Review

Advances in boron-10 isotope separation by chemical exchange distillation

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ABSTRACT

Advances in boron-10 isotope separation by chemical exchange distillation are reviewed in this article. With a brief introduction of the principle of the separation, the progress on the research of this method and the problems relating to the separation coefficient are discussed. Several new donors, including nitromethane, acetone, methyl isobutyl ketone (MIBK) and diisobutyl ketone (DIBK), which have large separation factors are introduced. The complexes of these new donors and boron trifluoride (BF$_3$) are more stable than those of using the donors examined before. Among these new donors nitromethane could be a promising substitute for donors in present use to develop new technology of separating boron-10.
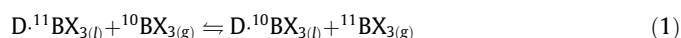
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1. Introduction

Natural boron consists of two stable isotopes: B-10 and B-11 with the abundances of 19.19% and 80.11% (Qiu, 1990) respectively. B-10 has a thermal-neutron capture cross-section of as large as five times that of natural boron and 7.7×10^5 times that of B-11 (Healy and Palko, 1958). Therefore, B-10 is widely used in nuclear industry, military industry (Ye and Zhou, 1998; Zhang, 1983; Verbeke et al., 2000), etc.

As the main production method, the separation of B-10 from natural boron has received wide attention for years (Palko and Drury, 1964; Saxena et al., 1961; Conn and Wolf, 1958; Palko, 1959; Liebscher et al., 2005; Zawisky et al., 2004; Gupta, 1992). Though a variety of methods are available for boron isotope separation, only chemical exchange distillation has been applied in industrial scale production of B-10 (Sergei, 2001). However, relatively low separation coefficients of donors, which would lead to large investment in equipment and the complexity of operation,

still remain an important issue of the separation of B-10 and B-11. In this article, advances in boron-10 separation by chemical exchange distillation are reviewed and some novel donors bringing better separation effect are introduced.

2. Boron-10 enrichment by chemical exchange distillation

The principle of boron-10 enrichment by chemical exchange distillation can be demonstrated by the following chemical reaction:

$$\text{D} \cdot {}^{11}\text{BX}_{3(l)} + {}^{10}\text{BX}_{3(g)} \rightleftharpoons \text{D} \cdot {}^{10}\text{BX}_{3(l)} + {}^{11}\text{BX}_{3(g)} \tag{1}$$

In Eq. (1), X represents H, CH$_3$ or halogen, D represents the donor (generally Lewis alkali) and D·BX$_3$ represents the complex compound.

The separation coefficient α of chemical reaction (1) is described with Eq. (2):

$$\alpha = \frac{[\text{D} \cdot {}^{10}\text{BX}_{3(l)}][{}^{11}\text{BX}_{3(g)}]}{[\text{D} \cdot {}^{11}\text{BX}_{3(l)}][{}^{10}\text{BX}_{3(g)}]} = \frac{[{}^{10}\text{B}/{}^{11}\text{B}]_{(l)}}{[{}^{10}\text{B}/{}^{11}\text{B}]_{(g)}} \tag{2}$$

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As shown in Table 1 (Frank, 1995), most separation coefficients are between 1 and 1.1060. It, therefore, would require hundreds of theoretical stages and considerably large reflux ratio which needs to large diameter of distillation columns for a specified product abundance of B-10. So it is vitally important to select appropriate donors for chemical exchange distillation.

The vapor of BX_3 and the liquid of $D \cdot BX_3$ contact stage by stage in distillation column during the isotope exchange reaction (Palko and Drury, 1967, 1969), thus B-10 and B-11 are enriched in the liquid phase and the vapor phase respectively. Halogen X and electron donor D are the dominant influence factors of exchange efficiency and their selection principles are as follows:

(1) Large separation coefficient α is preferred in order to decrease the number of theoretical plates needed for a specified product purity.
(2) Time needed to reach chemical exchange balance should be short so as to increase the production capacity.
(3) BX_3 must be easy to dissociate from the complex compound so that it is easy to obtain product and recover the donor for circulation use. This process can be described as chemical reaction Eq. (3) and the reversible reaction should be carried out quantitatively by heating and cooling.

$$BX_3 + D \leftrightharpoons BX_3D \qquad (3)$$

(4) High stability of $D \cdot BX_3$ is necessary, and therefore, undesired side reaction should be avoided.

According to principles (1)–(4), BF_3 is generally used at present to concentrate B-10 by chemical exchange for it is a good electron acceptor as Lewis acid (Healy and Palko, 1958). Nevertheless, only 9 kinds of atoms can act as electron donors to BF_3. They are H, N, O, F, P, S, Cl, Se and Te. Among them only N, O and S is in agreement with principles (1)–(4). Table 1 displays the separation coefficients of various electron donors as complex agent when separating B-10 (Frank, 1995; Palko et al., 1958; Palko and Drury, 1967; Jiang et al.).

3. Progress on B-10 separation

The separation of B-10 was started during World War II. Aether was originally selected as the donor (Palko and Drury, 1961a,b,1964; Saxena et al., 1961) and the process condition was: a glass distillation column with a height of 4 m and a diameter of 19 mm, and packing Dixon ring of 1.6 mm × 1.6 mm were adopted. The operation temperature was 70 °C and the pressure was 2.7 kPa at the top and 4.0 kPa at the bottom. The operation cycle lasted 88 days and the yield of B-10 was 2 kg/year with a mass purity of 83%. However, due to the irreversible decomposition of $(C_2H_5)_2O \cdot BF_3$, the decomposition rate of the feed was 12% per day. Higher temperature (70 °C) and high vacuum were required in this process, which consequently limited the production capacity.

Later, aether was replaced with ether and the industrial equipment which can yield 300 kg B-10 (95%) per year was built (Conn and Wolf, 1958). The process condition was as follows: 9 cascaded columns made of Monel steel were adopted. The diameters of the first 3, the second 3 and the final 3 columns were 457.2 mm, 304.8 mm and 152.4 mm respectively. The columns had an average height of 8.33 m and were packed with Stedman Packing. The operation pressures and temperatures were 20 kPa/90 °C at the top and 38.7 kPa/104 °C at the bottom. Compared with the former donor aether, although the irreversible decomposition still existed, the decomposition rate of the feed was only 1.2% per day and the vacuum was allowed to be ten times lower. Production yield increased obviously, yet a certain degree of vacuum was still necessary.

At present, anisole, instead of ether, is widely used in the production of B-10. Compared with ether, anisole has a higher single stage separation coefficient. The process condition is as follows: the whole apparatus consists of four parts: the exchange column, the decomposer column, the recombination device and the solvent purification tank. The copper exchange column is 81.3 m high and operates at 25 °C and normal pressure. The decomposition rate decreases remarkably to only 0.01% in every operation circle.

Katalnikov (Frank, 1995) explored the kinetics and thermodynamics in the separation of B isotopes by chemical exchange distillation using complex anisole, and demonstrated two ways to improve the process: (1) operate at a high pressure so that the capacity of the column would be increased and the kinetics would be improved and (2) apply ideal temperature gradient technology to optimize the separation process. In the past few years, Weijiang Zhang, et al. (Jiang et al., 2007; Han et al., 2007, 2006; Wang et al., 2006; Yu et al., 2005) experimentally studied problems such as decomposition reaction and evaluation of donors in chemical

Table 1
Separation of coefficient α of chemical exchange system for different donors.

Sequence number	Complex compound	Temperature (K)	α	$\log \alpha = a/T + b$
1	$(CH_3)_2O \cdot BF_3$	303	1.027	
2	$(C_2H_5)_2O \cdot BF_3$	293	1.034	
3	$(C_4H_9)_2O \cdot BF_3$	293	1.029	
4	$(CH_3)_2S \cdot BF_3$	298	1.036	$16.9/T - 0.0440$
5	$(CH_3)_2Se \cdot BF_3$	298	1.033	$8.13/T - 0.0131$
6	$(C_2H_5)_2N \cdot BF_3$	298	1.023	
7	$(ClC_2H_4)_2O \cdot BF_3$	298	1.040	$15.323/T - 0.03447$
8	$C_6H_5OH \cdot BF_3$	298	1.027	$10.315/T - 0.02423$
9	$C_6H_5OCH_3 \cdot BF_3$	298	1.030	$9.8753/T - 0.02005$
10	o-CH_3-$C_6H_4OCH_3 \cdot BF_3$	298	1.029	
11	m-CH_3-$C_6H_4OCH_3 \cdot BF_3$	298	1.033	
12	p-CH_3-$C_6H_4OCH_3 \cdot BF_3$	298	1.022	
13	p-Cl-$C_6H_4OCH_3 \cdot BF_3$	300	1.039	
14	$C_6H_4(OCH_3)_2 \cdot BF_3$	298	1.048	
15	$C_6H_5OC_2H_5 \cdot BF_3$	298	1.042	$12.918/T - 0.02573$
16	$C_6H_5OC_2H_4Cl \cdot BF_3$	298	1.054	
17	$CH_3COOC_2H_5 \cdot BF_3$	298	1.036	$32.50/T - 0.09354$
18	$CH_3Cl \cdot BF_3$	165	1.021	
19	$CHClF_2 \cdot BF_3$	165	1.017	
20	Cis-2-$C_4H_8 \cdot BF_3$	165	1.020	
21	$Trans$-2-$C_4H_8 \cdot BF_3$	165	1.011	
22	$SO_2 \cdot BF_3$	177	1.022	

exchange distillation. Modeling and simulation were also carried out by them to illustrate and optimize the separation process, which provide an effective way for further studies.

4. New donors for B-10 separation

Because of the crucial importance of B-10, significant progress on B-10 separation and concentration has been made in recent years and a plenty of new donors have been found. Any compound that can form a complex compound with BF$_3$ is a potential donor. However, it is difficult to experimentally explore the effectiveness of all these potential donors in the separation of B-10. Therefore, it is wiser to test some typical ones in group compounds. Many group compounds have been researched such as ethers, ammonia and sulfides (shown in Table 1).

Herbst and McCandless (1994) initially studied ketones as the donors in B-10 concentration of by chemical exchange distillation. First, ketones were tested to select the ones that form complex compounds with BF3. Second, the combination rate of the selected donors and the melting points of their complex compounds were found to determine the appropriate temperature for the measurement of the vapor–liquid equilibrium (VLE) data. Acetone, acetophenone, methyl isobutyl ketone (MIBK), nitromethane, diisobutyl ketone (DIBK) and dimethyl sulfoxide (DMSO) were experimentally studied and the result showed that acetone, MIBK and nitromethane are more suitable for the VLE experiment (the combination rates of them and the melting points of their complex compounds are presented in Table 2 (Frank, 1995)).

The single stage separation coefficients of CH$_3$NO$_2$, acetone, MIBK and DIBK have been measured at different temperatures and the fitting relation between separation coefficient α and temperature T has been obtained and presented in Table 3 (Herbst and McCandless, 1994).

The curves of the fitting equation in Table 3 are shown in Fig. 1 (Eldred et al., 2000; Ownby, 2004). The curve of theoretical maximum value in Fig. 1 is estimation curve calculated by the vibrational partition function of statistical thermodynamics. The maximum values of ketone are all greater than those of ether. The measured maximum value of CH$_3$NO$_2$ is much higher than its theoretical one, which makes it a unique compound. The probable reason is that CH$_3$NO$_2$ has two oxygen atoms and can provide two electron donating sites. Thus, it is still possible for excessive BF$_3$ in the liquid phase to form the complex compound with BF$_3$·CH$_3$NO$_2$ and the final molar ratio of BF$_3$ to CHNO$_2$ could be greater than 1:1. A similar compound C$_6$H$_5$NO$_2$ is also used as a donor to separate B-10. The separation coefficient of BF3·C$_6$H$_5$NO$_2$ is 1.030 at 280 K (Palko, 1965), while the maximum theoretical value is 1.050 when the temperature is lower than 300 K. It is experimentally observed that BF$_3$ is immiscible with BF$_3$·C$_6$H$_5$NO$_2$. The comparison between these two systems proves that the dual sites theory of isotope exchange is reasonable for the complex compound BF$_3$·CHNO$_2$. In a 435 h experiment, no decomposer of BF$_3$·CH$_3$NO$_2$ was discovered and CH$_3$NO$_2$ proved to be the most ideal donor to replace the existed donors for

Table 2
Melting point and combining rate of complex compounds formed by the combination of BF$_3$ and ketone.

Donor	Melting point of complex compound	Mole ratio of BF$_3$ to donor
Nitromethane	−46 to −48	1.4–1.6
Acetone	16–18	1.0–1.2
MIBK	16–18	1.0–1.2
DIBK	16–18	1.0–1.2

Table 3
Result of isotope exchange reaction for the combination of BF$_3$ and different donors.

Complex compound	Temperature (K)	α	$\log \alpha = a/T + b$
BF$_3$·CH$_3$NO$_2$·BF$_3$	273	1.081	$38.45/T - 0.0627$
	288	1.074	
	303	1.066	
BF$_3$·acetone·BF$_3$	298	1.041	$59.58/T - 0.1597$
	308	1.033	
	318	1.028	
BF$_3$·MIBK·BF$_3$	298	1.041	$9.504/T - 0.0071$
	308	1.036	
	318	1.039	
BF$_3$·DIBK·BF$_3$	298	1.045	$31.758/T - 0.0625$
	308	1.042	
	318	1.038	
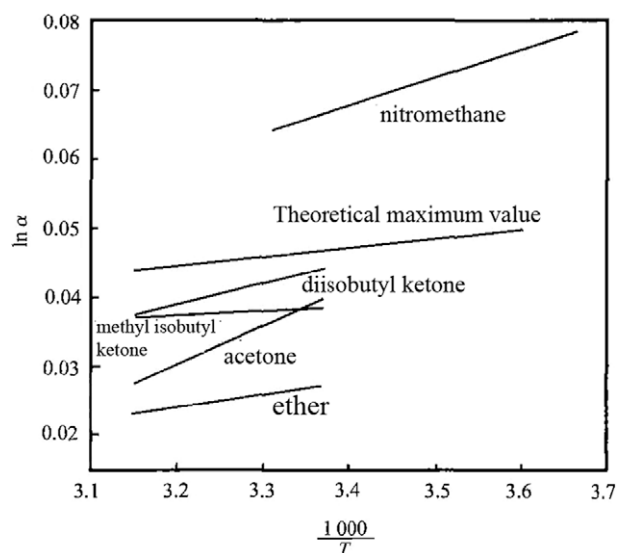
Fig. 1. The relation curve of temperature and separation coefficients of BF$_3$ combined with different donors.

B-10 separation because of its good performance. For instance, the equipment size could be remarkably reduced, which would consequently reduce the operation cost. According to modeling analysis, B-10 with a purity of 95% in mass can be produced using CH$_3$NO$_2$ as the donor with two columns with 95 and 71 theoretical stages. The operation pressure and temperature are atmospheric pressure and 25 °C respectively. Weijiang Zhang, et al. (Han, et al.) used anisole, nitromethane, acetone, methyl isobutyl ketone as the donors and prepared four complex compounds. In their research the basic properties of the four complex compounds were experimentally investigated respectively, which can provide the important data for pilot and industrial scale production of boron isotopes. These preliminary studies indicate that the boron fluoride with nitromethane or acetone system with higher separation coefficient is superior to the anisole system used currently. Considering the previous researches, CH$_3$NO$_2$ would possibly be the best donor at present for B-10 separation by chemical exchange distillation.

5. The explosive nature of nitromethane

Nitromethane has some odd properties, due to the singular weirdness of the nitro group. The electron-withdrawing nature of

the group makes it a decent acid; in neutral (i.e., pH 7) water, about 1 in 1000 molecules of nitromethane will have a formal negative charge on the carbon and exist as $CH_2NO_2^-$. These "carbon acids" are not plentiful, and their properties make them useful in organic synthesis. The "nitro" part of nitromethane does not disappoint if you associate the prefix/word with nitrous oxide and TNT, either; nitromethane is a very energetic compound and can be explosive (it was used in the Oklahoma City bombing). It is relatively insensitive especially compared to compounds like nitroglycerine and TNT. Still, the explosiveness of nitromethane was discovered by accident. One key element to explosives (and certain specialty fuels) is that they contain their own oxidizers; nitromethane can actually burn in the absence of air, yielding nitrogen, hydrogen, carbon monoxide, and water vapor. There is still energy to be obtained from the CO and H_2, though; with sufficient oxygen, it will go all the way to CO_2, nitrogen, and water. This is the case in drag racing and model airplanes; nitromethane contains about 25% of the energy of gasoline but takes only about an eighth the oxygen to burn completely. This means that engines can run much "richer" (i.e., with less air in the cylinder); hence the use in dragsters.

6. Conclusion

CH_3NO_2 and ketones such as acetone, MIBK and DIBK are all stable donors which can form stable complex compounds with BF_3. The separation coefficients of these four donors are all greater than those of two existed systems $(C_2H_5)_2O\cdot BF_3$, $(CH_3)_2O\cdot BF_3$ and $C_6H_5OCH_3\cdot BF_3$. Furthermore, the separation coefficient of CH_3NO_2 is greater than its theoretical maximum value. This makes CH_3NO_2 a highly effective and valuable donor for B-10 separation, which could markedly reduce the equipment investment and operation time. For boron-10 separation by chemical exchange distillation, the search for novel more effective donors and their application in industrial production, remains significant and still require further researches.

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