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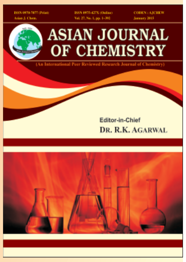

Preparation of Boric-10 Acid Applied in Shielded Materials of Nuclear Industry

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Because of the superior features of boron-10 isotope in absorbing hot neutrons, boric-10 acid ($H_3{}^{10}BO_3$) has been used widely in nuclear industry, like as additive in primary loop of pressurized water reactor and as control rod and other shielded materials in nuclear reactor. Boric-10 acid is obtained from boron-10 trifluoride ($^{10}BF_3$) by esterification and hydrolyzation. In this study, the preparation of trimethyl borate-10 [$(CH_3O)_3B$] from boron-10 trifluoride ($^{10}BF_3$) obtained through chemical exchange rectification was investigated. The kinetics of esterification reaction was controlled by second order pseudo homogeneous reaction. The activation energy was 685.5 KJ/mol. In addition, the hydrolyzation of trimethyl borate-10 was investigated as a function of pH, temperature and molar ratio of water to trimethyl borate-10. Under optimum process conditions, higher yield of boric-10 acid with nuclear industrial purity grade was realized.

Keywords: Boric-10 acid, Esterification, Trimethyl borate-10, Hydrolyzation.

INTRODUCTION

Boron ranks the 5th in the periodic table of chemical elements. It has two stable isotopes, ^{10}B and ^{11}B, with natural concentration of 19.9 and 80.1 %, respectively. Because of the superior features of ^{10}B in absorbing neutrons (3.837×10^{-25} m^2) compared with that of ^{11}B ($< 0.05 \times 10^{-28}$ m^2), much effort has been devoted to extracting ^{10}B from the natural mixture of boron isotopes[1]. The excellent features of ^{10}B isotope make it possible to be widely used in most industries, for the examples as follows[2-4]: **1) Nuclear industry:** some metals with ^{10}B isotope can be used as shielded materials for reactor emergency protection, nuclear waste storage and transportation; **2) Military industry:** ^{10}B isotope can be used to prevent activation in neutron exposure, such as nuclear protective clothing, neutron gun protective clothing and nuclear submarines; and **3) Medical and medicine field:** α-Particles and ^{7}Li nuclei formed by neutron can be made into targeted medicine to combat cancer by Neutron Capture Therapy. ^{10}B isotope is more preferable to protect normal cell away from hurting by X-ray or other radiations than other neutron absorbents do. The three applications above are based on the following reaction:

$$^{10}B + n \rightarrow [^{11}B] \rightarrow {}^{7}Li + {}^{4}He$$

Therefore, ^{10}B is widely used in nuclear reactors, nuclear physics and devices and so on. Enriched boron-10 isotope material is most widely used in the form of boric acid, because it's easier to transport and store solid production.

Boric acid (H_3BO_3) with nature abundance is white odorless crystalline solid, which is the trihydrate of boron oxide. It can also be dissolved in water, alcohol, glycerol, ether and essential oils. Boric acid is widely used in the manufacture of textiles, fiber glass and ceramic lasers and is an important raw material of national nuclear industry and national defense industry.

Boric acid (H_3BO_3) is produced industrially from borate minerals and brines. Alkali and alkaline earth metal borates, such as borax, colemanite, ulexite or kernite, react with strong acids to form boric acid. In China, boric acid is obtained by reaction and concentration from borax ($Na_2B_4O_7 \cdot 10\,H_2O$) with sulfuric acid, ascharite with ammonium bicarbonate, ascharite with sulfuric acid or ascharite with sodium carbonate and sulfuric acid by industrial production process[5]. The raw materials of the above sources in producing boric acid are boron minerals with natural abundance, which can meet the requirement of nuclear power plants in early period. However, with the continuous development of nuclear power technology, the boric acid with natural abundance has gradually exposed many problems, such as low utilization rate, high energy consumption, too many byproduct impurities, *etc.*, thus boron-10 boric acid with natural abundance cannot meet the requirement of new generation nuclear power plants. Therefore, a process of preparing baron-10 acid from boron trifluoride with high enrichment of ^{10}B obtained by chemical exchange rectification has been investigated.

For the sake of industrial applications of boron-10 isotope, the design and realization of boron isotopes separation processes had begun as early as the Second World War. Many kinds of ^{10}B isotope enrichment process were developed, such as low temperature rectification of BF_3, chemical exchange rectification of BF_3, ion exchange of boric acid and counter-current circulation of BF_3 in series film and so on[6-9]. Finally, a large industrial plant used the process of chemical-exchange rectification of the complex compound of boron trifluoride with dimethyl ether, aether or anisole was selected in boron isotopes separation processes[8,10,11].

There are many ways of preparing boron trifluoride and the mostly used industrial way is to add dropwise concentrated sulfuric acid to boron oxide and fluorite (calcium fluoride) by heaing to obtain boron trifluoride gas. While the method used in laboratory is usually to generate boron trifluoride by potassium fluoroborate and boron oxide. It can be seen that boron trifluoride and boric acid with natural abundance are prepared with fluorite as raw materials. Furthermore, boric acid is more expensive than boron trifluoride. But for the sake of the requirement of enriched ^{10}B boric acid in nuclear industry, enriched ^{10}B boron trifluoride must be prepared from boron trifluoride with nature abundance through chemical-exchange rectification to produce boric acid.

Trimethyl borate with natural abundance is prepared from boric acid and methanol with catalyst by esterification reaction, while boric-10 acid which meets the requirements of nuclear industry is prepared from boron-10 trifluoride with high abundance.

Preparation of boric acid ester from boron trifluoride with rich abundance is a complicated process. Boron trifluoride is a gas with a choking odor and its chemical property is very active. It reacts with many classes of both organic and inorganic substances. It fumes in the air due to reaction with water vapor.

Boron trifluoride can also react with water to generate boric acid. The composition and the properties of aqueous solutions of BF_3 of intermediate concentrations are essentially more intricate. First of all, the combination of BF_3 and H_2O is an acid in chemical property, which continually generate boron trifluoride dihydrate with water and then continue to react with water through complex changes and boric acid is obtained ultimately. The chemical reaction goes through several stages:

$$BF_3 + H_2O \rightarrow HBF_3OH$$
$$HBF_3OH + H_2O \rightarrow HF + HBF_2(OH)_2$$
$$HBF_2(OH)_2 + H_2O \rightarrow HF + HBF(OH)_3$$
$$HBF(OH)_3 \rightarrow HF + H_3BO_3$$

Although there is no boron consumption in the above steps, hydrofluoric acid is intensely corrosive and there will be a side reaction occurring subsequently:

$$BF_3 + HF \rightarrow HBF_4$$

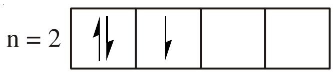
The byproduct, fluoroboric acid (HBF_4), is colorless and transparent liquid, miscible with water and alcohol. It's a strong acid, does not exist in pure state and is only stable in the form of ions. The generation of fluoroboric acid is a loss to boron.

Accordingly, there are two technical routes used to produce boric-10 acid by boron-10 trifluoride. One way is adding weakly alkaline substance to an aqueous solution timely so as to neutralize hydrofluoric acid to avoid the formation of fluoroboric acid. The other way is that boron trifluoride reacts with sodium alkoxide in alcohols and then boric acid is obstained by hydrolysis of boric acid ester. Using methanol as solvent has also some advantages than aqueous solution, because it doesn`t generate any impurity to the system and methanol also plays a role similar to catalyst. Thus boric acid finally produced is purer with higher yield. In this study, an attempt has been made to produce boric-10 acid from boron-10 trifluoride in methanol. The corresponding optimal technology conditions and reaction kinetic have been investigated. Meanwhile, an analysis of hydrolysis of trimethyl borate has been made.

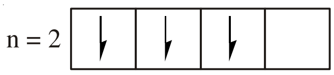
EXPERIMENTAL

Due to small radius and high ionization energy (800.6 KJ/mol), boron atom is mainly connected by covalent bond with other atoms. BF_3 (and other boron halides) will be in complex form with water, alcohol, aldehydes, amines, ethers, ketone, carboxylic acid or their derivatives, which can be explained by the features of their electron structure.

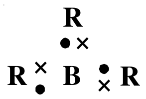
Peripheral electronic configuration of boron atoms is $2s^2 2p^1$



Easy to form sp^2 hybrid orbitals



To form a compound with triangle plane configuration



Boron atom is surrounded by six electrons on the hybrid sp^2-orbits and has a vacant *p*-orbit perpendicular to the plane of three sp^2-bonds. That's the reason why BF_3 has a forceful tendency to accept undivided pairs of electrons and to react with Lewis acid or Lewis base (donors of delectrons) to form complex compounds, *i.e.*, $F_3B \leftarrow NH_3$. Among these compounds, boron atom exhibits tetrahedral structure.

In addition, boron trifluoride will start association reaction with water in the air, generating toxic substances such as hydrogen fluoride and fluoroborate, which are extremely corrosive to equipment. Therefore, it requires the moisture content in the reaction system to be no more than 1 mg $(m^3)^{-1}$. Methanol was chose as a reaction solvent in the esterification reaction in the test. Sodium methoxide is sensitive to moisture, thus it's easy to absorb the water from the air and to hydrolyze to generate sodium hydroxide. Container should be kept dry, thus it was determined to use methanol solution with 30 % of sodium methylate in weight as a reactant and solvent.

The experiments were carried out in a 1,000 mL glass reactor with jacket, which was connected to a cryostat to heat and to control the temperature of the mixture. The reactor must be airtight to prevent reactant and resultant from escaping. The container was blown with nitrogen with high purity for 2 to 3 min to replace the air in it. The reactor was equipped with a mechanical stirrer with 3 blades. Before esterification reaction, certain amount of calcium chloride and methanol solution with 30 % of sodium methylate in weight were added into the reactor. The solution was stirred at 300 rpm and the temperature increased as a result of the heat generated from calcium chloride dissolving in methanol. Until the temperature of the mixture was cooled to the desired temperature by circulating cooling water, boron-10 trifluoride prepared by chemical exchange distillation was inlet slowly, thus complexation reaction took place simultaneously with added heat. It needed to increase the amount of cooling water remove heat timely, otherwise the system would result in elevated temperatures. At the end of the inlet, system was maintained stable for some time and the mixture was kept at a preset temperature. Boron-10 trifluoride decomposed from methanol complex and reacted with sodium methylate and calcium chloride in the following time. At the end of reaction, the temperature was lowered to room temperature. After separated with methanol mixture by centrifugation, trimethyl borate was passed into a series of follow-up process for hydrolysis, concentration, crystallization and desiccation and thereby to meet the requirements of nuclear industry.

Detection method of trimethyl borate-10 and boric-10 acid: Gas chromatography is an effective separation and analysis methods for organic compounds. The composition separated from capillary gas chromatography column (pure substance) was introduced directly into ionization chamber of mass spectrometer so as to perform qualitative analysis of the esterification reaction for whether trimethyl borate was generated or not.

A quantitative analysis of trimethyl borate from esterification reaction was carried out on SP 2100 gas chromatography with standard curve method. Chromatographic column: 5 Ms capillary column; column temperature :70 °C; flow rate of the carrier gas N_2 gas velocity was 50 mL/min; inlet temperature 130 °C; FID (Flame Ionization Detector) temperature 200 °C; inlet pressure 0.1 Mpa, hydrogen 0.08 Mpa, air 0.22 Mpa.

Sample was taken into a gas chromatography mass-line analyzer for analyzing trimethyl borate at regular intervals during reaction. Owing to the solubility of sodium fluoride (by product) and sodium methoxide (reactant) in methanol, most of the solid insolubles were removed by centrifugation and then the liquid was recycled by distillation prior analysis to prevent the pipeline of gas chromatograph from blocking. And then subsequently the content of the trimethyl borate was measured with the gas chromatograph.

Boric acid, after hydrolysis by trimethyl borate, was detected with a spectrophotometer. An Agilent 8453 UV-visible spectrophotometer (1 cm optical cell) was used to measure its absorbance at 543 nm. Adjustable micropipettes delivering volumes of 100, 500, 1000 and 5000 μL were used to inject samples and reagents to 50 mL screw cap polyethylene reaction bottles. The precision of the samples and reagents injection was ± 0.2 % using the micropipettes. 1 L polyethylene volumetric flask was used for preparing dilutions. To avoid possible B contamination, borosilicate glassware was not used in any analytical step.

4 mL sulfuric acid-acetic acid mixture and 6 mL curcumin reagent were added to the reaction bottle, mixed thoroughly and reacted to completion for 70 min, during which period an orange boron-curcumin complex (rosocyanin) was formed. Since excessive curcumin formed an interfering proton complex, it must be removed prior B analysis. This was achieved by the addition of 20 mL buffer solution to the reaction bottle and cooling to room temperature (15 min). The absorbance of the final solution was measured at 543 nm using a 1 cm cell.

RESULTS AND DISCUSSION

Sample liquid after esterification reaction and centrifugation was analyzed with gas chromatography-mass spectrometry. The Figure was compared with standard spectra of trimethyl borate. The results were shown in Figs. 1 and 2.

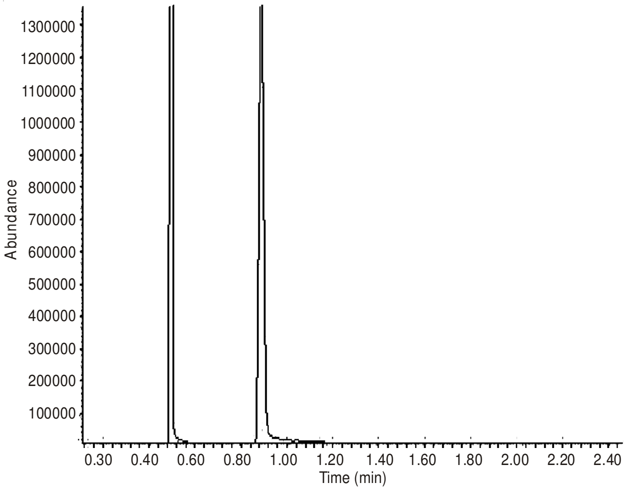


Fig. 1 Total ion current of the product

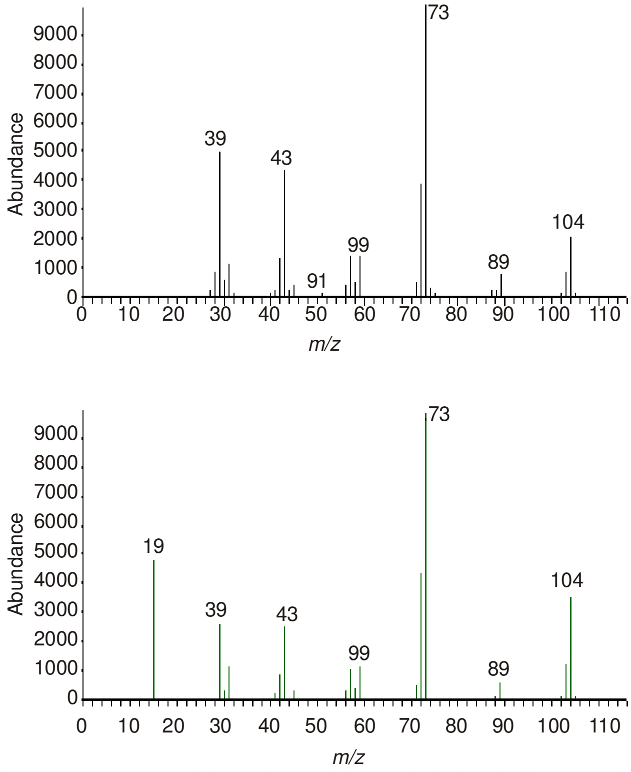
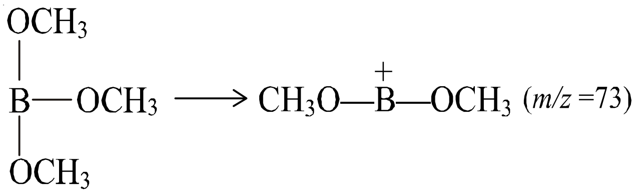


Fig. 2. Mass spectra of the product and the standard trimethyl borate under the same condition

Fig. 1 is a total ion chromatogram of the sample, with the peak at 0.49 min, showing methanol as a solvent. According to preliminary judgment, the peak at 0.90 min might be the peak of trimethyl borate. The component and a standard sample of trimethyl borate were analyzed, respectively with mass spectrometry under the same conditions. The results were shown in Fig. 2.

According to the peak of molecular ion in the mass spectrum of the target product, we can judge the relative molecular mass of the sample was 104, which was the same as that of trimethyl borate. The molecules of the sample in the ionization process would often be broken into fragments with electric charges, which correlates with mass peaks severally. Usually the mass peak was higher and the fragment ions was more stable. From the mass spectrum of the target product in Fig. 2 we can detect: The most stable fragment ion was those whose mass-to-charge ratio was 73, which was the same with the mass spectrum of the standard sample of trimethyl borate. The main reason was that trimethyl borate was easy to break in a high-energy ion source to form stable fragment ions with mass-to-charge ratio being 73. The fragmentation pattern can be considered as follows:



$$B(OCH_3)_3 \longrightarrow CH_3O\text{—}\overset{+}{B}\text{—}OCH_3 \ (m/z = 73)$$

In addition, according to comparison spectra between the target product and the standard sample of trimethyl borate under the same conditions, we can find out: The fragment ions with mass-to-charge ratio were 29, 43, 59 and 89, all appearing in two Figures. Combining with the retention time of 0.888 min in gas chromatography, we can judge trimethyl borate was generated in esterification reaction.

Analysis of reaction mechanism: Prior the experimental investigations discussed, boron fluoride was used to react with sodium methoxide and calcium chloride, respectively. Boron fluoride reacted with sole sodium methoxide and sodium fluoride was firstly formed, which was not a absolute deposit but slightly soluble in methanol, therefore the formation of sodium fluoride inhibited the reaction proceeded. On the other hand, when boron fluoride reacted only with calcium chloride in methanol, hydrogen chloride, which is difficult to volatilize from methanol and methyl borate, which is mixed with methanol, would be generated. Thus it's also not conducive to improve the conversion rate of boron fluoride.

The esterification reaction of boron fluoride with sodium methylate and calcium chloride in methanol were given in the following reactions:

$$^{10}BF_3 + 3CH_3ONa \rightarrow {}^{10}B(OCH_3)_3 + 3NaF \qquad (1)$$

$$2^{10}BF_3 + 6CH_3OH + 3CaCl_2 \rightarrow 2^{10}B(OCH_3)_3 + 6HCl\uparrow + 3CaF_2\downarrow \ (2)$$

Subsequently, the double decomposition reaction of foregoing resultant in methanol would continue:

$$2NaF + CaCl_2 \rightarrow 2NaCl + CaF_2\downarrow \qquad (3)$$

$$HCl + NaOCH_3 \rightarrow CH_3OH + NaCl \qquad (4)$$

The total reactions is as following:

$$6CH_3ONa + 3CaCl_2 + 2^{10}BF_3 \rightarrow 3CaF_2\downarrow + 2^{10}B(OCH_3)_3 + 6NaCl \qquad (5)$$

In the reaction process, although boron fluoride reacted with calcium chloride and sodium methylate, respectively in methanol, the final products were the same. In the above four-step reaction, boron fluoride reacted with sodium methoxide at the beginning since sodium methoxide was more alkaline than calcium chloride. Sodium fluoride as a resultant is slightly soluble in methanol. The slightly soluble sodium fluoride and the mixture of methanol and ester could form a colorless translucent gelatinous substance, which is extremely unfavorable for solid-liquid centrifugal separation. The reaction was inhibited to further step since sodium fluoride was not precipitate. However, the speed of reaction (2) was slower than that of reaction (1) in the later period. Sodium fluoride, which is slightly soluble in methanol, was saturated in methanol and partial sodium fluoride was precipitated from the solution with the proceeding of reaction (1). Once sodium fluoride precipitated, it's difficult to react with calcium chloride in liquid as in reaction (3). On the other hand, although the speed of reaction (2) was not as fast as that of reaction (1). The formation of the resultant calcium fluoride, which was infusible in methanol, can promote reaction (2) to go further. Since it's difficult to exhaust the resultant hydrogen chloride from this turbid liquid, alkaline sodium methoxide was needed for neutralization (as in reaction 4) instead of using a strongly alkali sodium hydroxide for neutralization (the resultant water would result in ester hydrolysis).

We tried to add sodium methylate solid powder first and then calcium chloride into methanol in early practice and two conclusions were found: First, the yield was not as high as that in the previous practice; Second, the above-mentioned translucent solid was almost all calcium fluoride and did not contain any sodium fluoride after distillation, which showed the conversion rate of boron trifluoride in reaction (1) was higher than that in reaction (2).

Effect of reactant ratio on yield of trimethyl borate: Reaction 1 to reaction 4 occurred simultaneously during the medium-term time, but sodium methoxide and calcium chloride were the mutual catalysts of reaction (1) and reaction (2). So they were needed to be added simultaneously. Through analyzing reaction (1) to reaction (4), it was determined that the molar amount of calcium chloride was twice times of that of sodium methoxide. It was found that excessive sodium methoxide and calcium chloride can increase the yield of trimethyl borate. The effect of molar ratio of $^{10}BF_3$ to sodium methoxide on the yield of enriched ^{10}B trimethyl borate was examined in range of 1 to 1.3 under the conditions of the reaction temperature being 55 °C, the reaction time of more than 35 h to ensure complete esterification reaction. The results were shown in Fig. 3.

As can be seen from Fig. 3, the yield of trimethyl borate increased with gradual augment of $n[CH_3ONa]{:}n[BF_3]$, because the excess of sodium methoxide and calcium chloride can direct reaction equilibrium towards the creation of trimethyl borate. The yield of trimethyl borate reached maximum at the

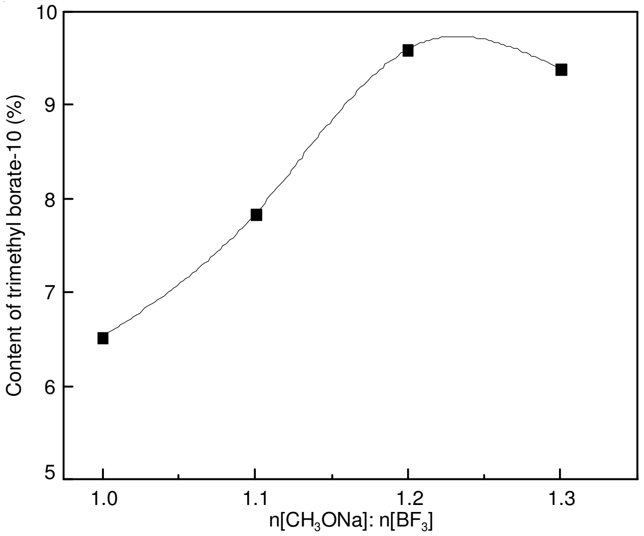


Fig. 3. Effect of raw materials' proportion on the yield of trimethyl borate-10

point of n[CH$_3$ONa]: n[BF$_3$] = 1.2. When n[CH$_3$ONa]: n[BF$_3$] reached 1.3, the yield of trimethyl borate became lower on the contrary. The reason was that the solution became viscous and difficult to be stirred because of excessive sodium methoxide and calcium chloride. Besides, excessive sodium methoxide could form complex with trimethyl borate, which prevented the increase of the yield of trimethyl borate. So n[CH$_3$ONa]: n[BF$_3$] = 1.2 was appropriate.

Effect of temperature and time on yield of trimethyl borate-10: Under the condition of n[CH$_3$ONa]: n[BF$_3$] = 1.2, the effect of reaction temperature and time on the esterification reaction was investigated and the results were shown in Fig. 4.

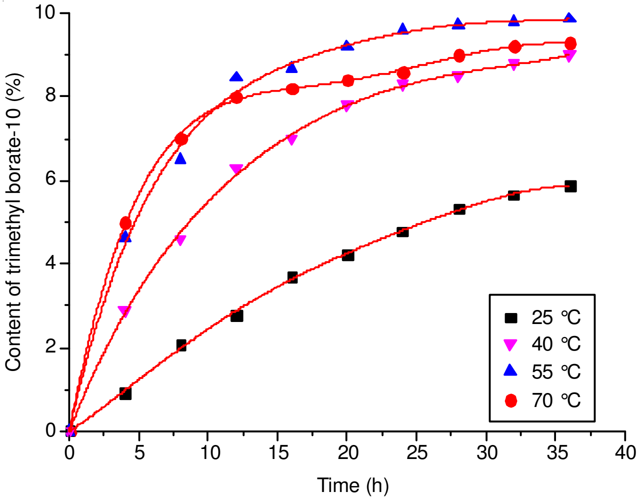


Fig. 4. Effect of reaction time and temperature on the yield of trimethyl borate-10

Because the complex reaction between boron trifluoride and methanol is strong exothermic, the reaction needs to be carried out in an environment of low temperature, or even water at freezing point was used in jacket. After blowing, complex compound of boron trifluoride and methanol was formed in glass reactor. As the temperature was increased, boron trifluoride was released gradually from methanol and reacted with calcium chloride and sodium methoxide to form trimethyl borate.

The yield of trimethyl borate was below 6 % at 25 °C. Boron trifluoride gas as reactant was released from methanol slowly, and the complexation of boron trifluoride and methanol plays a major role at low temperature with little gas emission. As a result of temperature increase, the amount of boron trifluoride gas released increased and the yield of trimethyl borate increased gradually. Generally speaking, increasing reaction temperature had advantages for the whole process. During the first 10 h of the reaction time, the content of trimethyl borate at 65 °C improved faster. The reason is that much boron trifluoride complex can be released and it reacts with other reactants faster at higher temperature. On the other hand, because the release rate of boron trifluoride is faster than the reaction rate of boron trifluoride at higher temperature after 10 h, boron trifluoride escaped to the gas phase without reaction. Therefore, the yield of trimethyl borate declined when the reaction temperature reached 65 °C. Meanwhile, the azeotropic point of the mixture of trimethyl borate and methanol was 54.6 °C, partial azeotrope, which was formed by trimethyl borate and methanol, lost (mass fraction of trimethyl borate was 68 %). Accordingly, 55 °C was chosen as an appropriate reaction temperature.

It can be seen from Fig. 4, the content of trimethyl borate was not high at the initial stage of the reaction. This was because it would take some while for boron trifluoride to escape from methanol. Over time, with the desorption of boron trifluoride from methanol increasing gradually, the content of trimethyl borate increased. The maximum content of the trimethyl borate in the liquid occurred at 27th h and then decreased slightly, which showed that the rate of reaction (2) reduced gradually, while reaction (4) played a major role. Although the resultant methanol in reaction 4 caused the content of trimethyl borate in liquid decreased slightly, the quality of trimethyl borate did not decrease in Fig. 4. The yield of trimethyl borate decreased until reaction (2) and reaction (4) had stopped. The yield of trimethyl borate almost increased no longer after 30 h. At this point the reaction had reached equilibrium. Therefore, it's appropriate to take reaction time as 0.5 h and the conversion rate of trimethyl borate reaches above 92 %.

Kinetic analysis: The rate of reaction between a solid and a fluid can be expressed with homogeneous and heterogeneous models. The kinetic data here did not fit any heterogeneous model, but it was determined that second order pseudo homogeneous reaction model fits very well with the data.

$$kt = \frac{1}{c_A} - \frac{1}{C_{A0}} = \frac{1}{c_{A0}}\left(\frac{X_A}{1 - X_A}\right)$$

where, c_A = consistency of boron trifluoride
c_{A0} = initial consistency of boron trifluoride
X_A = fractional conversion of boron trifluoride
t = time
k = rate constant

Fig. 5 shows the relation between $\frac{1}{c_{A0}}\left(\frac{X_A}{1 - X_A}\right)$ *versus* reaction time, which gives almost perfect straight lines indicating agreement of the experimental results with second order pseudo homogeneous reaction model at different reaction temperatures.

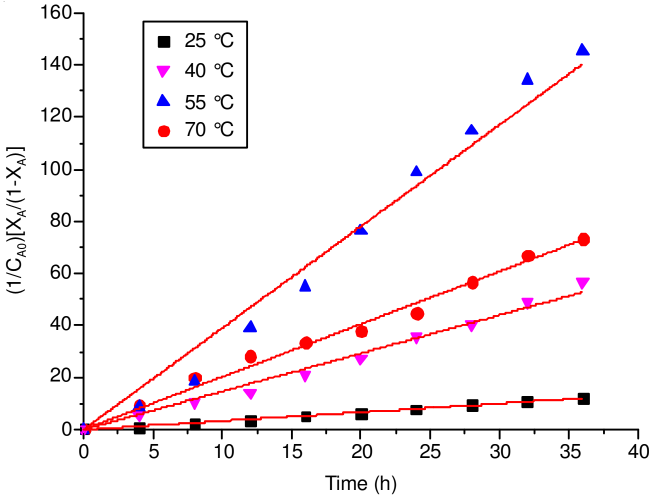


Fig. 5. Agreement of experimental data with second order pseudo homogeneous kinetic model

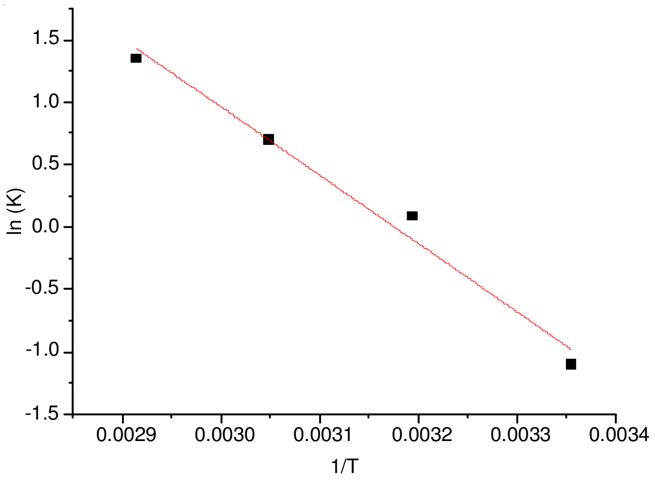


Fig. 6. Arrhenius plots for the synthesis of trimethyl borate-10

Activation energies: The temperature dependence of the chemical reactions can be given by Arrhenius equation:

$$k = -Ae^{-E_a/RT}$$

where, k = rate constant

A = a pre-exponential factor

E = activation energy

R = gas constant

T = temperature

Another form of Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + B$$

According to this equation, the slope of the curve between ln k *versus* 1/T should give a straight line, whose slope equals to $-E_a/R$. Fig. 6 shows the Arrhenius plots for the formation of trimethyl borate-10 from sodium methoxide, calcium chloride and boron-10 fluoride in methanol. The activation energies derived from this curve was found as kJ/mol K for this reaction.

$$(-E_a/R) = -5474.85, \; B = 17.39$$

$$k = 3.568 \times 10^7 \; e^{-658.5}/RT$$

Hydrolysis of trimethyl borate-10: According to the appropriate material proportioning of esterification reaction, hydrolysis of trimethyl borate-10 proceeded with 50 % methanol contained after esterification. Trimethyl borate-10 hydrolyzes easily even if exposed to air and boric-10 acid will be synthesized and adhered to the brim of bottle. The presence of methanol influences hydrolysis of trimethyl borate-10 more or less, so it's different from the hydrolysis of pure trimethyl borate-10.

There are several methods for separating trimethyl borate-10 and methanol in the following ways: Salting out, extraction, distillation and ion exchange process, *etc*. Some of them are often used together to achieve a higher purity of trimethyl borate-10. Compared with hydrolysis of pure trimethyl borate-10, reducing methanol content in the mixture of methanol and trimethyl borate-10 has advantage for hydrolysis. However, there is no need to separate methanol restrictly prior to hydrolysis for economical consideration. Hereinafter, hydrolysis of liquid mixture of trimethyl borate-10 and methanol after esterification was investigated.

Analysis of product: The samples were detected in infrared spectroscopy as Fig. 7. Compared with standard infrared spectra of boric acid as Fig. 8, it was confirmed that enriched 10B product of boric acid can be prepared in this method.

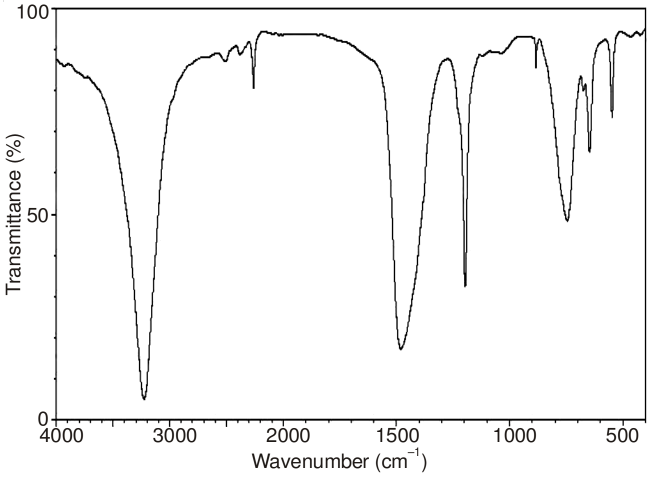


Fig. 7. Infrared spectra of pure boric acid

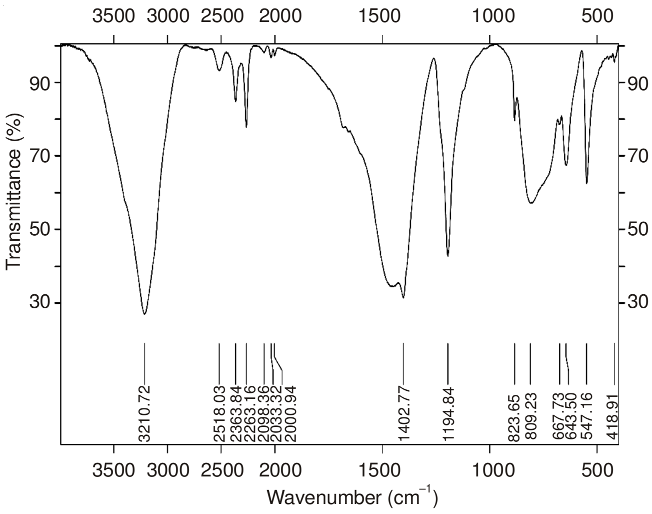


Fig. 8. Infrared spectra of sample

0.4 g of sample (accurate to 0.0002 g) was taken into a 250 mL Erlenmeyer flask with 60 mL of water. Consequently, titration of boric acid was carried out with 0.2 mol /L of standard volumetric solution of sodium hydroxide in the presence of 7 g of mannitol, using 5 drops of phenolphthalein indicator for end point determination. The purity of boric acid was calculated by titration value and mass of product. The yield of boric acid can be calculated by titration value and theoretical output of boric acid.

Effect of pH value on the hydrolysis yield of trimethyl borate-10: Sufficient water was added to ensure that it was a dilute solution after hydrolysis. The impact of the medium on hydrolysis was investigated. Boric-10 acid is a weak acid in aqueous solution, so hydrolysis of trimethyl borate-10 cannot be enhanced in a relatively acid environment. Theoretically, hydrolysis of trimethyl borate-10 can be promoted in alkaline aqueous solution so as to increase the yield of trimethyl borate-10. The formation of borate-10 will affect the crystallization yield and the purity of boric-10 acid, so higher yield and purity of boric-10 acid can be achieved in a neutral environment. Trimethyl borate-10 reacts with water directly. Unhydrolyzed trimethyl borate-10 can be recycled with methanol from distillation to subsequent esterification.

Effect of water content on hydrolysis yield: Trimethyl borate-10 content in methanol was about 15 % after the esterification. The effect of water content on hydrolysis yield was investigated at 25 °C (Fig. 9). The purity of boric-10 acid maintained above 99 % and the yield of boric-10 acid increased with increase of molar ratio of H_2O to $^{10}B(CH_3O)_3$. When $n(H_2O)$: $n[^{10}B(CH_3O)_3]$ was above 45, the curve tended to slow down. If continue to increase water content, subsequent concentration and crystallization would be overburdened. Accordingly, $n(H_2O)$: $n[^{10}B(CH_3O)_3] = 45$ was appropriate.

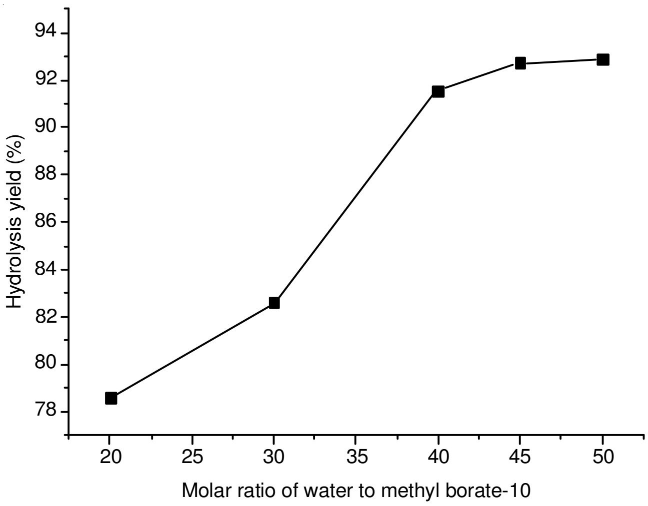


Fig. 9. Effect of water content on hydrolysis yield

Effect of temperature on hydrolysis yield: Increasing temperature helps reduce water content, thereby reduce the losses of boric-10 acid in subsequent concentration process. The solubility of boric-10 acid in water changes greatly with temperature and does the same in methanol. In an aqueous medium, hydrolysis of pure trimethyl borate-10 is an exothermic reaction. But for this experiment, methanol in water would absorb some heat. Besides, the mass ratio of trimethyl borate-10 to water was 1:8.3. Therefore, total temperature changed a little. The azeotropic temperature of methanol and trimethyl borate-10 was 58 °C. Therefore some trimethyl borate-10 will evaporate at high temperature without hydrolysis, resulting in yield loss.

Crystallization and refination: The solubility of enriched ^{10}B boric acid at different temperature is shown in Fig. 10. It can be seen that boric acid could be obtained by the way of evaporation cooling crystallization. Enriched ^{10}B boric acid solution was evaporated to supersaturated state and then at cooling speed of 0.5-1 °C/min, stirring speed of 200 rad/min for crystallization. Enriched ^{10}B boric acid crystal was obtained by filtering after maintaining an hour at temperature of 15-20 °C.

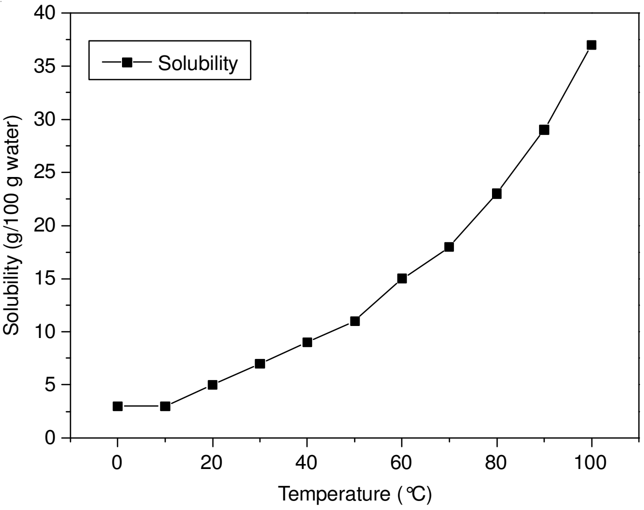


Fig. 10. Solubility curve of boric-10 acid

However, the enriched ^{10}B boric acid cannot meet the standard that used in nuclear technology without refining. Some treatment of enriched ^{10}B boric acid crystal such as crystallization, adsorption and ion exchange methods were chosen to compare.

The enriched ^{10}B boric acid crystals was washed by deionized water at temperature of 15-20 °C. Next, the solution was heated up to 70 °C and crystallized by cooling directly to 10 °C. Refined enriched ^{10}B boric acid crystals were dried in vacuum drying oven at temperature of 45 °C for 5 h. The drying temperature was kept low with vacuum as a result of enriched ^{10}B boric acid starts to loose crystal water over 60 °C. The purity of enriched ^{10}B boric acid was improved to above 99.9 %.

Conclusions

- The practicability of the preparation of boric-10 acid from boron-10 trifluoride through esterification and hydrolyzation was demonstrated through experiments. According to the analysis of technological process of the synthesis of trimethyl borate-10 and the hydrolyzation of trimethyl borate-10, the reaction mechanism was exposited in detail.
- The optimum reaction conditions of synthesis of trimethyl borate-10 were determined. The reaction took place at 55 °C for 30 h in methanol with n (boron-10 trifluoride): n(sodium methylate): n(calcium chloride) = 1:1.5:3, the yield

of trimethyl borate reached 80 % and the purity higher than 99 %. It was determined that the reaction kinetics of esterification in methanol was controlled by second order pseudo hogeneous reaction. The activation energy was 685.5 KJ/mol.

- The hydrolyzation of trimethyl borate-10 with methanol existenting was investigated. It was determined that under the condition of neutral pH value and at 25 °C temperation, the feasible ratio of water to trimethyl borate-10 was 7.5, with a small amount of production loss. Boric-10 acid obtained in this process is qualified for nuclear industry.

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