ortho-Fluoroanisole: A New Donor for Boron Isotopes Separation by Chemical Exchange Distillation

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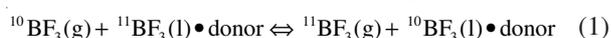*Corresponding authors: Tel: +86 13662126469; E-mail: chemeng114_tju@163.com

[10]B is an effective neutron absorbent, which endows its duty in nuclear industry as a protecting agent. The only industrialized process for preparation of [10]B is chemical exchange distillation using anisole as a complexing agent. The drawbacks such as low isotope separation factor and instability under process conditions inspired continuous interests to find a replacement. A new complexing agent, *o*-fluoroanisole, was selected and evaluated for boron isotopes separation. *O*-fluoroanisole demonstrates better properties such as higher separation factor, lower freezing point of the complex and longer cycle life compared with those of anisole, which suggest it as a noteworthy agent used for separating isotopes.

Keywords: Boron isotope, Isotope separation, *o*-Fluoroanisole, Separation factor, Cycle life, Stability, Pyrolysis.

INTRODUCTION

Boron has two stable isotopes, [10]B and [11]B, with natural concentration of 19.9 and 80.1 %, respectively. Because of the superior ability of [10]B in absorbing neutrons (3.837×10^{-25} m^2) compared to that of [11]B (0.05×10^{-28} m^2), great efforts have been devoted to extract [10]B from the natural mixture of boron isotopes[1,2]. The [11]B isotope is used relatively less in absorbing neutrons. Nevertheless, it is used as an additive in seamless steels that are used in the construction of reactors to enhance their heat and radiation resistance without destroying the neutron physics of the reactor's active zone[3].

Different donors have been studied[4-8] for their efficiency and practical utility in the isotopic exchange reaction,

$$^{10}BF_3(g) + {}^{11}BF_3(l) \bullet donor \Leftrightarrow {}^{11}BF_3(g) + {}^{10}BF_3(l) \bullet donor \quad (1)$$

$$^{10}BF_3 \cdot donor \rightarrow {}^{10}BF_3 + donor \quad (2)$$

The only complexing agent used in industry is anisole. The eqn. (1) shows that [10]B is concentrated in the liquid phase during exchange distillation. The eqn. (2) shows the complexes are cracking into [10]BF$_3$ gas and complexing agent by heating. Separation factor (a) is an important parameter for the process of chemical exchange distillation. Boron trifluoride is the sole boron species in the gas phase and BF$_3$·donor is the sole boron species in the liquid phase, then K = α. It may be written as a ratio of as follows[9]:

$$\alpha = \frac{\left[{}^{11}BF_{3(g)} \right]\left[{}^{10}BF_3 \cdot donor_{(l)} \right]}{\left[{}^{10}BF_{3(g)} \right]\left[{}^{11}BF_3 \cdot donor_{(l)} \right]} = \frac{\left[{}^{10}B / {}^{11}B \right]_{(natural)}}{\left[{}^{10}B / {}^{11}B \right]_{(g)}} \quad (3)$$

For anisole system, the factor α (1.030 at 293.15 K) is relatively small[10]. In order to obtain 99.5 % [10]B in bottom stream and 99.0 % [11]B in top stream, the number of minimum theoretical plates is calculated to be 335 at ambient temperature and pressure by Fenske equation. The large number of theoretical plates increases separation equipment cost and difficulty of the operation. For the purpose of finding more ideal complexing agents, many studies had been done[11-14].

For anisole, there are some deficiencies in the pyrolysis process which are listed as follows:

(1) Under the catalysis of strong acid like BF$_3$ and HF, which produced by BF$_3$ and H$_2$O in the air or materials, some unwanted phenolic byproducts were formed during pyrolysis process, which may cause a loss of anisole.

(2) Those phenolic byproducts can also react with BF$_3$ to form complexes, which cannot be dissociated completely at the anisole's boiling point, hence, the separation efficiency was inevitably damaged.

(3) Molecular addition compounds of BF$_3$ with phenols have viscosity 3 to 5 times higher than that of complex Anisole·BF$_3$. So, it greatly influence mass and heat transfer of system. The accumulating of by-products reduce the cycle-life of the anisole, so anisole with concentration of any phenol impurity exceeds 0.3 % should be replaced.

Considering these defects of anisole in industry application, it is advisable to find a replacement. We expected to solve some of existing problems through introducing a electronegative group like fluorine atom on the benzene ring of anisole, which is thought to reduce electron density of benzene

ring and prevent undesired electrophilic side reactions in pyrolysis process. A chloride-containing anisole was evaluated as a donor, which showed an increase in the separation factor[2]. Thinking of avoiding introduce of other atom in BF_3 system, some fluorine-substituted anisoles were studied in this paper. Through screening, *o*-fluoroanisole was selected because of its relative good properties, such as the separation factor, freezing point, stability during pyrolysis. These data are measured for the engineering design and operation of a boron isotopic separation system, including column parameters, complexing agent cycle life, *etc*.

EXPERIMENTAL

Analytical Reagent grade compounds were used in the complexing and pyrolysis experiment. The BF_3 used in all experiments was purchased from the Zibo Linzi Xinqiang Chemical Co., Ltd with a minimum purity of 99.99 %. The anisole, *o*-fluoroanisole, *p*-fluoroanisole and *m*-fluoroanisole used for these experiments were obtained from Shanghai Tong Yuan Chemical Co., Ltd. These compounds were dehydrated with 4 A molecular sieves to water content of 30-50 ppm before use.

The schematic diagram of apparatus used in these experiments is shown in Fig. 1. These apparatus consisted essentially of two parts, complexation equipment and pyrolysis equipment, both were made of stainless steel (SUS304L) with volume of 300 mL avoiding HF etching glass. Considering the rapid reaction of BF_3 with water, the equipment needed to be purged with nitrogen and all the procedures described henceforth occurred inside a dry box with ambient water vapor maintained below 50 ppm.

The water content of the complexing agent was detected by sf-3 micro calorimeter moisture analyzer manufactured by Zibo Zifen Instrument Co., Ltd. The GC was manufactured by Lunan Analytical Instrument., Led. The $^{10}B/^{11}B$ ratio was detected by the inductively coupled plasma mass spectrometer was made from Thermo Electron Corporation, USA[15]. The accuracy of thermocouples was 0.1 °C. The range of all pressure gauges made by Xi'an Instrument Factory was -0.1-0.25 Mpa with an accuracy of 2 Kpa.
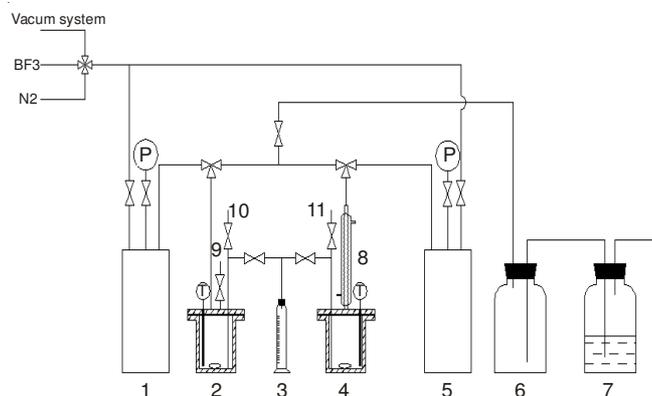

Fig. 1. Schematic diagram of experimental equipment, 1. BF_3 tank 1 with 5L; 2. Complexing kettle; 3. cylinder with stopper; 4. Dissociation kettle; 5. BF_3 tank 2 with 5L; 6. buffer bottle; 7. NaOH solution; 8. condenser; 9. complexing agent inlet and gas sampling port; 10. adduct sampling port; 11. sampling port for dissociation

Isotopic separation factor (α)

The single stage Isotopic separation factor (α), for the reaction (1): If the amount of BF_3 in the gas phase is kept small compared to the amount of BF_3 used as complex in the liquid phase, the second relationship may be assumed because the ratio of $^{10}B/^{11}B$ was almost constant in the liquid[16].

The amount of gas removed from the gas phase during equilibration must be so small that isotopic equilibrium is not disturbed during sampling.

For the sake of data reliability, the isotopic separation factor (α) in four temperature points is indispensable. Therefore, the temperatures of 0, 10, 20 and 30 °C were chosen in the experiments. All sets of data were fitted by least squares to the equation:

$$\lg \alpha = a/T + b \qquad (4)$$

Procedure for measuring α: The complexing reaction took place in the complexing kettle. Procedure for determination of α was as follows: (1) the entire dried and cleaned system was evacuated by vacuum system, (2) BF_3 tank 1 was disconnected with the dissociation system and complexing system to avoid BF_3 entering. (3) About 50 mL of complexing agent was pumped into the 300 mL complexing kettle. (4) BF_3 tank 1 was aerated with BF_3 until the pressure reached 0.3 Mpa and then the valve between tank 1 and complexing kettle (valve 1) was opened. Boron trifluoride reacted with the complexing agent in the complexing kettle under agitation and cooled by cold water. As the reaction proceeded, the pressure within the reactor decreased.

Valve1 was closed at the end of the complexing reaction and then the complexing kettle became an independent closed system. The BF_3 at the headspace of the complexing kettle was then chemically exchanged with BF_3 from the complex. The kettle was then maintained sealed at 0, 10, 20 and 30 °C, respectively, for 24 h. Then, BF_3 sample was taken from gas sampling port (9) with plastic syringe and stored in vials. Three airtight, plastic vials (10 mL each) were half-filled with calcium nitrate drawn from the same batch as the substrate. Then samples of the liquid and gas phases from each vial were then injected (separately) into inductively coupled plasma mass spectrometer and the $^{10}B/^{11}B$ ratio measured. The $^{10}B/^{11}B$ of each sample measured by inductively coupled plasma mass spectrometer.

Density: Volumetric vials, with an accuracy of 0.01 mL, filled with complex were weighed on a digital balance, with an accuracy of ± 0.001 g. The accuracy of the system was verified using distilled water as a reference before measuring the density of *o*-fluoroanisole; the density of water was measured accurately with a mean deviation of 0.003 g/cm³ [17]. Three separate measurements of the density of *o*-fluoroanisole yielded an average density of 1.384 g/cm³ which was 23 % higher than that of the pure *o*-fluoroanisole.

Freezing point of complexes: The freezing point of the complex determined the lowest operation temperature in actual industrial separation. The chemical exchange reaction took place on the gas-liquid interface. Therefore, lower freezing point means less limitation in industrial application. The capillary method is a simple and convenient way to determinate melting point of the complex[18].

BF$_3$/*o*-Fluoroanisole ratio by titration: This technique consisted of dissolving a certain amount of complex in calcium nitrate solution, titrating with 1N NaOH to the neutral inflection point, adding excess mannitol to make hydrolysis of boric acid completely and then titrating with 0.1 N NaOH to the second end-point. The volume of 0.1 N NaOH allowed the quantity of BF$_3$ to be calculated.

Pyrolysis: The types and contents of by-products formed under various temperatures varied. In order to find a suitable temperature, the pyrolysis temperatures were controlled at 80, 110, 140, 160 and 180 °C, respectively. To avoid the mutual interference of by-products, fresh complexing agent was used at each temperature point.

The complexing agent vaporized during pyrolysis was condensed with a condenser. Boron trifluoride steam was cooled to room temperature and the vapor pressure of *o*-fluoroanisole is small at room temperature, so the small amount of *o*-fluoroanisole volatilized was fully condensed so that the gas flow out of the condenser was boron trifluoride gas only. The same operations were conducted for anisole as the complexing agent for comparison. The contents of by-products were tested by GC.

Procedure for pyrolysis: After the complexing process finished, the complex was pressured to container 3 and then to dissociation kettle with a volume of about 30 mL. The dissociation kettle was heated with hot oil to 80, 110, 140, 160 or 180 °C, respectively. In the dissociation kettle, the complex would pyrolyze into complexing agent and BF$_3$. When the pressure of tank 2 stopped increasing, the pyrolysis reaction was completed.

At each temperature, the operation procedures were comprised of recording pyrolysis time and taking samples periodically from port 11 to detect pyrolysis degree and analyze the impurities of the pyrolysis product[19].

We replaced the oil bath pot with cold water pot to cool the pyrolysis kettle down to 20 °C and opened the valve between pyrolysis kettle and tank 5, to start complexing. The pyrolysis and complexation process were repeated four times.

RESULTS AND DISCUSSION

The new complexing agents were compared with anisole in various aspects.

Comparison of isotopic separation factor: The first objective of this study was to determine the isotopic separation factor, which was measured and compared with that of anisole. According to the data in Table-1 (1.0326 < 1.0323 < 1.0352 < 1.0447), *o*-fluoroanisole has the greatest separation factor among these halogenated anisoles.

According to the data in Table-1, linear extrapolation given as follows and shown in Fig. 2:

$$\lg \alpha = 22.69/T - 0.05763 \quad (R^2 = 0.99308) \tag{5}$$

And for anisole, this relationship is expressed as follows:

$$\lg \alpha = 10.94/T - 0.02332 \quad (R^2 = 0.97940) \tag{6}$$

The minimum theoretical plate (N) as shown in Table-2 is calculated by Fenske equation based on that the product composition of ^{10}B in bottom stream is 99.5 % and the ^{11}B in top stream is 99 %. Where Fenske equation:

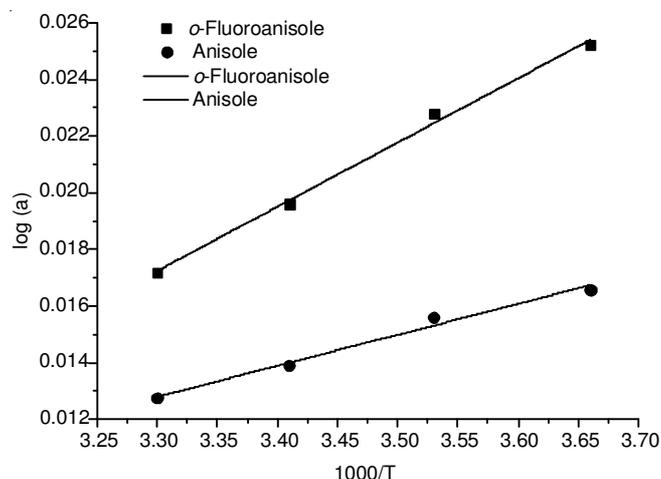$$N_{min} + 1 = \frac{\ln\left(\dfrac{x_D}{1-x_D} \cdot \dfrac{1-x_W}{x_W}\right)}{\ln \alpha} \tag{7}$$

Fig. 2. Separation coefficient *vs.* reciprocal temperature

Freezing point of complexes: The freezing point of anisole·BF$_3$ is 1 °C, while that of *o*-fluoroanisole is -40 °C. Because of the low outdoor temperature in winter, anisole is easy to freeze and stick on the packing which may cause certain industrial production problems. So *o*-fluoroanisole is more suitable than anisole when used in winter. On the other hand, chemical exchange at lower temperature usually has a larger separation factor

TABLE-1
EXPERIMENTAL RESULTS OF THE COMPLEXATION REACTIONS

Agent	Temperature (T/K)	α	log α = a/T + b	Freezing point (°C)	BF$_3$/donor ratio
Anisole	273.15	1.0389	log α = 10.94/T-0.02332	~1	0.9712
	283.15	1.0366			
	293.15	1.0326			
	303.15	1.0298			
o-Fluoroanisole	273.15	1.0598	log α = 22.69/T-0.05763	-40	0.9617
	283.15	1.0588			
	293.15	1.0447			
	303.15	1.0404			
p-Fluoroanisole	293.15	1.0323		~5	0.8867
m-Fluoroanisole	293.15	1.0352		~40	0.8011

TABLE-2
COMPARISON OF THE ISOTOPIC SEPARATION
FACTOR AND THEORETICAL PLATE NUMBER

T (K)	α_1	N_1	α_2	N_2
273.15	1.0389	260	1.0510	197
283.15	1.0366	283	1.0488	206
293.15	1.0326	308	1.0447	211
303.15	1.0298	337	1.0404	248

α_1: Separation coefficient of anisole system, α_2: Separation coefficient of *o*-fluoro anisole system, N_1: Minimum theoretical plates of anisole, N_2: Minimum theoretical plates of *o*-fluoroanisole

BF$_3$/*o*-fluoroanisole ratio: The BF$_3$/anisole ratio equals to 0.9712 at 20 °C, is in good agreement with reported result[1] and verified the reliability of the instrument and operations. The BF$_3$/*o*-fluoroanisole ratio measured in experiment is 0.9617, which indicates that the energy of B-O in *o*-fluoroanisole BF$_3$ is smaller than that in anisole BF$_3$.

Comparison of pyrolysis: All pyrolysis data are summarized in Table-3. The pyrolysis process completed quickly[1]. As shown in Fig. 3, the degree of pyrolysis increases with the pyrolysis temperature. At low temperature, the pyrolysis degree is independent with the heating time. The anisole·BF$_3$ pyrolyze completely at above 160 °C[20], as *o*-fluoroanisole is above 140 °C.
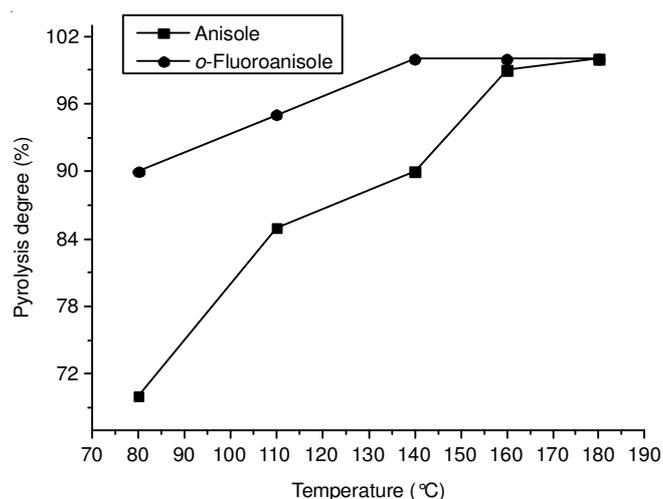

Fig. 3.   Pyrolysis degree-temperature curve for BF$_3$ anisole and BF$_3$ *o*-fluoro-anisole

Regarding to unwanted reactions, Fig. 4 shows that the optimal temperature of anisole is 160 °C and that of *o*-fluoroanisole is 140 °C. The lower temperature means less energy conservation. The content of byproduct of *o*-fluoroanisole is lower than that of anisole at the corresponding optimum temperatures. However, the amount of by-products is proportional to the temperature after the complexing is pyrolyzed completely, so the temperature must be controlled strictly. One of the anisole by-products is phenol, which produces complexes that are not able to dissociate completely. Meanwhile, the main by-product of *o*-fluororanisole is anisole.
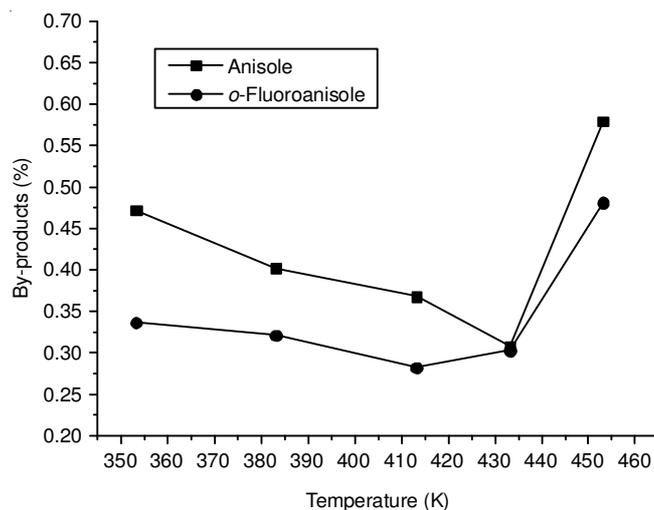

Fig. 4 Curves of by-product content with the increase the temperature

The by-products accumulate as reaction time lapse, with an increasing accumulation rate. The relation of by-product content with cycle times is shown in the Fig. 5. The enrichment rate of *o*-fluoroanisole by-product is smaller than that of anisole at each temperature point as shown in the Figs. 6 and 7, which means the *o*-fluoroanisole has a longer cycle life than anisole. It can save materials cost of complexing agent due to its chemical stability.

Conclusion

ortho-Fluoroanisole and anisole is compared in this work regarding to various properties, such as isotope separation factor, density, stability, cycle life and freezing point. Chemical and physical properties of *o*-fluoroanisolewere studied using

TABLE-3
EXPERIMENTAL RESULTS OF THE PYROLYSIS

Agent	Pyrolysis (T/K)	Main by-products	Degree of pyrolysis (%)	Content of by-product (%)			
				1	2	3	4
	353.15		70	0.6722	0.7894	1.0900	1.2340
	383.15		85	0.4022	0.5235	0.6458	0.8896
Anisole	413.15	Phenol	90	0.3684	0.4094	0.4339	0.4890
	433.15		100	0.3075	0.3592	0.3778	0.4202
	453.15		100	0.5793	0.7897	1.0905	1.1100
	353.15		90	0.3073	0.4995	0.5112	0.6242
	383.15		95	0.3213	0.4566	0.4792	0.5033
o-Fluoroanisole	413.15	Anisole	100	0.2822	0.2907	0.3004	0.3204
	433.15		100	0.3037	0.3838	0.4065	0.4434
	453.15		100	0.4818	0.5983	0.6026	0.6785

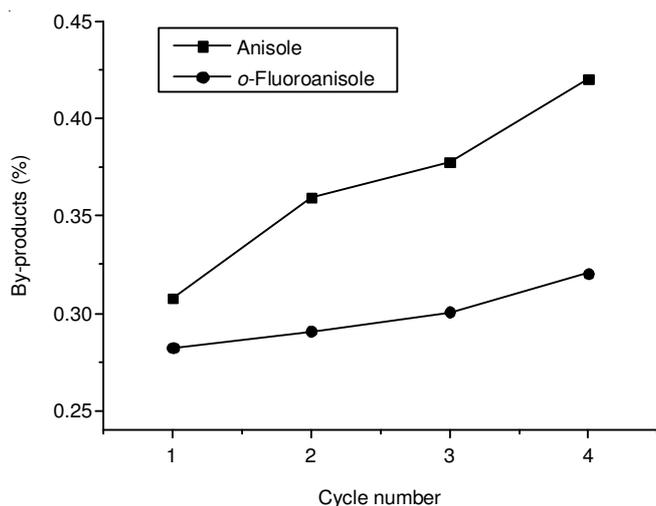1, 2, 3, 4: Cycle number of complexation and pyrolysis

Fig. 5. Curves of by-product content with the increase of cycle number
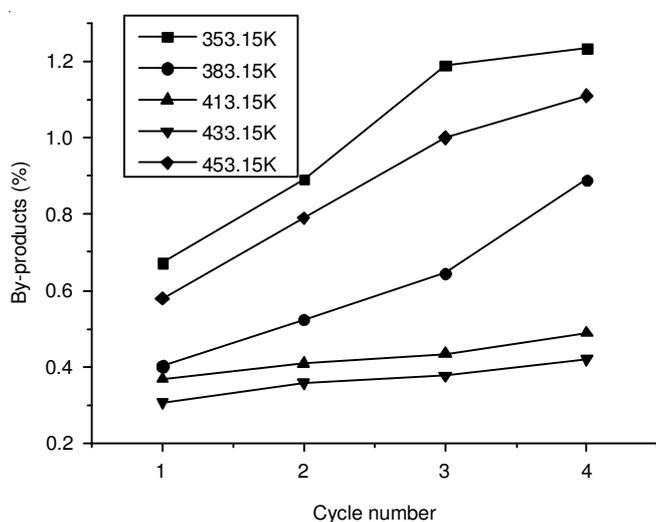

Fig. 6. Curves of by-product content with the increase of cycle number for BF₃ anisole at each temperature
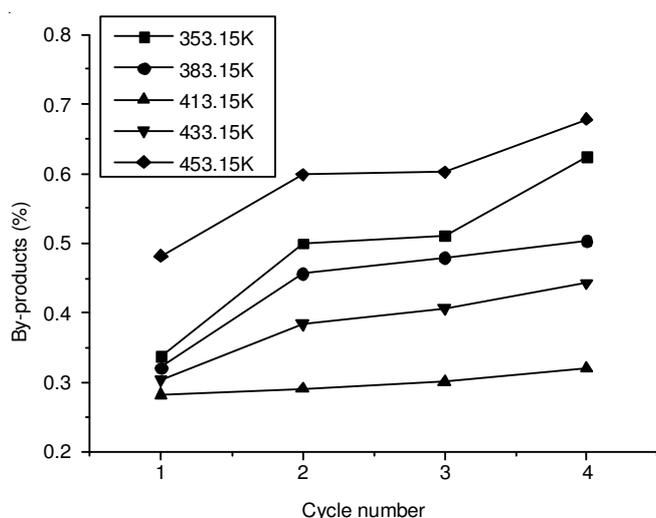

Fig. 7. Curves of by-product content with the increase of cycle number for BF₃·*o*-fluoroanisole at each temperature

a variety of techniques. The density was found to be 1.384 g/cm³. The isotope separation factor of *o*-fluoroanisole is larger than that of anisole, which can reduce the number of theoretical plates in distillation. It was found that *o*-fluoroanisole is a more stable complexing agent, because (1) the content of by-product after pyrolysis is lower than anisole; (2) the accumulation ratio of by-product during multiple cycles of pyrolysis and complexing is lower than anisole. So the cycle life of *o*-fluoroanisole is longer than anisole. The BF₃/*o*-fluoroanisole ratio is 0.9617, similar to that of anisole (0.9712). The higher α can lead to reduction in the column height. Moreover, the lower freezing point of *o*-fluoroanisole (-40 °C < 1 °C) is more suitable for industrial boron isotope separation, especially in winter. According to the eqn. (3) the separation factor is larger at a lower temperature. So, low freezing point is favorable in the separation of isotopes. Apparently, *o*-fluoroanisole is a better complexing agent for boron isotope separation in both complexing and pyrolysis. In summary, it can be concluded that *o*-fluoroanisole is a promising donor to replace the current anisole in the chemical exchange separation of ^{10}B and ^{11}B.

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