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Improved Donors for the Separation of the Boron Isotopes by Gas–Liquid Exchange Reactions

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ABSTRACT

Chemical exchange between gaseous boron trifluoride (BF_3) and the liquid BF_3·dimethyl ether complex has been used extensively for the commercial fractionation of boron isotopes. Several compounds never before studied as donors in the isotope exchange reaction were examined to determine if they were viable replacements for the dimethyl ether system. For the first time, ketones were studied as donors in the boron isotope exchange reaction. The ketones examined were acetone, methyl isobutyl ketone, and diisobutyl ketone. The ideal single stage separation factors, α, measured for these ketones were between 1.038 and 1.043 at 30°C. The observed separation factor for a fourth donor system, nitromethane, was 1.067 at 30°C, well above that predicted by theory or observed for any known BF_3/donor system. For each of the systems studied, the separation factors were greater than the value of $\alpha = 1.027$ reported for the dimethyl ether/BF_3 system at 30°C. In view of the experimentally observed separation factors, these donor systems are potential replacements for dimethyl ether in large-scale boron isotope fractionation schemes. It is concluded that plant size could be significantly reduced by using any of these donors rather than dimethyl ether.

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INTRODUCTION AND BACKGROUND

Naturally occurring boron is comprised of two isotopic forms. The mass 10 isotope, ^{10}B, has a relative abundance of 19.8 atom% while the remainder, or 80.2%, consists of the mass 1 isotope, ^{11}B.

The impetus for the isotopic fractionation of boron arises primarily from the contrasting difference in thermal neutral capture cross sections. Boron-10 has a thermal neutral capture cross section of 3837 barns, while that of ^{11}B is only 0.005 barns. As a composite of the two isotopes, naturally occurring boron has a thermal neutron capture cross section of approximately 750 barns. Consequently, ^{10}B is roughly 5 times more effective than naturally occurring boron, 20 times more effective than lead, and nearly 500 times more effective than concrete as a neutron shielding material. It is precisely this propensity for thermal neutron capture which makes ^{10}B enriched materials a useful commodity.

The nuclear related industries are the predominant consumers of ^{10}B. Enriched boron-10 compounds are used for standby liquid control systems in boiling water reactors. Breeder reactors use ^{10}B enriched carbide for control rods. Boron-10 enriched boric acid is used as a chemical shim for reactivity control in pressurized water reactors. Boron-10 enriched alloys are used for criticality control in nuclear fuel casks, as construction material in storage racks, and as neutron shielding around reactors. It is also used in instrumentation for both neutron density and dosage. Medical research with ^{10}B enriched compounds has indicated a promising method for the nonsurgical removal of malignant brain tumors.

Goals of this study included the examination of several donors for isotope exchange systems which have not been previously reported in the literature.

Isotope Exchange Processes

Isotope exchange processes for ^{10}B enrichment are characterized by reactions of the type

$$^{10}BX_{3(g)} + {}^{11}BX_3{\cdot}Donor_{(l)} \rightleftharpoons {}^{11}BX_{3(g)} + {}^{10}BX_3{\cdot}Donor_{(l)} \qquad (1)$$

where X is generally H, CH_3, or a halogen. The "complex," $BX_3{\cdot}Donor$, is a molecular addition compound, and the donor is a Lewis base or electron pair donor. The equilibrium constant for Reaction (1) is given by

$$K_{eq} = \frac{[^{11}BX_{3(g)}][^{10}BX_3{\cdot}Donor_{(l)}]}{[^{10}BX_{3(g)}][^{11}BX_3{\cdot}Donor_{(l)}]} = \frac{[^{10}B/^{11}B]_{(l)}}{[^{10}B/^{11}B]_{(g)}} \qquad (2)$$

where brackets represent the equilibrium concentrations of the respective species.

Most known exchange systems pertinent to boron isotopes have values of the equilibrium constant in the range of $1 \leq K_{eq} < 1.06$. That the equilibrium lies slightly to the right in Reaction (1) forms the basis for the separation. The small value of K_{eq} suggests the need of a multistage exchange process in order to obtain a significant degree of separation.

Utilization of the isotopic exchange reaction requires the passage of gaseous BX_3 and liquid complex in a stagewise process. Thus, ^{10}B concentrates in the liquid phase while ^{11}B concentrates in the gaseous phase. Pertinent considerations focus primarily on the selection of X and the donor molecule in Reaction (1). These considerations include:

(a) The largest possible value of the equilibrium constant, K_{eq}, in order to minimize the necessary number of stages for a given enrichment.

(b) The equilibrium must be rapidly established, e.g., isotopic exchange needs to be kinetically rapid in order to maintain a high throughput in a continuous system.

(c) BX_3 must be readily liberated from the complex for product recovery, recirculation, and reuse of the separative agent or donor. In this regard, it is desirable that the formation reaction

$$BX_3 + \text{Donor} \rightleftharpoons BX_3\cdot\text{Donor} \tag{3}$$

be quantitatively reversible simply by addition or removal of heat.

(d) The BX_3·donor complex must be sufficiently stable so as not to decompose into unwanted reaction products. Such irreversible decomposition would result in ^{10}B enriched product losses with the attendant loss of BX_3 and donor.

Selection of X

Virtually all systems studied to date have used the first member of the halogen family, fluorine, as X in the isotopic exchange reaction. This consideration largely stems from Criteria (a) and (d) above and is associated with the excellent electron acceptor capabilities of BF_3 (3, 4). Use of BF_3 as the Lewis acid in the isotope exchange reaction has been justified on theoretical grounds as well (24). Consequently, the isotope exchange reaction may be rewritten for subsequent discussions as

$$^{10}BF_{3(g)} + {}^{11}BF_3\cdot\text{Donor}_{(l)} \rightleftharpoons {}^{11}BF_{(3)} + {}^{10}BF_3\cdot\text{Donor}_{(l)} \tag{4}$$

In addition to BF_3, several brief studies utilizing BCl_3 as the Lewis acid in the isotopic exchange reaction have been conducted (3, 4, 10, 12). In all reported instances, the equilibrium constant for the BF_3 systems was larger than for similar BCl_3 systems. Consequently, the use of BCl_3 as the acid in isotopic exchange was abandoned.

Donor Selection

The species BF_3·Donor in Eq. (4) is a molecular adduct formed between BF_3 and an electron pair donor. This type of compound formation is a classical example of Lewis acid–base chemistry. The Lewis acid, BF_3, accepts a lone electron pair from the basic donor atom which is typically bound in a molecular species.

Boron trifluoride has been touted as the most powerful acceptor molecule (Lewis acid) known, yet the number of atomic species capable of donating electrons to BF_3 is relatively small (2). The nine elements H, N, O, F, P, S, Cl, Se, and Te, in certain of their compounds, are capable of donating electrons to BF_3 (3).

Of the aforementioned criteria, (a) and (d) limit the donor atom to predominantly N, O, or S, although systems containing other donors have been examined (3, 4). Table 1 lists the donor molecules which have been studied, the associated equilibrium constants, and the literature references for the pertinent study.

The standard by which an "improved" isotope separation process is compared is the production scale method involving BF_3 and the BF_3–dimethyl ether complex. From Table 1, the equilibrium constant at 30°C for this system is $K_{eq} = 1.027$. The actual separation factor observed for the process is $\alpha = 1.014$ with the reduction due primarily to incomplete dissociation of the complex in the vapor phase and solubility of BF_3 in the liquid complex (1, 3, 19).

The donor species listed in Table 1 were studied pursuant to development of an improved separation process with respect to the dimethyl ether–BF_3 system. An improved system would be subject to all criteria previously outlined. Examination of Table 1 is indicative that a number of exchange systems possess a larger equilibrium constant (Criterion a) than the dimethyl ether system. Most of these systems were dismissed based on failure to meet one or another of the remaining criteria. In a number of cases, a donor was eliminated prior to obtaining experimental equilibrium data.

Studies with anisole as the donor species in the isotope exchange reaction indicated this system was indeed superior to dimethyl ether (3, 13). The promising experimental results for the anisole–BF_3 exchange reaction prompted both bench-scale and pilot-plant studies (21, 22). The conclusion of these studies was that the anisole process was a definite improvement

TABLE 1

Review of Previously Studied Donor Molecules in the Isotopic Exchange Reaction (4)

Donor		K_{eq}[a]		References
		30°C	0°C	
Oxygen Donors				
1. Methyl ether	$(CH_3)_2O$	1.027	1.034	3,4,9
2. Ethyl ether	$(C_2H_5)_2O$	1.031	1.037	3,4,14
3. *n*-Butyl ether	$(C_4H_9)_2O$	—	—	3,4,9
4. Tetrahydrofuran	$(CH_2)_4O$	1.026	1.031	3,4,10
5. Phenol	C_6H_5OH	1.024	1.040	3,4,11,12
6. Anisole	$C_6H_5OCH_3$	1.030	1.039	3,4,12,13
7. Phenetole	$C_6H_5OC_2H_5$	1.039 1.042 (25°C)	1.051	3,4,5
8. *n*-Butyl phenyl ether	$C_6H_5OC_4H_9$	1.026 (25°C)	—	4,7
9. Ethyl formate	$HCOOC_2H_5$	1.029 (20°C)	—	4,8,9
10. Ethyl acetate	$CH_3COOC_2H_5$	1.033 (28°C)	—	4,6
11. Ethyl propionate	$C_2H_5COOC_2H_5$	1.019 (43°C)	—	4,6
12. Sulfur dioxide	SO_2	—	—	17,18
13. Dimethyl sulfoxide[b]	$(CH_3)_2SO$	1.040	1.036	16
14. Diphenyl ether	$(C_6H_5)_2O$	—	—	3
15. Nitrobenzene	$C_6H_5NO_2$	1.03 (7°C)	—	3,10
Sulfur Donors				
16. Methyl sulfide	$(CH_3)_2S$	1.037	1.046	3,4,9,20
17. Ethyl sulfide	$(C_2H_5)_2S$	1.037	1.043	3,4,14
18. *n*-Butyl sulfide	$(C_4H_9)_2S$	1.032	1.040	3,4,12,15
19. Diphenyl sulfide	$(C_6N_5)_2S$	—	—	3,10
20. Thiophenol	C_6H_5SH	—	—	3,10
21. Ethyl mercaptan	C_2H_5SH	—	—	3
22. Butyl mercaptan	C_4H_9SH	—	—	3
Nitrogen Donors				
23. Triethyl amine	$(C_2H_5)_3N$	1.022	1.028	3,4,14
24. *N*-Methyl diphenyl amine	$(C_6H_5)_2NCH_3$	—	—	3,10
25. *N*,*N*-Dimethyl aniline	$C_6H_5N(CH_3)_2$	—	—	3,10
Miscellaneous				
26. Methyl selenide	$(CH_3)_2Se$	1.032	1.039	3,4,9
27. Methyl telluride	$(CH_3)_2Te$	—	—	3,9
28. Methyl isocyanide	CH_3NCO	—	—	3,10

[a] Equilibrium temperatures other than 30 or 0°C are given in parentheses.

[b] Isotopic equilibrium between the gas and solid phases:

$$^{10}BF_{3(g)} + {}^{11}BF_3\cdot DMSO_{(s)} \rightleftharpoons {}^{11}BF_{3(g)} + {}^{10}BF_3\cdot DMSO_{(s)}$$

over the dimethyl ether system and was amenable to plant-scale application. Despite the positive results suggesting its use as the separative agent, anisole use was never incorporated into the large-scale process for fractionation of the boron isotopes process.

It was postulated that phenetole would be a better donor for isotope fractionation than anisole, but the appropriate bench-scale and pilot-plant studies have not been performed (4).

The purpose of the current study was to examine previously unstudied donors to determine if such donors would be viable replacements for the dimethyl ether/BF_3 system. The separation factor α rather than the "true" equilibrium constant, K_{eq}, was experimentally measured for the new donors to accomplish this goal.

Theoretical Maximum K_{eq}

Vibrational partition functions obtained from statistical thermodynamics and the appropriate spectroscopic data provide the theoretical basis for estimating the maximum obtainable equilibrium constant of any BF_3·Donor system. At 303 K, the maximum theoretical equilibrium constant corresponds to K_{eq} = 1.047; at 250 K the maximum value corresponds to K_{eq} = 1.056 (24). The linear extrapolation of K_{eq} as a function of temperature through these two points is of interest and is given by

$$\ln \alpha = \frac{12.233}{T(\mathrm{K})} + 0.00556 \qquad (5)$$

Equation (5) represents the theoretical maximum value the separation factor may assume at a given temperature. The separation factors for the donor systems studied in this work will subsequently be compared with the theoretical maximum values of α from Eq. (5). Note that if the appropriate spectroscopic data for a particular complex is available, the expected equilibrium constant for any BF_3·Donor system may be theoretically determined at a specified temperature (24).

EXPERIMENTAL DETERMINATION OF SEPARATION FACTORS

The number of molecular species capable of forming complexes with BF_3, and thus potentially useful as donors in the isotope exchange reaction, is virtually limitless. As indicated previously (refer to Table 1), only a select few of the vast number of potential donors have been examined in the isotope exchange reaction. The systematic examination of each possible donor compound would be a horrendous undertaking. Rather, a more prudent approach is the systematic examination of a number of species from characteristic classes of compounds to determine the potential usefulness of these materials in the exchange reaction. This is apparently the approach taken by previous researchers, and a number of classes of compounds have been examined, e.g., ethers, amines, sulfides, etc.

Examination of the relevant literature indicates that carbonyl compounds have never been studied as donor species in boron isotope exchange reactions. Furthermore, studies utilizing ketones as the donor have never been reported. Molecular addition compounds between BF_3 and the carbonyl groups of acetone, acetaldehyde, trimethyl acetaldehyde, methyl nonyl ketone, and camphor are known (2). This study was directed at examining various carbonyl compounds, specifically ketones, as the donor species in the isotope exchange reaction. Emphasis was placed on determination of the separation factors for these $BF_3 \cdot$Donor systems.

Numerous compounds were prescreened as donors to determine if the BF_3 complexes with these materials actually existed. Once the existence of the complex was established, the molar ratio of BF_3 absorbed per mole of donor material and the freezing point of the resultant liquid complex were also determined. These prescreening experiments provided a measure of the solubility of gaseous BF_3 in the liquid complex and were used to determine the appropriate temperatures at which gas/liquid equilibrium data could be obtained.

Prescreening experiments with acetone, acetophenone, methyl isobutyl ketone (MIBK), diisobutyl ketone (DIBK), nitromethane, and dimethyl sulfoxide (DMSO) were performed. Based on these initial experiments, the donors selected for study in equilibrium experiments with BF_3 were acetone, MIBK, DIBK, and nitromethane. Due primarily to unacceptable physical properties, the acetophenone/BF_3 and DMSO/BF_3 systems were found to be unsuitable for boron isotope fractionation by chemical exchange methods.

Experimental Reagents

Unless otherwise noted, materials were used as received with no attempt at further purification.

Boron trifluoride, BF_3, was obtained from the Matheson Gas Company and was of chemical purity (c.p.) grade with a minimum reported purity of 99.5% BF_3. This gas was used as the boron feed in all experiments. Mass spectral analysis indicated the boron isotopes were present in approximately the natural abundance (19.7% ^{10}B, 80.3% ^{11}B).

High purity helium was obtained from the Linde Company with a minimum reported purity of 99.995% He. The high purity helium (HP He) was used as a purge gas to eliminate entrained air, and thus atmospheric moisture, from experimental equipment prior to use of BF_3.

Other chemicals were obtained from Aldrich Chemical Co. in the highest purity available and used without further purification, with the exception of nitromethane which was redistilled to remove residual water.

Experimental Equipment and Procedures

Details of the experimental procedure for determination of α together with analytical procedures can be found in Reference 23, but are briefly outlined here for continuity.

The experimental equilibrium cell designed to obtain separation factors associated with the isotope exchange reaction is shown in Fig. 1. The cell consisted of a cylindrical vessel machined from 316 stainless steel. The internal volume of the cell was approximately 265 mL. The cell lid was secured by machine screws and incorporated a Viton O-ring to facilitate a leak-free seal. The cell lid contained gas inlet and outlet ports, a thermowell, and a pressure transducer port. A liquid circulating pump withdrew the liquid phase from a port near the bottom of the cell body and returned the liquid near the top of the cell through a sparger placed in the

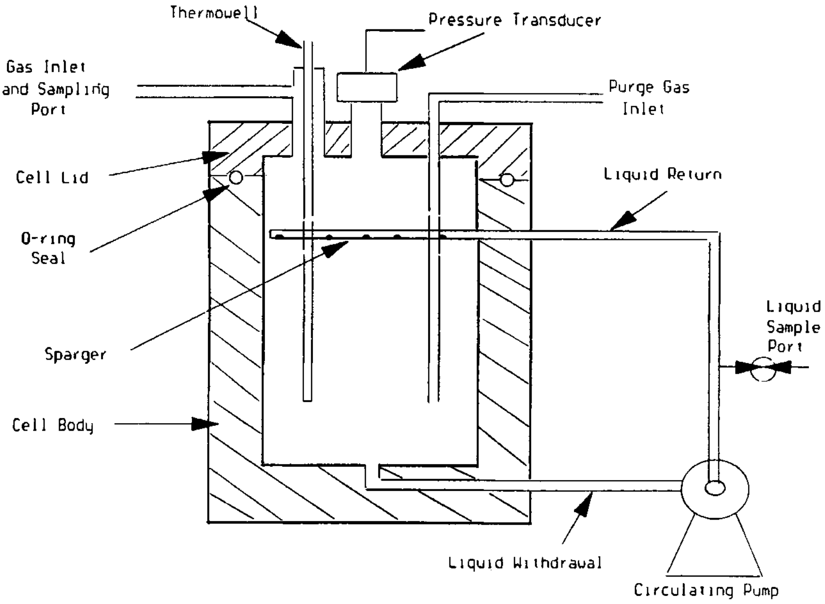

FIG. 1 Schematic of the equilibrium cell used to obtain isotopic equilibrium data.

vapor space just under the cell lid. The circulation and sparging action of the liquid phase provided agitation of the cell contents. A valved, small diameter tube placed in the circulating pump return line between the pump and the cell body provided a simple means of removing a small amount of the liquid complex for the isotopic abundance analysis.

A known volume (≈45 to 65 mL) of the donor liquid was placed into the equilibrium cell. The cell lid was then sealed in place. The cell was purged with high purity helium and evacuated under vacuum to remove any entrained air (and thus atmospheric moisture) from the cell. Once the cell was evacuated, only the pure donor material remained sealed in the equilibrium cell. Donor losses were expected during the evacuation process, but the amount of material lost was unknown. The cell was then placed in a constant temperature bath preset to the desired equilibrium temperature. Once the cell and its contents reached the temperature of the bath, BF_3 was slowly added to the system. The internal pressure was continuously monitored during BF_3 addition. Thus, the liquid complex was formed in situ, and after the pressure stabilized at between 8 to 14 psig, the complex formation process was assumed complete and the BF_3 feed to the cell was shut off.

The cell and its contents were then allowed to stand at the desired equilibrium temperature for an appropriate length of time. Usually 12 to 24 hours were allowed to establish the isotopic equilibrium between the two phases. Samples of both the gas and liquid phases were withdrawn from the cell, and the boron isotopic ratios were determined by mass spectroscopy. The separation factor for the given BF_3/donor at the specific equilibrium temperature was then evaluated from this information. The sampling and analysis process was repeated several times at a given equilibrium temperature. The temperature was then changed, and the associated separation factor was determined in an analogous manner at the new equilibration temperature. Thus, a single experiment provided the separation factor for a particular BF_3/donor system as well as the temperature dependence of α.

Mass Spectroscopic Isotopic Abundance Analysis

An analysis of the boron isotope abundance ratio for both the gas and liquid phases was required to determine the separation factor, α, evaluated from the relationship

$$\alpha = \frac{[^{10}B/^{11}B]_{(l)}}{[^{10}B/^{11}B]_{(g)}} \tag{6}$$

The separation factor was determined directly from Eq. (6) using mass spectroscopic analysis of the two phases. Consequently, the molar quantities of BF_3 and pure donor in the equilibrium cell were not required for the evaluation of α. It was only necessary that an excess amount of gaseous BF_3 be present in the cell for exchange with the BF_3 bound in the liquid complex.

The analysis of the isotopic ratio in the liquid phase, $[^{10}B/^{11}B]_{(l)}$, presents a number of problems due to the difficulties associated with sampling the liquid phase and quantitative recovery of BF_3 from the liquid complex. Therefore, previous researchers have not attempted isotopic analysis of the liquid molecular addition compound. These problems were overcome by developing a novel analytical technique for determining the boron isotopic ratio in the equilibrated liquid phase (23). The evaluation of the liquid phase isotopic composition constitutes the first known attempt at such an analysis. Consequently, this work was expected to provide actual values of α for the first time.

RESULTS AND DISCUSSION

Since the experimental and analytical techniques used to study chemical exchange in this research were new and untested, it was necessary to establish their validity. This task was accomplished by examination of a BF_3/Donor system studied by previous researchers with results available in the literature. Once the validities of the experimental and analysis procedures were proven, new systems could be confidently examined with these techniques.

The BF_3/phenetole system was chosen to further develop and test the experimental and analytical techniques. Phenetole was chosen as the donor material since the $BF_3\cdot$phenetole complex is reported to have a respectable separation factor of $\alpha = 1.051$ at 0°C (3). Furthermore, this liquid complex is reportedly quite stable with regards to irreversible decomposition (4).

Several experiments were conducted to validate the new experimental technique and analytical procedure with the phenetole/BF_3 isotope exchange system. Details of these preliminary experiments are presented in Reference 23. The agreement between the experimental separation factors and those reported in the literature for the BF_3/phenetole system were sufficient to lend credibility to the newly developed experimental technique and analytical procedure.

Certain physical properties of the various $BF_3\cdot$Donor compounds are of interest. For example, the freezing point of the liquid complex fixes the lower temperature at which the gas–liquid equilibrium could be measured and determines the minimum operating temperature of process scale fractionation facilities. It is also of practical interest to know the molar

TABLE 2
Selected Properties of the BF_3·Donor Complexes

Donor	Freezing point (°C)	Moles BF_3 absorbed per mole of donor
Nitromethane	−46 to −48	1.4 to 1.6
Acetone	16 to 18	1.0 to 1.2
MIBK	16 to 18	1.0 to 1.2
DIBK	16 to 18	1.0 to 1.2

ratio of BF_3 absorbed per mole of donor species. This determines the amount of material necessary to form the respective BF_3·Donor complexes. Since references to the complexes formed between BF_3 and nitromethane, acetone, MIBK, or DIBK are unavailable in the literature, these physical properties were measured directly during this work. These properties are summarized in Table 2.

Tables 3 through 6 indicate separation factor as a function of temperature obtained experimentally for the different BF_3·Donor systems examined. Reported values of α for the BF_3·dimethyl ether system are also indicated for comparative purposes. Note that for any given temperature,

TABLE 3
Experimental Results in the Isotopic Exchange Reaction (4) between BF_3 Gas and the BF_3Nitromethane System[a]

Temperature	Separation factors, α	Average α	Reported α BF_3·dimethyl ether
0°C (273 K)	1.075		
	1.079		
	1.085	1.081 ± 0.004	1.034
	1.085		
	1.082		
15°C (288 K)	1.075		
	1.079	1.074 ± 0.006	1.030
	1.067		
30°C (303 K)	1.064		
	1.066	1.066 ± 0.002	1.027
	1.066		

[a] Best fit linear equation through the above BF_3·nitromethane experimental data:

$$\ln \alpha = \frac{38.45}{T\,(\mathrm{K})} - 0.0627$$

TABLE 4
Experimental Results in the Isotopic Exchange Reaction (4) between BF_3 Gas and the BF_3·Acetone System[a]

Temperature	Separation factors, α	Average α	Reported α BF_3·dimethyl ether
25°C (298 K)	1.044		
	1.038	1.041 ± 0.003	1.028
	1.042		
35°C (308 K)	1.033	—	1.027
45°C (318 K)	1.030		
	1.027	1.028 ± 0.002	1.024
	1.028		

[a] Best fit linear equation for the above BF_3·acetone experimental data:

$$\ln \alpha = \frac{59.58}{T\,(\mathrm{K})} - 0.1597$$

TABLE 5
Experimental Results in the Isotopic Exchange Reaction (4) between BF_3 Gas and the BF_3·MIBK System[a]

Temperature	Separation factors, α	Average α	Reported α BF_3·dimethyl ether
25°C (298 K)	1.030		
	1.040		
	1.044		
	1.043	1.041 ± 0.005	1.028
	1.041		
	1.042		
	1.044		
35°C (308 K)	1.029		
	1.041	1.036 ± 0.007	1.027
	1.043		
	1.031		
45°C (318 K)	1.045		
	1.038		
	1.034	1.039 ± 0.004	1.024
	1.037		
	1.041		
	1.040		

[a] Best fit linear equation for the BF_3·MIBK experimental data:

$$\ln \alpha = \frac{9.504}{T\,(\mathrm{K})} - 0.0071$$

TABLE 6
Experimental Results in the Isotopic Exchange Reaction (4) between BF_3 Gas and the BF_3·DIBK System[a]

Temperature	Separation factors, α	Average α	Reported α BF_3·dimethyl ether
25°C (298 K)	1.047 1.045 1.044	1.045 ± 0.002	1.028
35°C (308 K)	1.043 1.042 1.040	1.042 ± 0.002	1.027
45°C (318 K)	1.044 1.038 1.033	1.038 ± 0.006	1.024

[a] Best fit linear equation for the BF_3·DIBK experimental data:

$$\ln \alpha = \frac{31.758}{T\,(\mathrm{K})} - 0.0625$$

the separation factors associated with each of the donor systems are substantially higher than those associated with the dimethyl ether/BF_3 system. The benefits of increasing the separation factor include the potential to substantially reduce the size of the necessary process equipment associated with large-scale fractionation of boron isotopes. This effect will be discussed subsequently (vide infra). The best fit linear equation relating the natural logarithm of separation factor, ln α, to temperature (Kelvin scale) are also indicated for each of the donor systems. These equations were obtained by linear regression of the experimental data presented in each table.

Comparison of Experimentally Studied Systems

The scope of this study focused primarily on the experimental determination of the separation factor as a function of temperature for the various systems examined. The temperature dependence and magnitude of the separation factor for the BF_3/donor systems studied in this research are presented in Fig. 2. Literature data for the dimethyl ether system are also indicated in Fig. 2 for comparison.

The separation factor, α, increases with decreasing temperature, as indicated by the positive slope of the lines shown in Fig. 2. The positive slope indicates that the exchange process is exothermic. This trend is expected and predicted from theory and also from the results of previous research-

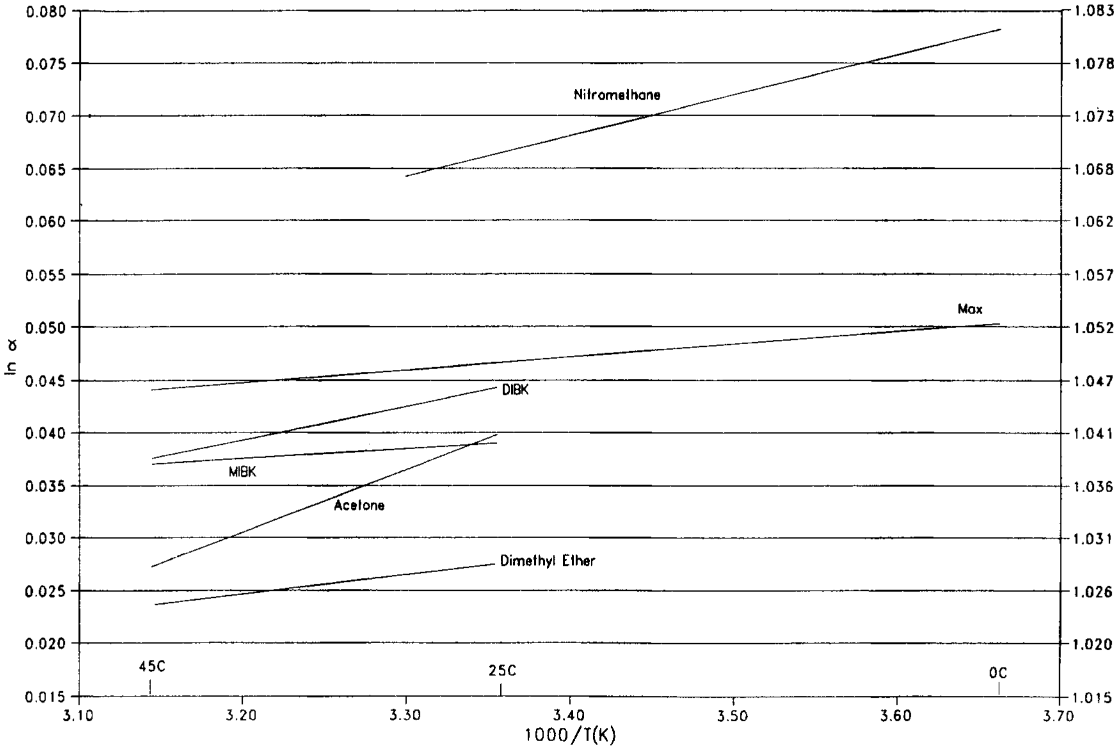

FIG. 2 Comparison of experimental systems studied in isotopic exchange.

ers for similar exchange systems (24). Based on the slope of the experimental lines shown in Fig. 2, the temperature dependence of separation factor varies from donor to donor and increases in the order

Acetone > Nitromethane > DIBK > MIBK

Depending on the BF_3/donor system, the variation of α with temperature may be an important consideration in the design and operation of a large-scale cascade. For a strongly temperature-dependent donor, such as acetone or nitromethane, a substantial increase in cascade performance may be realized by isothermal operation of the exchange column.

The magnitude of α at a specific temperature varies from donor to donor. This variation is a result of differences in substituent groups attached to the basic center in the donor molecule. The increasing inductive effect of larger alkyl groups should strengthen the BF_3—donor bond and result in lower values of the separation factor (4). The opposite trend was observed with the ketones studied in this work, with separation factor increasing in the order DIBK > MIBK > acetone. This is attributed to steric interferences, presumably between the β- or γ-carbon in the isobutyl group and the normal positioning of fluorine in BF_3.

As indicated in Fig. 2, the nitromethane/BF_3 experimental results are substantially greater than those predicted by the theoretical maximum. The nitromethane/BF_3 system is the only known instance in BF_3 gas/liquid isotope exchange where separation factors in excess of the theoretical maximum have been observed. These extraordinary results may be justified based on the unique properties of the nitromethane molecule.

The donors which have been examined in this study, and nearly all of those examined by previous researchers, have been *single site* donors. Consequently, there is only *one* basic center containing the required lone pair of electrons necessary for bonding in formation of the BF_3–donor molecular addition compound. The nitromethane molecule contains two oxygen atoms, and consequently has *two* such donor sites available. It is conceivable that excess BF_3 dissolved in the liquid phase beyond that mandated by a 1:1 molar complex could be associated or weakly bound to the second oxygen of the nitromethane/BF_3 complex. The isotope effect between the complex and the excess BF_3 could potentially result in larger values of the separation factor than for the corresponding single site donors.

The only system similar to nitromethane which has been previously examined and is briefly described in the literature (10) is that of nitrobenzene, $(C_6H_5)NO_2$. In that work a separation factor for the nitrobenzene/BF_3 system of 1.03 at 7°C was reported. This is well below the theoretically predicted maximum of $\alpha = 1.05$ at 7°C. That study also reported BF_3 gas was virtually insoluble in the liquid nitrobenzene/BF_3 complex. Comparison of these two systems provides some evidence regarding the existence of a double site mechanism in isotope exchange for the nitromethane/BF_3 system. Furthermore, the dramatic effect of substituent groups attached to the basic center of the donor molecule is indicated.

During the nitromethane/BF_3 experiment, the liquid complex was in contact with the gas phase for 435 hours (≈18 days). During this extended period of time, decomposition products were never observed in the mass spectra of the equilibrated gas or liquid samples. It was concluded that this system was extremely stable with regards to irreversible decomposition of the complex. Furthermore, nitromethane was never observed in the gas-phase samples, which indicated a relatively low vapor pressure for this complex.

The experimental evidence outlined above for the nitromethane/BF_3 system strongly suggests much potential exists for the use of nitromethane as a viable alternative donor in the boron isotope fractionation scheme. Based on the extraordinary magnitude of the separation factor, it is conceivable that a "super donor" has been discovered in this system. Further work is certainly required and strongly suggested with the nitromethane/BF_3 system to validate this supposition.

Usefulness of the Improved Donor Solvents

The benefits of increasing the separation factor in large-scale isotope fractionation is easily brought into perspective with a simple comparison based on the familiar Fenske–Underwood equation:

$$n = \frac{\ln[y_p(1 - x_w)/(1 - y_p)x_w]}{\ln \alpha} \tag{7}$$

Equation (7) provides the minimum number of ideal stages, n, required for a specified separation in an exchange column operated at total reflux. For a cascade producing 95 mol% ^{10}B product ($y_p = 0.95$) and a 5 mol% ^{10}B waste stream ($x_w = 0.05$), Eq. (7) can be simplified:

$$n = \frac{5.889}{\ln \alpha} \tag{8}$$

Minimum stage requirements are listed in Table 7 for the various donor systems based on reported values of the separation factor and Eq. (8). It is apparent that a slight increase in separation factor results in a concomitant decrease in the minimum ideal stage requirements. Consequently, a dramatic reduction in the size of the required process equipment can be

TABLE 7
Minimum Ideal Stage Requirements for a Boron Isotope Fractionation Cascade Operating at Total Reflux

Donor	Separation factor, α	Minimum number for ideal stage
Dimethyl ether	1.014	424
Acetone	1.041	147
MIBK	1.041	147
DIBK	1.045	134
Nitromethane	1.081	77

achieved if a ketone or nitromethane is used as the donor rather than dimethyl ether.

CONCLUSIONS

(1) Acetone, MIBK, DIBK, and nitromethane are suitable donors and form relatively stable liquid complexes with BF_3.

(2) Each of these four donors exhibits larger values of the separation factor than dimethyl ether in the boron isotope exchange reaction. In this regard, each is more amenable to large-scale fractionation than the dimethyl ether/BF_3 system.

(3) Nitromethane exhibits separation factors substantially higher than those predicted theoretically or for any known system in boron isotope chemical exchange reactions. This anomaly is postulated to be due to a dual site exchange mechanism. An understanding of the cause of this anomaly could provide valuable insight into the isotope exchange process and donor selection.

(4) The increased separation factor for any of the donors studied could dramatically reduce the size of a large-scale boron isotope fractionation plant and the associated process equipment.

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