Experimental and Theoretical Investigation of Boric Acid Production through Reactive Dissolution of Oxalic Acid Crystals in Borax Aqueous Solution

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Abstract−Reaction of oxalic acid crystals with borax solution was experimentally investigated in a 1.5 L batch reactor at different operating conditions. The reaction was fast and took place very near to the surface of solid reactant. The dissolution process was found to be bulk diffusion controlled. A surface reaction model considering particle shrinkage was proposed for description of the process. Predicted fractional conversion of oxalic acid crystals were in good agreement with experimental values at different operating conditions. Conversion of oxalic acid crystals was significantly affected by the initial mean size of the solid reactant, while the temperature had the smallest effect. The activation energy of the dissolution process was determined as 12.89 kJ mol^{-1}. The proposed process can be used as an alternative way for boric acid production.
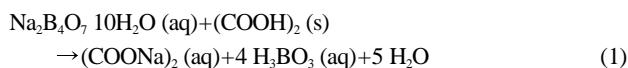
Key words: Boric Acid Production, Solid Oxalic Acid, Borax Solution, Reactive Dissolution, Diffusion Controlled

INTRODUCTION

Boric acid has a surprising variety of applications in both industrial and consumer products [Gerhartz, 1985]. It serves as a source of boron in many fused products, including textiles, fiber glass, optical and sealing glasses, heat resistant borosilicate glass, ceramic glazes and porcelain enamels. It is added directly to the water coolant of closed cycle pressurized water power nuclear reactors for control of power level or neutron flux.

In the industrial two stage process of boric acid production from sodium borates, borax ($Na_2B_4O_7$ $10H_2O$) particles are reacted with sulphuric acid and the product boric acid is then recovered from the solution phase by cooling crystallization [McKetta, 1999]. The low solubility of dissolved boric acid at high acid concentrations reduces the dissolution rate of borate particles and hence the production rate may decrease.

In this work, production of boric acid through reaction of solid oxalic acid with borax solution is proposed. The reaction can be presented by the equation:

$$Na_2B_4O_7 \; 10H_2O \; (aq) + (COOH)_2 \; (s)$$
$$\rightarrow (COONa)_2 \; (aq) + 4 \; H_3BO_3 \; (aq) + 5 \; H_2O \qquad (1)$$

In this case due to the moderate solubility of boric acid in the mother liquor, the solid reactant dissolves easily in the alkaline solution of borax such that the phenomenon of mineral blinding in the conventional process does not occur. Effects of process variables namely, stirrer speed, temperature, reactant concentration and mean size of oxalic acid crystals on the fractional conversion of solid reactant are experimentally investigated and the mathematical modelling of the process is presented.

EXPERIMENTAL PROCEDURE

Effect of different process variables were investigated by using

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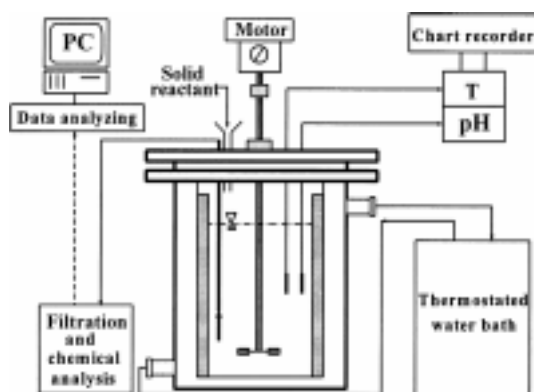E-mail: zarenezhad@yahoo.com

Fig. 1. Experimental apparatus for the stirred batch reactor.

a 1.5 L jacketed baffled cylindrical reactor (11 cm i.d., height 16 cm) maintained at constant temperature (Fig. 1). Four vertical stainless steel baffles with a width of about 1/10th of the tank diameter were mounted against the vessel wall at 90° intervals around the vessel. The off-bottom clearance was set at 2.5 cm according to Shimizu et al. [1995]. A six blade stainless steel disk turbine impeller was used to ensure that all particles were completely suspended. The stirrer was rotated by a variable speed stirrer motor (RZR-200, Heidolph) and the impeller speed was set at the required values using a digital tachometer (Heidolph) attached to the motor. Both pH and temperature were traced by a chart recorder.

In a typical experiment the required amount of water was first filtered and then charged into the reactor. Borax crystals were added and the contents were stirred to dissolve the crystals and a clear solution of known composition was obtained. A known amount of monosize oxalic acid crystals, sieved in the size range of 320-1,200 μm, was quickly added to the solution at the start of an experiment. The addition point was carefully fixed to be midway between the shaft of stirrer and the vessel wall throughout the series of experiments by using a plastic funnel. Sampling was achieved by pipetting about 5 ml of the contents from the reactor at different time

Table 1. Ranges of run conditions for the reaction of borax solution with oxalic acid crystals

Run	c_{Bo} (mol/kg water)	N_{so}/M (mol/kg water)	N (Hz)	L_{Ao} (μm)	T (K)
R1-R6	0.04-0.14	0.04-0.14	7	320	293
R7-R12	0.05	0.05	8-18	1,024	293
R13-R18	0.07	0.07	11	320-1,200	293
R19-R24	0.11	0.11	10	320	293-313

intervals and filtering it through a 0.4 μm pore size filter paper.

The samples of solids and filtrates were weighed and finally analysed to determine changes in the overall compositions of the solid and solution phases during the process. The fractional conversion of the solid reactant, described as X=(the weight of reacted oxalic acid crystals)/(the weight of original oxalic acid crystals), versus time was measured. A dual pH titrimetric method was used to determine the composition of borax and boric acid in the solution phase [Jeffery et al., 1989]. A weighed quantity of the solution phase sample was diluted with 50 ml of distilled water. The solution was first titrated with 0.05 M sulphuric acid for determination of borax concentration and then back-titrated with 1.0 M sodium hydroxide solution using proper amount of mannitol for evaluating the boric acid concentration.

The ranges of process variables used in twenty four series of experiments are displayed Table 1. In run R1 a few drops of cresol red (an indicator with a colour change interval of 0.2-1.8 in pH scale) was also added to the borax solution to facilitate the visual observation of the dissolution process.

MODELLING OF THE PROCESS

The preliminary experiment indicated that the reaction of borax solution with oxalic acid crystals was fast and took place very near to the oxalic acid crystal surface. Therefore it was assumed that the diffusion through the liquid film surrounding the solid surface was rate controlling while the reaction occurred at surface of shrinking solid oxalic acid. The model proposed by Levenspiel [1998] for this type of mechanism is applied and extended to obtain a correlation for predicting the fractional conversion of oxalic acid crystals in terms of all influencing process variables.

In order to obtain the relation between conversion and time, the rate of disappearance of solid oxalic acid (A), R_A, must be equated with the rate of consumption of borax (B). By taking the stoichiometry into account, we get:

$$R_A = -\frac{1}{A_{ex}}\frac{dN_s}{dt} = \frac{N_{so}}{A_{ex}}\frac{dX}{dt} = \rho_1\beta k_d c_B \tag{2}$$

where N_s is the number of moles of solid reactant (oxalic acid), A_{ex} is the external surface of spherical oxalic acid crystals, ρ_1 is the density of free water, β is the stoichiometric ratio of the reactants (=1), c_B is the borax concentration in the solution phase and k_d is the solid-liquid mass transfer coefficient.

For the range covered experimentally in the present study ($0.5 < Re_p < 600$ and $700 < Sc < 1,200$), the correlation proposed by Asai et al. [1986] is used for determination of the solid-liquid mass transfer coefficient. This correlation can be written as:

$$Sh = 2 + 0.61 Re_p^{0.58} Sc^{1/3} \tag{3}$$

where $Sh = k_d L_A/D_A$
$Re_p = L_A^{4/3}(N_p\rho_s N^3 D^5/V)^{1/3}/\nu$
$N_p = 6$ (for disk turbine)
$Sc = \nu/D_A$

Neglecting the first term of Eq. (3) at prevailing turbulent mixing condition leads to the following semi empirical correlation:

$$k_d = k_T L_A^{-0.22} N^{0.58} \tag{4}$$

where k_T is a temperature dependent term.

According to Eq. (1), the variation of borax (B) concentration with solid oxalic acid conversion, X, can be written as:

$$c_B = c_{Bo}\left(1 - \frac{N_{so}}{Mc_{Bo}}X\right) \tag{5}$$

where M is the mass of free water.

During the dissolution process, the oxalic acid crystals shrink in size and thus the particle diameter at any time during the reaction can be obtained by the relation:

$$L_A = L_{Ao}(1-X)^{1/3} \tag{6}$$

where L_{Ao} is the initial mean diameter of oxalic acid crystals and L_A is the average diameter at solid reactant conversion, X.

Combining Eqs. (2), (4)-(6), the rate of solid oxalic acid conversion can be derived as:

$$\frac{dX}{dt} = 6\frac{\rho_1 k_T c_{Bo}}{\rho_s L_{Ao}}(1-X)^{2/3}\left(1 - \frac{N_{so}}{Mc_{Bo}}X\right)L_A^{-0.22}N^{0.58} \tag{7}$$

In order to determine k_T, Eq. (7) is integrated using Eq. (6) and the boundary condition X=0 at t=0 to give:

$$\frac{\rho_s L_{Ao}^{1.22}}{6\rho_1 c_{Bo}N^{0.58}}\int_0^x \frac{dX}{(1-X)^{0.59}\left(1 - \frac{N_{so}}{Mc_{Bo}}X\right)} = k_T t \tag{8}$$

For stoichiometric amounts of reactants ($N_{so}=Mc_{Bo}$), this equation can be integrated analytically to give:

$$(1-X)^{-0.59} - 1 = 3.54\frac{\rho_1 c_{Bo}N^{0.58}}{\rho_s L_{Ao}^{1.22}}k_T t \tag{9}$$

Assuming the following Arrhenius type correlation [Mullin, 1993]:

$$k_T = k_{T_o}\exp\left(-\frac{E_D}{RT}\right) \tag{10}$$

the following correlation can be derived:

$$\ln\left[\frac{\rho_s L_{Ao}^{1.22}}{3.54\rho_1 c_{Bo}N^{0.58}}\frac{(1-X)^{-0.59}-1}{t}\right] = \ln k_{T_o} - \frac{E_D}{RT} \tag{11}$$

The values of k_{T_o} and E_D can thus be obtained by plotting the left hand side of Eq. (11) against 1/T at different operating conditions.

RESULTS AND DISCUSSION

Fig. 2. shows the pH variation of the solution during the reaction in run R1. The pH changed from 9.2 to 5 in about 20 s. Since the colour of cresol red indicator changes from yellow to red at pH=
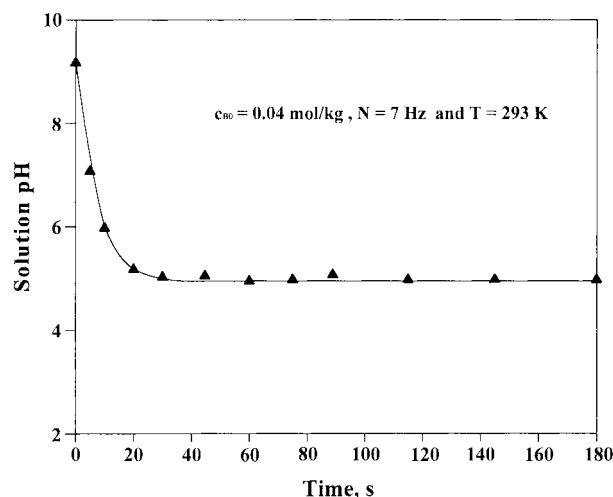
Fig. 2. pH variation of the solution during the dissolution of oxalic acid crystals in borax solution.
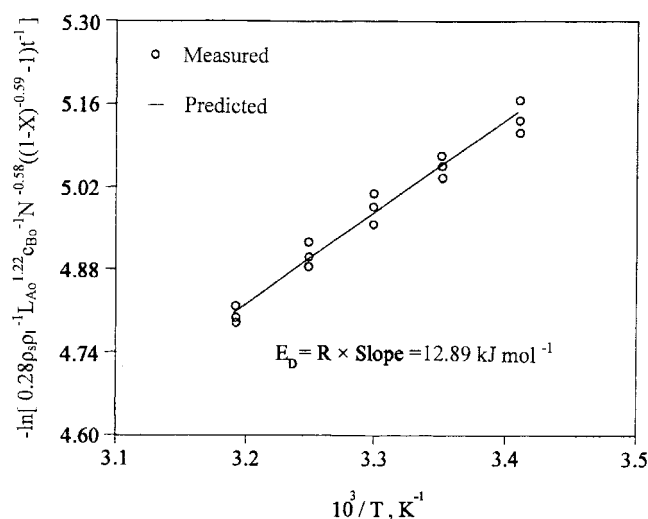

Fig. 3. Comparison of the predicted result with the measured data at different temperatures.

1.8, no colour change was observed in this case. However, after addition of tiny particles of oxalic acid in excess of the stoichiometric proportion with respect to borax, an abrupt change of colour from yellow to red was observed near to the solid surface during the dissolution of the oxalic acid crystals. After complete dissolution of these crystals the solution pH dropped to 4 and the final colour of the solution was still yellow. The rapid change of pH suggested that the reaction is fast and the colour indicator confirmed that the reaction takes place very near to the oxalic acid crystal surface. Thus the assumption a diffusion controlled dissolution process is appropriate.

Predicted results are compared with the measured data in Fig. 3. Linear regression analysis of 100 data points from 24 experimental runs at different stirrer speed, initial concentration, oxalic acid crystal size and temperature gave values for k_{To} and E_D of $(9.47\pm0.51) \times 10^{-3}\ m^{1.22}\ s^{-1.58}$ and $12.89\pm1.4\ kJ\ mol^{-1}$ in Eq. (11) respectively. The individual standard errors represent 95% confidence limits.

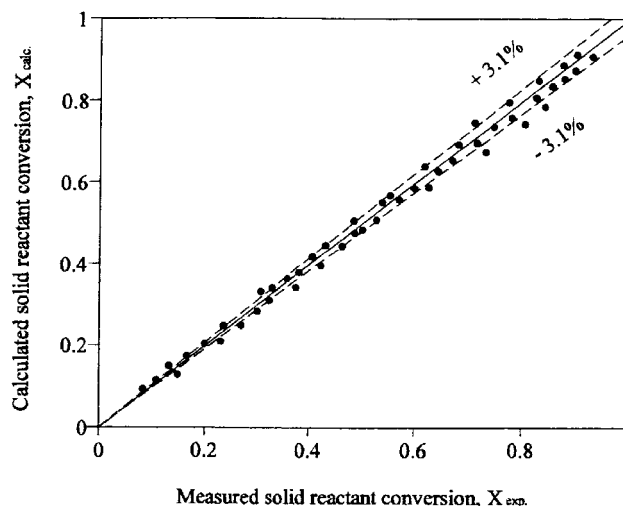Having the values of k_{To} and E_D, Eq. (11) may be written in the following form:

Fig. 4. Comparison of the measured and predicted solid reactant conversion.

$$(1-X)^{-0.59} - 1 = 0.0335\frac{\rho_l c_{Bo} N^{0.58}}{\rho_s L_{Ao}^{1.22}}\exp\left(\frac{-1550.4}{T}\right)t \qquad (12)$$

Thus the fractional conversion, X of the solid reactant as a function of time can be finally written as:

$$X = 1 - \frac{1}{\left[1 + 0.0335\frac{\rho_l c_{Bo} N^{0.58}}{\rho_s L_{Ao}^{1.22}}\exp\left(\frac{-1550.4}{T}\right)t\right]^{1.695}} \qquad (13)$$

The relationship between calculated and measured solid conversion for all runs at relative deviation of $\pm3.1\%$ is shown in Fig. 4. The predicted conversions are in good agreement with the measured values.

CONCLUSIONS

Production of boric acid through the reaction of oxalic acid crystals with borax solution was investigated. A diffusion controlled surface reaction model considering particle shrinkage was used for description of the dissolution process. The measured fractional conversions of the solid reactant were in good agreement with the predicted values. The time variation of oxalic acid conversion was much more influenced by the initial mean size of the solid reactant. Effect of solution temperature on the solid conversion was not significant. These results in addition to low value of dissolution activation energy ($=12.89\ kJ\ mol^{-1}$) confirmed the assumption of a diffusion controlled process. The effect of different process variables namely, initial mean size of oxalic acid crystals, initial borax concentration, stirrer speed and temperature on the conversion of solid reactant were well predicted by Eq. (13).

NOMENCLATURE

A_{ex} : external surface of oxalic acid crystals [m²]
c_B : concentration of borax in the solution [mol (kg free water)⁻¹]
D_A : diffusion coefficient of borax in the bulk solution [m²s⁻¹]
D : impeller diameter [m]
E_D : activation energy for volume diffusion [kJ (mol)⁻¹]

k_d : solid-liquid mass transfer coefficient [ms^{-1}]
k_T : temperature dependent term in Eq. (4) [$m^{1.22} s^{-0.42}$]
k_{T_o} : constant used in Eq. (10) [$m^{1.22} s^{-0.42}$]
L_A : mean size of oxalic acid crystals [m]
M   : mass of free water [kg]
N   : stirrer speed [Hz]
N_s : number of moles of oxalic acid crystals [mol]
R   : gas constant (=8.314) [$J mol^{-1} K^{-1}$]
R_A : rate of disappearance of solid oxalic acid [$mol\ m^{-2}s^{-1}$]
T   : temperature [K]
t   : time [s]
V   : solution volume [m^3]
X   : fractional conversion of oxalic acid crystals, dimensionless

Greek Letters

ρ_l : density of free water at a given temperature [$kg\ m^{-3}$]
ρ_s : molar volume of solid oxalic acid [$mol\ m^{-3}$]
β : stoichiometric ratio of the reactants (=1), dimensionless
ν : kinematic viscosity [m^2s^{-1}]

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