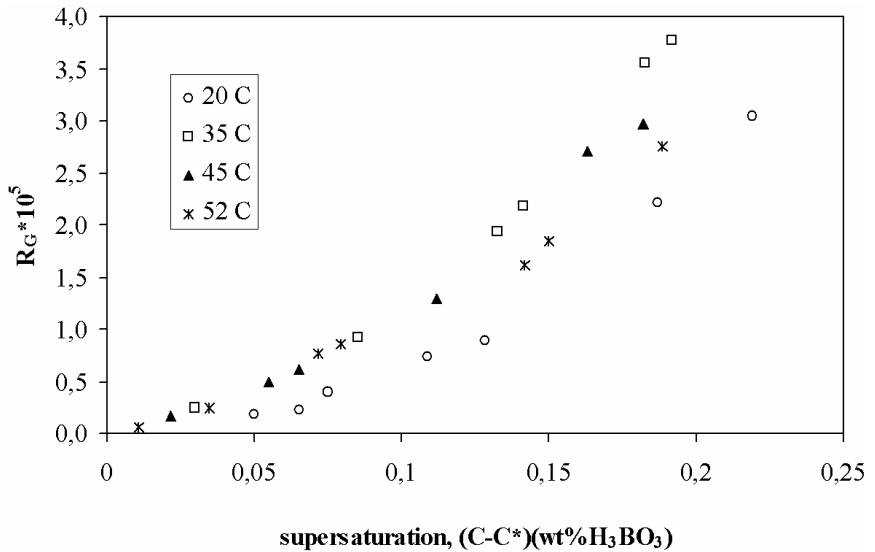


Fig. 5: Growth rates of -0.600+0.500 mm boric acid crystals as a function of supersaturation at different temperatures under one D.C voltage.

Effect of electrical field on the crystal growth rate

Figure 5 demonstrates the changing of crystal growth rates with supersaturation under 1.00 DC volt at different temperatures. As can be seen in this figure, increase in temperature cause to decrease in the growth rate comparing to the results obtained in the absence of electrical

field for the same concentration driving force. The current in fluidized bed at the temperatures of 20 °C, 35 °C, 45 °C, 52 °C has the values of 2.7 μA, 4.6 μA, 8.3 μA, 14 μA respectively. The growth rate data obtained under 1.00 DC volt are utilized by using Eq.5 to compute the overall rate coefficient, K_G and the growth order, g for each temperature. The variation of K_G with temperature is given in Table 1.

Table 1: Best fit parameters of Eq.4 and Eq.5 for growth rate of boric acid crystals at different temperatures.

Temp. (°C)	Absence of electrical field					
	g	$K_G \cdot 10^4$	r	$k_r \cdot 10^4$	$k_d \cdot 10^2$	$s \cdot 10^4$
20	1.813	4.286	1.814	4.303	8.200	1.860
35	1.369	5.943	1.370	5.977	10.480	1.280
45	1.347	8.027	1.384	8.076	13.200	1.300
52	1.283	9.188	1.284	9.249	14.110	0.770
Temp. (°C)	Presence of electrical field					
	g	$K_G \cdot 10^4$	r	$k_r \cdot 10^4$	$k_d \cdot 10^2$	$s \cdot 10^4$
20	1.960	5.707	1.962	5.745	6.224	2.650
35	1.484	4.088	1.486	4.134	3.630	2.190
45	1.396	3.034	1.398	3.067	2.799	2.290
52	1.365	2.567	1.367	2.597	2.149	3.360

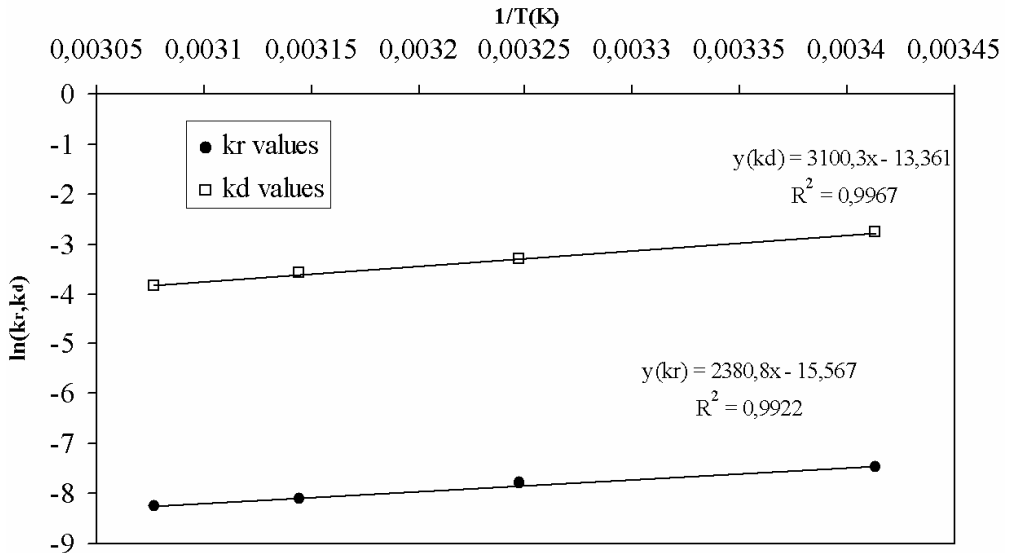


Fig. 6: Plot of Arhenius Eqs.11,12 for both the reaction rate constant and diffusion coefficient found under one DC volt.

It can be seen from the comparison of the results in absence and in the presence of electrical field (Table 1) that electrical field leads to decrease overall rate coefficients and to increase growth rate orders at all temperatures, except at 20 °C. The overall growth rate data obtained

in the presence of electrical field (Table 1) are applied in Eq.7 for calculating diffusion coefficient, k_d reaction constant, k_r and reaction order, r under one DC volt at the temperatures set 20 °C, 35 °C, 45 °C, 52 °C by trial and error method. Table 1 displays these constant values(k_d , k_r , r) and their standard deviations calculated according to Eq.9. Since the values of k_d are much more greater than the k_r values, it can be said that the growth rate of boric acid is mainly controlled by reaction step under 1.00 DC volt. Table 1 illustrates that increasing temperature is the major reason in decreasing reaction order, r reaction constant k_r and diffusion coefficient, k_d in the presence of one DC volt electrical field. In order to calculate the activation energy in the presence of electrical field, the plots of $\ln(k_r, k_d)$ versus $1/T$ are shown in Figure 6. In this figure the slope of both lines have the positive values which implies that the activation energy is not a meaningful under this condition. The reason is that these constants (K_G , k_r , k_d) of crystal growth are increased with temperature in pure conditions whereas electrical field decrease the constants(K_G , k_r , k_d) of crystal growth with increasing temperature. In the temperature above 30 °C, electrical field dominates the temperature effect on the crystal growth. constants(K_G , k_r , k_d)

Conclusions

Diffusion and reaction steps effect the growth rate of boric acid. However, growth rate of boric acid realized at the temperature of 20, 35, 45, 52 is mainly controlled by surface-integration step. The effect of integration step on crystal growth increases much more rapidly with temperature than does the diffusion process. The temperature dependency of the overall growth rate coefficient, K_G reaction rate constant, k_r and diffusion coefficient, k_d for the growth rate of boric acid can be correlated with the Arrhenius equation in order to obtain activation energies of 19.22 kJ/mol, 19.287 kJ/mol and 13.927 kJ/mol, respectively. Electrical field decrease the values of overall growth rate coefficient, K_G reaction order, r reaction constant, k_r and diffusion coefficient, k_d with increased temperature. Because, increasing temperature cause increasing the electrical current passed in fluidized bed. As a result of this behavior, electrical field dominate the temperature effect on the kinetic parameters(K_G , k_r , k_d , r). In the presence of electrical field, Arrhenius equation can not be used to calculate activation energy since it decrease the values of kinetic parameters(K_G , k_r , k_d , r) with increasing temperature.

The kinetic parameters at different temperature are determined for both normal condition and presence of electrical field by trial and error method. In both condition, these parameters shows that it is a good approach to take $r = g$ instead of $r = 2$ for boric acid. As a result, this method can be easily applied to determine K_G , k_r , k_d , r parameters of other material.

Notation of Symbols

C	concentration of the crystallized substance in a supersaturated solution, kg of hydrate/kg of water
C*	equilibrium concentration at the crystal surface, kg of hydrate/kg of water
ΔC	supersaturation of the crystallized substance, kg of hydrate/kg of water
C_i	concentration of the crystallized substance at the surface of Volmer layer, kg of hydrate/kg of water
k_d	mass transfer coefficient of the crystallized substance, $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
k_r	surface reaction constant, $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
K_G	overall crystal growth rate constant, $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
g	overall crystal growth rate order, $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$

α	volume shape factor
β	surface shape factor
ρ_c	crystal density (kg/m^3)
L_1	initial crystal size (m)
L_2	final crystal size
t	time (s)
M_1	initial weight of crystals (g)
M_2	final weight of crystals (g)
G	overall linear growth rate (m/s)
R_G	crystal growth rate, $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
K	constant($\text{number}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{volt}^{-1}$)
B°	nucleation rate($\text{number}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$)

References

- BOMIQ, P., BOURNE, J.R., DAVEY, R.J.: J.Crystal Growth 30 (1975) 77-85
 BUDZ, J., KARPINSKI, P.H., NURUC, Z.: AIChE Journal, 31(1985) 2
 DALAS, E., KOUTSOUKOS, P.G.: J.Crystal Growth, 96 (1989b) 802
 GARSIDE, J., MERSMANN, A., NYVLT, J.: Measurement of Crystal Growth Rates, 1st ed. European Federation of Chemical Engineering, 1990
 KARAKAYA, C., BULUTCU, A.N., ULRICH, J.: Doga-Tr.J.Chem. 16(1992)144
 KARPINSKI, P.H.: Chem.Eng.Sci. 35 (1980)23, 21
 KOZLOVSKII, M.I.: Kristallografiya, 7 (1962)157
 KOZLOVSKII, M.I., in: Growth of Crystal, Vol.4, Consultant Bureau, New York, p.20, 1966
 PHILLIPS, V.R., EPSTEIN, N.: AIChE J., 20(1974) 4
 ROULLEAU, M., CAPUS, J.: Electric field effect on the phenyl salicylate crystallization rate, C.R.Acad.Sci. Paris, Ser. C265(18), 961-4(1967)(Fr)
 SAHİN, O., SAYAN, P., BULUTCU, A.N.: J.Crystal Growth 216(2000) 475-482
 SHABLA KH, M., DISSADO, L.A. AND HILL, R.N.: J.Chem.Soc. Faraday Trans, 2, 1983,79,1443
 SHÖHNEL, O., MULLIN, J.W.: Chemistry&Industry June 356 (1988b)
 SHUBNIKOV, A.V.: Crystal in Science and Technol.(in Russian) Izd. AV SSSR, Moscow, 1956
 SHUBNIKOV, A.V., PORVOV, V.F.: Kristallografiya, 6 (1961) 443
 SOB CZAK, E.: Chem.Eng.Sci. 45 (1990)2, 561-564
 TANRIKULU, S.U., EROGLU, I., BULUTCU, A.N., OZKAR S.: J.Crystal Growth 194(1998)220

Contact information:

Ömer SAHİN
 Dept. of Chemistry
 Harran University
 S.Urfa
 Turkey

e-mail: sahinomer@turk.net