Kinetic Study on Preparation of High-Purity Enriched Boric-10 Acid Used in Nuclear Power Plants

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Although entiched boron-10 trifluoride had been industrialized, it can not be applied to nuclear industry or other fields directly. To take advantages of the superior features of boron-10 isotope, boron-10 trifluoride should be inverted into boric-10 acid ($H_3{}^{10}BO_3$). The study of reaction of boron trifluoride methanol complex with aqueous solution of lithium hydroxide is rare. In this paper, mechanism of the reaction was discussed as well as proper reaction conditions like reaction temperature, the mass of water and the ratio of reactants were determined. The kinetics of the system were examined using homogeneous kinetic models and was determined to be a pseudo-second-order homogeneous reaction control model. The activation energy was calculated to be 43.67 kJ/mol.

Keywords: Boron trifluoride methanol complex, Lithium, Boron.

INTRODUCTION

Boric acid is used in pressurized water reactors as a neutron poison to slow down the rate at which fission is occurring. It is reported that the absorption cross section of natural boron for thermal neutrons is 752 barns; for pure boron-10 and boron-11, the corresponding values are 3837 and 0.005 barns, respectively[1]. It can be seen that as a neutron shield, isotopically pure boron-10 is five times more effective than natural boron. The large cross section of boron-10 for thermal neutrons and the α particle emission subsequent to neutron capture have hinted the immense potential use of enriched boron-10 compounds for nuclear power plants, protection materials and neutron therapy of malignant tissue[2]. Enriched boric-10 acid is also the raw material to produce enriched boron-10 power[3,4].

Some methods to produce enriched boric-10 acid were reported. The first method was column chromatographic boron isotopes separation with diluted natural boric acid solution[5,6]. The second was to make boron-10 trifluoride or its complex as raw material and converted to methyl borate. Then the intermediate product of methyl borate was hydrolyzed into boric acid[7-9]. This method could gain high purity boric acid, but has a low yield. The last one was that BF_3 complex, such as boron trifluoride ether complex, reacted with calcium carbonate or lithium carbonate in water to produce boric acid[10,11].

Yan and Tang[12] had studied the reaction of boron trifluoride with water by density functional theory. They proposed two different reaction path in hot and cold water and concluded that H_3BO_3 and HBF_4 were the main products in hot water.

When Gilpatric[13] synthesised sodium hydroxytrifluoroborate, he indicated that H_3BO_3 would be generated when temperature raised and low pH would make the $NaBF_3OH$ decompose to $NaBF_4$. It means that high temperature and high pH are conducive to the generation of H_3BO_3. As a Lewis acid, boron trifluoride can react with Lewis base, such as sodium hydride[14] or form complexes with electron donors, such as H_2O, N_2, CH_3OH, *etc*.[15]. So this paper selected LiOH and boron trifluoride methanol complex as reactants reacting in the water to seek for a economical and effective method to produce enriched boric-10 acid.

EXPERIMENTAL

Lithium hydroxide monohydrate and calcium chloride dihydrate, produced by Guangfu Fine Chemicals Co., both are analytical purity. The purity of Boron trifluoride gas, produced by Liufang Gas Co., is 99.5 %. Boron trifluoride complexes and the enriched boron-10 trifluoride complex were made in our laboratory. Amberlite IR-120 ion exchange resin was purchased from Guangfu Fine Chemicals Co.

The experiments can be carried out using boron trifluoride gas, but choosing boron trifluoride complex can transform the reaction from gas-liquid two phase reaction to liquid phase reaction. To make the reaction easier, this change can decrease the mass transfer resistance between gas phase and liquid phase. Comparing to other kinds of complexes, boron trifluoride methanol complex is relatively more stable[15] and has been realized commercial production. Meanwhile methanol has a

low boiling point and is miscible with water. All these factors made the reaction proceed smoothly.

Preparation of BF_3-CH_3OH complex: The complex solution was produced in a jacket packing tower as shown in Fig. 1. The complex can be obtained when the boron trifluoride flowed into the bottom of the tower and met the methanol pumped from the methanol tank. Whether it is natural or enriched boron-10 trifluoride complex depended on the boron trifluoride source. The boron trifluoride mass fraction of the produced solution is within the range of 0.300 to 0.679.
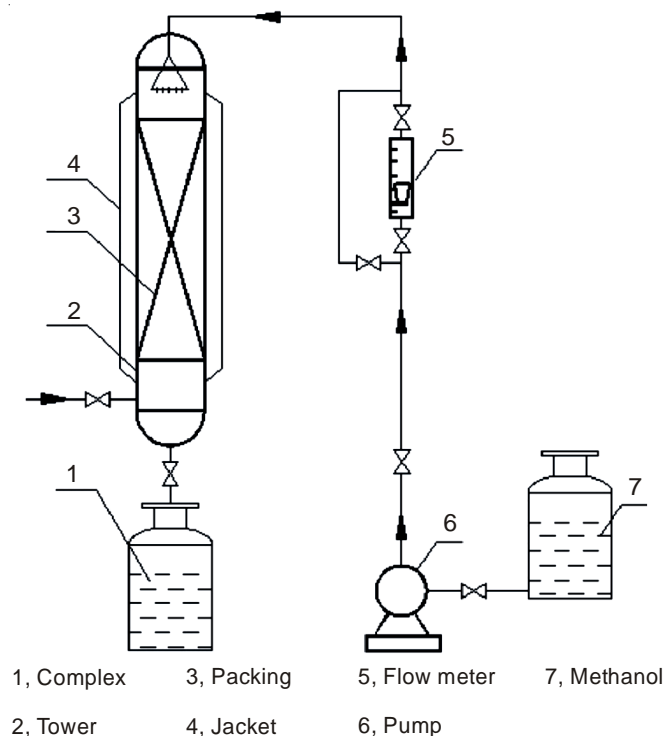

1, Complex   3, Packing   5, Flow meter   7, Methanol

2, Tower   4, Jacket   6, Pump

Fig. 1. Complex production equipments

Determination of boron trifluoride concentration of the complex and purity of lithium hydroxide monohydrate: About 1-2 g (accurate to 0.0001 g) boron trifluoride complex was sucked by 5 mL syringe and about 20 g $CaCl_2$ solution (20 w %) was added which was neutralized to methyl orange endpoint advanced by hydrochloric acid (0.1 M). Then the mixture was titrated to the methyl orange end point using standard sodium hydroxide (0.5 M) and boiled 0.5 h once a time till the methyl orange was no longer turn to red. At last, the mixture was cooled to room temperature, added 5-6 g mannital and titrated to the phenolphthalein endpoint using standard sodium hydroxide (0.5 M). This volume of sodium hydroxide was used to calculate boron trifluoride concentration.

The purity of lithium hydroxide monohydrate, according to GB/T 11062-1989, is 90 %.
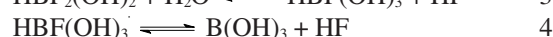
Reaction between BF_3-CH_3OH and lithium hydroxide: The reaction was carried out in a 1000 mL three-neck round-bottomed flask at atmospheric pressure. A mechanical agitator with a digital display was used to stir the solution. A programmable refrigerated bath/circulator was applied to keep the reaction medium at a constant temperature. An allihn condenser was used to avoid solution loss by evaporation. The temperature
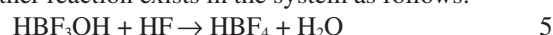
of solution in the flask was measured with a digital temperature controller. The complex (55.04 g, 0.25 mol BF_3) was added dropwise to the stirring lithium hydroxide aqueous solution (34.97 g, 0.75 mol $LiOH \cdot H_2O$; 300 g distilled water) in water/oil bath. After feeding, the temperature of water/oil bath was set. When the reaction was stopped, the mixture was filtered; the wet solid was dried in oven; the filtrate was purified through ion exchange resin which had been pretreated by sodium hydroxide and hydrochloric acid. The purified liquid was evaporated and concentrated and stopped heating when the first crystalline grain formed. Then crystallized and obtained boric acid crystal.
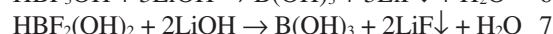
RESULTS AND DISCUSSION

Mechanism: When boron trifluoride is bubbled into water, some equilibria are developed[16]. The mechanism of the reaction between BF_3 and H_2O is shown as the following equations:

$$BF_3 + H_2O \rightarrow HBF_3OH \qquad\qquad 1$$
$$HBF_3OH + H_2O \rightleftharpoons HBF_2(OH)_2 + HF \qquad 2$$
$$HBF_2(OH)_2 + H_2O \rightleftharpoons HBF(OH)_3 + HF \qquad 3$$
$$HBF(OH)_3 \rightleftharpoons B(OH)_3 + HF \qquad\qquad 4$$

Another reaction exists in the system as follows:

$$HBF_3OH + HF \rightarrow HBF_4 + H_2O \qquad\qquad 5$$

When LiOH was added into the BF_3-H_2O system, this paper considered that a series of reaction shown as follows occurred:

$$HBF_3OH + 3LiOH \rightarrow B(OH)_3 + 3LiF\downarrow + H_2O \quad 6$$
$$HBF_2(OH)_2 + 2LiOH \rightarrow B(OH)_3 + 2LiF\downarrow + H_2O \quad 7$$
$$HBF(OH)_3 + LiOH \rightarrow B(OH)_3 + 3LiF\downarrow + H_2O \quad 8$$
$$HF + LiOH \rightarrow LiF\downarrow + H_2O \qquad\qquad 9$$
$$HBF_4 + LiOH \rightarrow LiF_4 + H_2O \qquad\qquad 10$$

Taking account of the slowest rate of reaction 5, side reaction 10 was suppressed due to the timely remove of HF by LiOH[16].

Analysis of boric acid: The product was determined by IR, TENSOR 27 as shown in Fig. 2. The purity of the boric acid was determined by the acid-base titration using standard sodium hydroxide (0.2 N) after addition of mannitol.

Effect of mass of water on the yield of boric acid: Water in need should satisfy the dissolution of lithium hydroxide and boric acid. The experiments were performed in an alkaline aqueous solution where the mass of water ranged from 250 to 450 g, with a mole ratio 3 of lithium hydroxide and boron trifluoride at boiling point, a reaction period of 20 h and a stirring speed of 200 rpm and the results are given in Fig. 3. When the mass of water was 250 g, the solution approach to saturation and the yield of boric acid was lower than the mass 300 g. When water added more than 300 g, the reaction rate slowed down for the dilution of the reagents. As a consequence, the yield of boric acid decreased. So the mass of water of the system should be 300 g, that is to say the required water was about 8.6 times the mass of LiOH.

Effect of reactant ratio on the yield of boric acid: To determine the effect of mole ratio of lithium hydroxide and boron trifluoride on the yield of boric acid, experiments were performed with the mole ratio of 3.0, 3.5, 4.0, 4.5, 5.0 at boiling point, a reaction period of 20 h and a distilled water of 300 g, a stirring speed of 200 rpm. Results are given in Fig. 4 which
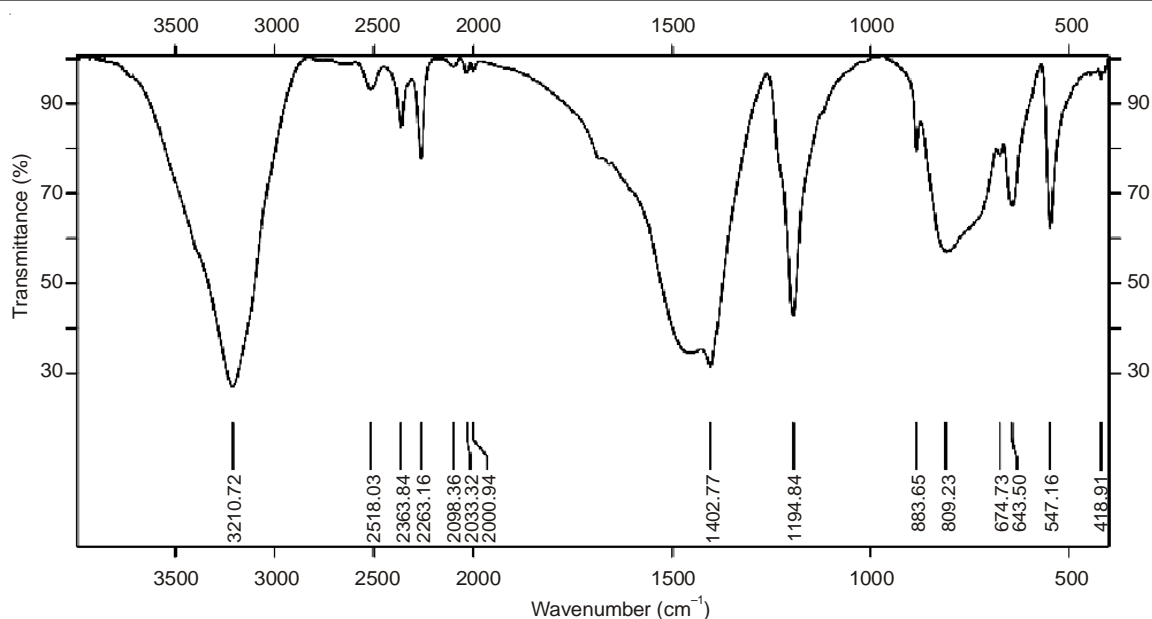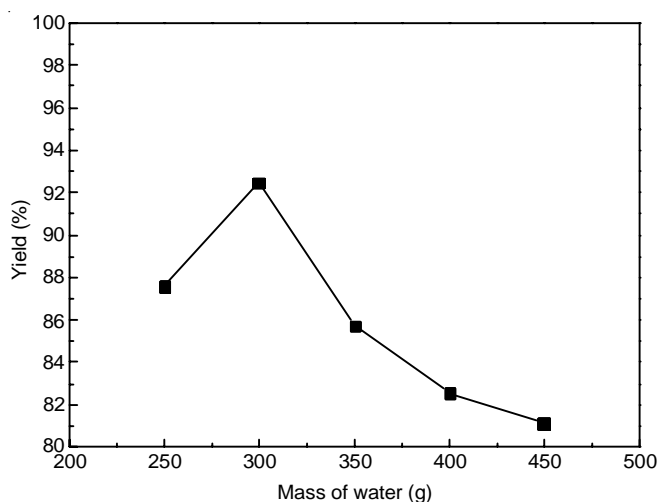
Fig. 2. Infrared spectra of product

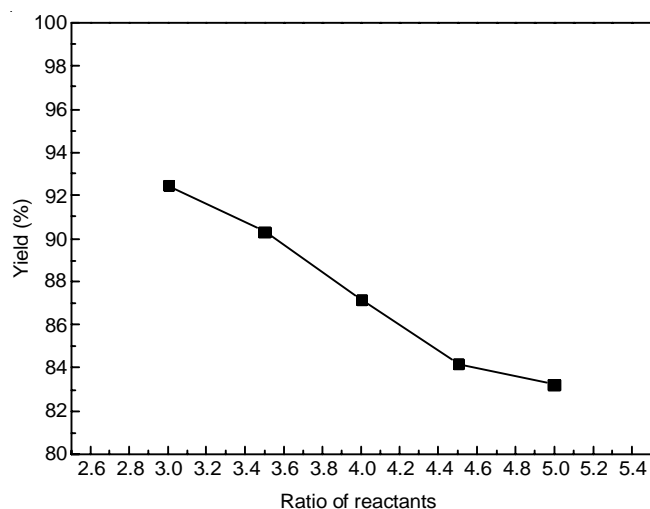Fig. 3. Effect of mass of water on the yield of boric acid

Fig. 4. Effect of reactant ratio on the yield of boric acid

showed that the increase in the mole ratio caused a decrease in the boric acid yield. When the mole ratio was over 3.0,

product H_3BO_3 might be consumed by excessive LiOH. In addition, considering the complexity of the reaction between BF_3 and H_2O, perhaps some side reactions we unknown might happen in the system. So the production dropped.

Effect of reaction temperature on the yield of boric acid: To determine the effect of temperature on the yield of boric acid, experiments were performed at 80, 85, 90 °C and boiling point which was depended on the concentration of complex and the yield was investigated at a reaction period of 10-30 h, a stirring speed of 200 rpm, a lithium hydroxide-boron trifluoride ratio of 3 and a distilled water of 300 g. Results are given in Fig. 5, which shows that the yield of boric acid increased rapidly during the first 10 h and then slowed down. When the reaction time was more than 20 h, the rate of reaction decreased to the most. At the same time, as temperature increasing from 80 to boiling point, the yield of boric acid increased. In this way, the yield of boric acid at boiling point reached 94.82 %.
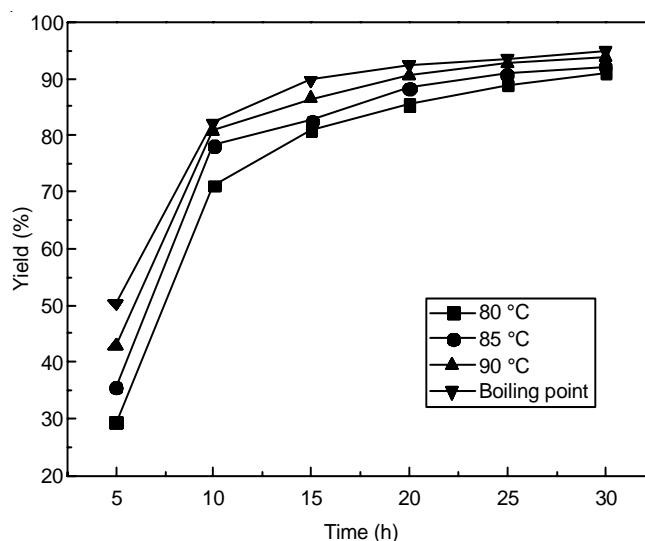

Fig. 5. Effect of reaction temperature on the yield of boric acid

After being purified through ion exchange resin and crystallized, the purity of obtained boric acid was above 99.95 %.

Our laboratory had tried other methods to produce boric-10 acid, for instance, boron-10 trifluoride methanol complex react with sodium methoxide in methanol or calcium carbonate in water, or lithium carbonate in water. Although these methods had been optimized, they still remain some shortcomings. For example, the reaction between boron-10 trifluoride complex and sodium methoxide is an esterification reaction. To ensure its yield, the reaction system should control water content as low as possible, otherwise the intermediate product-trimethyl borate would hydrolyze and could not be isolated which will make the yield of boric acid no more than 90 %. The last two methods are two-phase reactions. Because there exists mass transfer resistance between liquid and solid, the granularity of calcium carbonate and lithium carbonate would influence the reaction kinetics. When using calcium carbonate, the filtration resistance of filter cake is too high so that it needs higher filtration pressure than this paper's method to filter out the side product, mainly CaF_2, from filtrate. The method described in this paper do not need strict environment and its side product is easy to be removed.

Kinetic analysis: The rate of this reaction can be described by homogeneous control models. For this process, a successful reactor design depends mainly on kinetic data. Pseudo-second-order reaction-control models were used as the homogeneous models in this study. The results of the yield of boric acid at different temperatures are given in Fig. 5. These results were analyzed using the equations of homogeneous reaction control models. The values of these models were plotted against time to determine their slopes. In the mean time, the k and regression coefficient (R^2) values of these models for each temperature were calculated using the slopes of the lines. The pseudo-first-order homogeneous reaction-control model did not produce a linear relationship. However, a high regression coefficient was obtained for the pseudo-second-order homogeneous reaction-control model. The kinetics of a pseudo-second-order reaction-control model is given by the following equation:

$$\frac{d[A]}{dt} = -k[A][B] \qquad 1$$

where A = BF_3, B = LiOH

As the mole ratio of LiOH and BF_3 was 3, that is [B] = 3 [A] Then

$$\frac{d[A]}{dt} = -3k[A] \qquad 2$$

$$\frac{X}{C_{A0}(1-X)} = 3kt \qquad 3$$

where C_{A0} is initial mole concentration of boron trifluoride.

The second order reaction control models can be fitted due to linear regression. The regression coefficients and k values are given in Table-1 for the second order reaction control model. The results show that the k values increased with the reaction temperature.

When the dissolution temperature was increased from 80 to 90 °C, the k values increased nearly 2 times. A plot of the pseudo-second-order homogeneous reaction-control model,

TABLE-1
VARIATION OF REACTION RATE WITH TEMPERATURES

Temperatures (K)	k	R^2
353.15	0.1525	0.9927
358.15	0.1763	0.9976
363.15	0.2323	0.9906
368.15	0.2728	0.9973

$\dfrac{X}{C_{A0}(1-X)}$ *versus* time results in a linear relationship at different temperatures as shown in Fig. 6.

Activation energies: To calculate the activation energy for the reaction, an Arrhenius graph of -lnk *versus* 1/T was drawn using the data in Fig. 6. Then Fig. 7 was obtained.
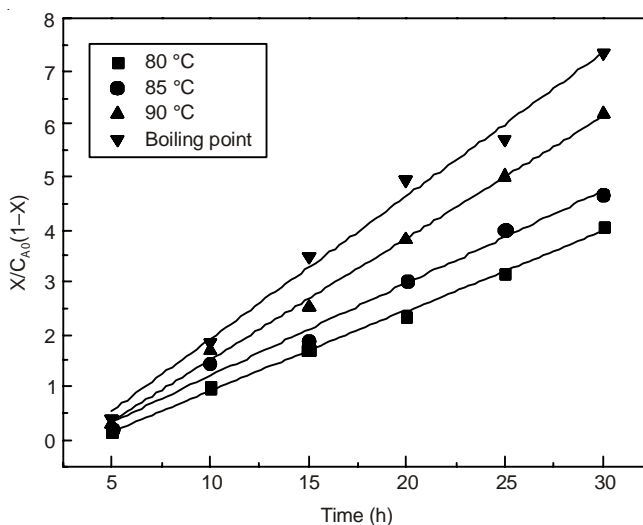

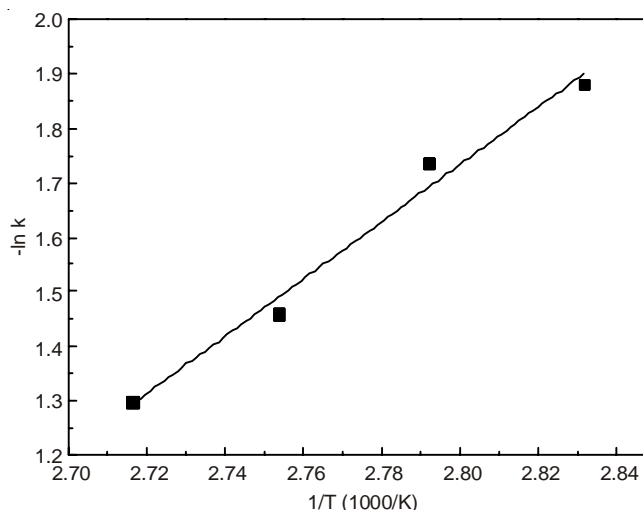Fig. 6. Variation in $\dfrac{X}{C_{A0}(1-X)}$ with time at different temperature

Fig. 7. Arrhenius plot of the reaction

The reaction control model of boron trifluoride and lithium hydroxide in water was determined to follow a pseudo-second-order homogeneous reaction-control model. The activation energy of the reaction was calculated from the Arrhenius eqn. 4 as follows:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \qquad 4$$

-ln(k) *versus* 1/T gives a straight line of slope E/R. From the slope of this line, the k_0 values and the activation energy, E, of the reaction rate of lithium hydroxide and boron trifluoride in water were determined as follows:

$$\frac{X}{C_{A0}(1-X)} = 3k_0 \exp\left(-\frac{5252.2}{T}\right) t$$

$$E = 43.67 \text{ kJ/mol}$$

Activation energy of 43.67 kJ/mol was calculated from the slope of the Arrhenius graph of the reaction of boron trifluoride and lithium hydroxide in water.

Conclusion

The most important parameters were found to be the reaction temperature and reaction time, while the least important was the mass of water. The maximum yield of boric acid was 92.47 % after 20 h at boiling point. The reaction rate increased with increasing reaction temperature. The reaction control model of boron trifluoride in lithium hydroxide aqueous solution follows a pseudo-second-order homogeneous reaction-control model. The activation energy of boron trifluoride in lithium hydroxide aqueous solution was calculated to be 43.67 kJ/mol. This study can offer an alternative solution to prepare enriched boron-10 acid and provide some data for reactor design and industrial scale production.

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