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ION EXCHANGE, ISOTOPE EXCHANGE AND ISOTOPE SEPARATION

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SUMMARY

Ion-exchange and isotope-exchange reactions are discussed mainly from the theoretical point of view in order to find a general expression for the isotope separation factor (eqn. 14). The theoretical expression for the separation factor of boron isotopes is derived from eqn. 14 for the system containing aqueous boric acid with an anion-exchange resin (eqn. 20). Some experimental results for boron isotopes are given and are discussed with the use of eqn. 20.

Results obtained from a small column are also presented in order to show a new, simple procedure for boron isotope separation, which needs only boric acid as raw material, a column of a weakly basic anion-exchange resin for chromatographic purposes and water as eluting agent.

INTRODUCTION

Since Taylor and Urey¹ proposed the possibility of ion-exchange separations of isotopes in 1937, many studies have been carried out, not only to acquire fundamental knowledge but also to find practical separation systems. Among these studies, the most important work might be the theoretical work of Glueckauf² and the successful separation of nitrogen isotopes by Powell *et al.*³

In this paper, on the basis of fundamental facts of ion-exchange and isotope-exchange reactions, the further possibility of ion-exchange separation of isotopes is considered, using the case of boron isotopes as an example.

ION-EXCHANGE REACTION

The thermodynamics of pure ion-exchange reactions (with no complex formation in the system) have been intensively investigated by Gregor and Frederick⁴⁻⁶ and by Glueckauf⁷, who obtained different results. The reason for the difference has been discussed and the general expression for the equilibrium constant of pure ion-exchange reactions has been derived⁸.

The ion-exchange reaction is expressed in general as



where A and B are solvated cations having charges p and q , respectively, and R is the resinous anion.

The equilibrium constant of reaction 1, K , is given by

$$\ln K = \ln \frac{(\bar{a}_B)^p (a_A)^q}{(\bar{a}_A)^q (a_B)^p} = \frac{(\pi - P)}{RT} (q\bar{v}_{A'} - p\bar{v}_{B'}) - [q(\bar{h}_A - h_A) - p(\bar{h}_B - h_B)] \ln a_w \quad (2)$$

where a_A , a_B and a_w denote the activities of solvated cations A and B and free water W in the external solution, \bar{a}_A and \bar{a}_B are the activities of solvated cations A and B in the resin phase, π is a complicated function caused mainly by the structural strain of the resin and having the dimension of pressure, P is the external pressure, $\bar{v}_{A'}$ and $\bar{v}_{B'}$ are the partial molal volumes of the solvated cations A and B in the resin phase, and h and \bar{h} denote the solvation numbers of each cation in the external solution and the resin phases, respectively.

The definitions of the separation factor, S and the distribution coefficient, D are

$$S \equiv \frac{[\bar{B}] \cdot [A]}{[\bar{A}] \cdot [B]} \quad (3)$$

and

$$D \equiv \frac{[\bar{B}]}{[B]} \quad (4)$$

where $[]$ and $[\bar{ }]$ denote the concentrations of each species in the external solution and the resin phases, respectively.

Combining eqns. 2 and 3, we obtain

$$\ln S = \left(\frac{q}{p} - 1 \right) \ln \frac{[\bar{A}]}{[A]} + \frac{1}{p} \ln \frac{(\bar{\gamma}_A)^q (\gamma_B)^p}{(\bar{\gamma}_B)^p (\gamma_A)^q} + \frac{1}{p} \cdot \frac{\pi - P}{RT} (q\bar{v}_{A'} - p\bar{v}_{B'}) - [q(\bar{h}_A - h_A) - p(\bar{h}_B - h_B)] \ln a_w \quad (5)$$

and combining eqns. 2 and 4, we obtain

$$\ln D = \frac{q}{p} \ln \frac{[\bar{A}]}{[A]} + \frac{1}{p} \ln \frac{(\bar{\gamma}_A) (\gamma_B)^p}{(\bar{\gamma}_B)^p (\gamma_A)^q} + \frac{1}{p} \cdot \frac{\pi - P}{RT} (q\bar{v}_{A'} - p\bar{v}_{B'}) - [q(\bar{h}_A - h_A) - p(\bar{h}_B - h_B)] \ln a_w \quad (6)$$

where γ and $\bar{\gamma}$ denote the activity coefficients of each solvated ion in the external solution and the resin phases, respectively.

Eqns. 5 and 6 are the general expressions for the separation factor and the distribution coefficient of a pure ion-exchange reaction. The first term in each equation is the concentration term, which is very important when $p \neq q$, the second term is the activity coefficient term, the third is the pressure-volume term and the fourth is the solvation term.

If the system contains complex formation reactions such as



in the external solution and



in the resin phase, the general expression for the separation factor is⁹

$$\ln S_A^B = \ln S + \ln \frac{\sum_n \sum_t \beta_{nt}^A [X]^n [F]^t}{\sum_n \sum_t \beta_{nt}^B [X]^n [F]^t} - \ln \frac{\sum_n \sum_s \beta_{ns}^A [\bar{X}]^n [\bar{Y}]^s}{\sum_n \sum_s \beta_{ns}^B [\bar{X}]^n [\bar{Y}]^s} \quad (9)$$

where the β values are the stability constants of eqns. 7 and 8.

ISOTOPE-EXCHANGE REACTION

If A and B are the isotopes of a certain element M, the stability constants in reactions 7 and 8 can be expressed in terms of the isotopic reduced partition function ratio¹⁰:

$$\frac{f_{nt}}{f_{00}^0} = \frac{\beta_{nt}^A}{\beta_{nt}^B} \quad (10)$$

$$\frac{\bar{f}_{ns}}{\bar{f}_{00}^0} = \frac{\beta_{ns}^A}{\beta_{ns}^B} \quad (11)$$

where f_{nt} and \bar{f}_{ns} are the reduced partition function ratios of the chemical compounds MX_nF_t and MX_nY_s and f_{00}^0 and \bar{f}_{00}^0 are the reduced partition function ratios of the atom (M) itself in the external solution and the resin phases, respectively.

The expression for the reduced partition function ratio was skillfully derived by Urey and Rittenberg¹¹ and Bigeleisen and Mayer^{12,13}:

$$\frac{s}{s'} f = \frac{s}{s'} f \left(\frac{m'}{m} \right)^{3n/2} = \prod_{i=1}^{3N-6} \left\{ \frac{u_i}{u'_i} \cdot \frac{e^{-u_i/2}}{1 - e^{-u_i}} \cdot \frac{1 - e^{-u'_i}}{e^{-u_i/2}} \right\} \quad (12)$$

or

$$\begin{aligned} \frac{s}{s'} f &= 1 + \sum_{i=1}^{3N-6} \left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i-1}} \right) \Delta u_i \\ &= 1 + \sum_{i=1}^{3N-6} G(u_i) \Delta u_i \end{aligned} \quad (13)$$

where $(s/s')f$ is the reduced partition function ratio, f is the partition function ratio, m and m' are the atomic weights for the heavy and light isotopes, n is the number of isotopic atoms exchanged, s and s' are the symmetry numbers, u_i and u'_i are equal to $h_c \nu_i / kT$ and $h_c \nu'_i / kT$ for the heavy and light isotopic compounds and Δu_i is equal to $u'_i - u_i$.

TABLE I

REDUCED PARTITION FUNCTION RATIOS OF BORON COMPOUNDS AND EQUILIBRIUM CONSTANTS FOR BORON ISOTOPE EXCHANGE REACTIONS AT 300°K

	${}^{10}\text{B}^{19}\text{F}_3$	${}^{10}\text{B}^{19}\text{F}$	${}^{10}\text{B}({}^{16}\text{O}^{-}\text{H})_3$	${}^{10}\text{B}({}^{16}\text{OH})_4$	${}^{10}\text{B}({}^{12}\text{CH}_3)_3$	${}^{10}\text{B}^{35}\text{Cl}_3$	${}^{10}\text{BH}_3\text{CO}$	$\text{HCN}^{10}\text{BCl}_3$	${}^{10}\text{BH}_4$	${}^{10}\text{B}^{79}\text{Br}_3$	${}^{10}\text{B}^{35}\text{Cl}_4$	${}^{10}\text{B}^{79}\text{Br}_4$	${}^{10}\text{B}^{127}\text{I}_3$
sf/s'	1.2387	1.2178	1.1979	1.1760	1.1693	1.1356	1.1319	1.1271	1.1190	1.1127	1.1072	1.0898	1.0893
${}^{10}\text{B}^{19}\text{F}_3$	1.0000	1.0172	1.0341	1.0533	1.0594	1.0908	1.0944	1.0990	1.1070	1.1132	1.1188	1.1366	1.1372
${}^{10}\text{B}^{19}\text{F}_4$	1.0000	1.0166	1.0355	1.0355	1.0415	1.0724	1.0759	1.0805	1.0883	1.0945	1.0999	1.1175	1.1180
${}^{10}\text{B}({}^{16}\text{OH})_3$		1.0000	1.0186	1.0186	1.0245	1.0549	1.0583	1.0628	1.0705	1.0766	1.0819	1.0992	1.0997
${}^{10}\text{B}({}^{16}\text{OH})_4$			1.0000	1.0000	1.0057	1.0356	1.0390	1.0434	1.0509	1.0569	1.0621	1.0791	1.0796
${}^{10}\text{B}({}^{12}\text{CH}_3)_3$				1.0000	1.0000	1.0297	1.0330	1.0374	1.0450	1.0509	1.0561	1.0729	1.0734
${}^{10}\text{B}^{35}\text{Cl}_3$						1.0000	1.0033	1.0075	1.0148	1.0206	1.0257	1.0420	1.0425
${}^{10}\text{BH}_3\text{CO}$					-		1.0000	1.0043	1.0115	1.0173	1.0223	1.0386	1.0391
$\text{HCN}^{10}\text{BCl}_3$							1.0000	1.0000	1.0072	1.0129	1.0180	1.0342	1.0347
${}^{10}\text{BH}_4$									1.0000	1.0057	1.0107	1.0268	1.0273
${}^{10}\text{B}^{79}\text{Br}_3$										1.0000	1.0050	1.0210	1.0215
${}^{10}\text{B}^{35}\text{Cl}_4$											1.0000	1.0160	1.0164
${}^{10}\text{B}^{79}\text{Br}_4$												1.0000	1.0005

Eqns. 12 and 13 make it possible to calculate the reduced partition function ratio, if the spectroscopic data are known for each isotopically different compound. Further, even if the spectroscopic data for the rarer isotopic compounds are not known, the approximate estimation of the reduced partition function is possible with use of the G and F matrix method¹⁴.

The reduced partition function ratios of boron compounds and the equilibrium constants of isotope exchange reactions between two boron compounds are calculated and shown in Table I.

ION-EXCHANGE SEPARATION OF ISOTOPES

Combining eqn. 9 with eqns. 10 and 11:

$$\ln S_A^B = \ln \sum_{n=0}^r \sum_{t=0}^T x_{nt} f_{nt} - \ln \sum_{n=0}^r \sum_{s=0}^S \bar{x}_{ns} f_{ns} \quad (14)$$

where x_{nt} and \bar{x}_{ns} are the mole fractions of each chemical species in the external solution and the resin phases, respectively, and are expressed as

$$x_{nt} = \frac{\beta_{nt}^B [X]^n [F]^t}{\sum_{n=0}^r \sum_{t=0}^T \beta_{nt}^B [X]^n [F]^t} \quad (15)$$

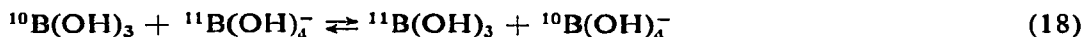
$$\bar{x}_{ns} = \frac{\bar{\beta}_{ns}^B [\bar{X}]^n [\bar{Y}]^s}{\sum_{n=0}^r \sum_{s=0}^S \bar{\beta}_{ns}^B [\bar{X}]^n [\bar{Y}]^s} \quad (16)$$

Eqn. 14 is the general expression for the isotope separation factor with complex formation reactions and describes the relationship among three different kinds of quantities, the separation factor, the reduced partition function ratio and the mole fraction, each of which can be measured experimentally by different methods.

In the case of boron isotopes, if boric acid is dissolved in water, the slight dissociation



will occur and the isotope exchange equilibrium



will be maintained.

The equilibrium constant of reaction 18 is simply the ratio of the reduced partition function ratio of B(OH)_3 to that of B(OH)_4^- and, as shown in Table I, the value is 1.0186 at 300°K.

This means ¹¹B will prefer to move in the neutral species B(OH)_3 and ¹⁰B in the anionic species B(OH)_4^- and the isotopic difference is 1.0186 which is very high as the isotopic standard. This high value, however, is not unexpected if it is remembered that the structural change between two species is very great, from a triangle in

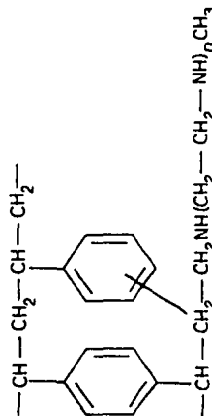
TABLE II

VALUES FOR THE SEPARATION FACTOR OF BORON ISOTOPES OBTAINED BY EQUILIBRIUM AND BREAKTHROUGH EXPERIMENTS AT 25°C AND THE VALUES FOR THE MOLE FRACTION OF $B(OH)_3$ IN THE RESIN PHASE ESTIMATED BY EQN. 20

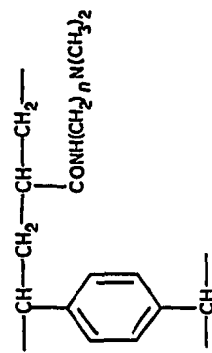
Parameter	Resin*								
	Diaion WA-21	Diaion WA-10:	Diaion PA-312:						
Boron concentration in the external solution (mole/l)	0.0107	0.102	0.518	0.101	0.0991	0.501	0.0104	0.109	0.501
Boron concentration in the resin phase (mole/l)	0.09	2.0	11	0.05	1.1	8.6	4.2	9.5	14
$S^{0.0}$: equilibrium expt.	1.015	1.013	1.011	1.016	1.012	1.007	1.019	1.013	1.007
$S^{0.0}$: breakthrough expt.	1.019	1.014	1.012	1.016	1.014	1.010	—	—	—
$\bar{x}_{B(OH)_3}$	0.10	0.31	0.42	0.16	0.31	0.52	0.00	0.31	0.63
pH in the resin phase	8	8	7	9	8	7	10	8	7

* Structures:

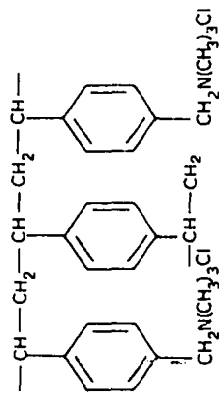
Diaion WA-21:



Diaion WA-10:



Diaion PA-312:



$B(OH)_3$ to a tetrahedron in $B(OH)_4^-$. This potentiality of isotopic difference in boric acid solution can be realized by the use of an anion-exchange resin, which prefers to pick up the anion $B(OH)_4^-$.

Involving only two chemical species, $B(OH)_3$ and $B(OH)_4^-$, a simple expression for the isotope separation factor can be derived from the general eqn. 14:

$$\ln S_{11}^{10} = \ln f_{B(OH)_3} - \ln [\bar{x}_{B(OH)_3} f_{B(OH)_3} + (1 - \bar{x}_{B(OH)_3}) \bar{f}_{B(OH)_4}] \quad (19)$$

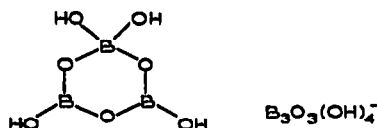
As the difference of the reduced partition function ratios of same chemical species between the external solution and the resin phases is very small, we can make the approximations $f_{B(OH)_3} = \bar{f}_{B(OH)_3}$ and $\bar{f}_{B(OH)_4} = f_{B(OH)_4}$ and, using the value 1.019 for $f_{B(OH)_3}/f_{B(OH)_4}$, eqn. 19 is reduced to

$$S_{11}^{10} = [\bar{x}_{B(OH)_3} + 1.019^{-1} (1 - \bar{x}_{B(OH)_3})]^{-1} \quad (20)$$

BORON ISOTOPE SEPARATION WITH USE OF ANION-EXCHANGE RESIN

The experimental results obtained by equilibrium and breakthrough experiments are summarized in Table II. The values for the mole fraction of $B(OH)_3$ in the resin phase, $\bar{x}_{B(OH)_3}$, are calculated by means of eqn. 20 and are shown in Table II. The separation factor of boron isotopes is not much influenced by the kind of anion-exchange resin used, but is very much influenced by the boric acid concentration in the external solution: the higher the concentration the lower is the separation factor or, in other words, the higher the value of $\bar{x}_{B(OH)_3}$, the lower is the separation factor.

The presence of the neutral species, $B(OH)_3$, in the anion-exchange resin phase may be caused by the formation of polyborate anions such as



As observed in the above structure, the polyborate anions contain not only the $B(OH)_4^-$ structure but also the $B(OH)_3$ structure and it is reported that the amount of polyborate is large at high concentrations of boric acid especially at pH 7-8 (ref. 15). In Table II, the high values for $\bar{x}_{B(OH)_3}$ can be seen in the resin phases of high boron concentrations and of pH 7-8.

As mentioned above, the separation factor is not much influenced by the kind of the anion-exchange resin, but if we use a weakly basic anion-exchange resin such as Diaion WA-21, the boric acid absorbed on the resin column can easily be eluted with water. This may be a very useful attribute in the practical separation of isotopes. If we used a strongly basic anion-exchange resin column, we must start by preparing the resin column in the free base form, then prepare a boric acid band, elute the band

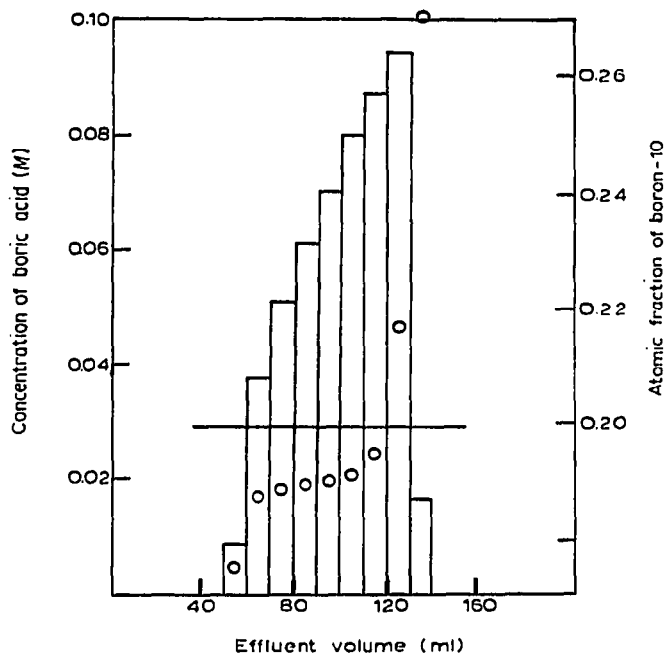


Fig. 1. Results obtained using a column of Diaion WA-21, 100-200 mesh, with a load of 10 ml of 0.501 *M* boric acid at a temperature of 40°C, flow-rate 10 ml/h·cm² and water as eluting agent. □, Concentration of boric acid; ○, atomic fraction of boron-10; —, atomic fraction of boron-10 in natural sample.

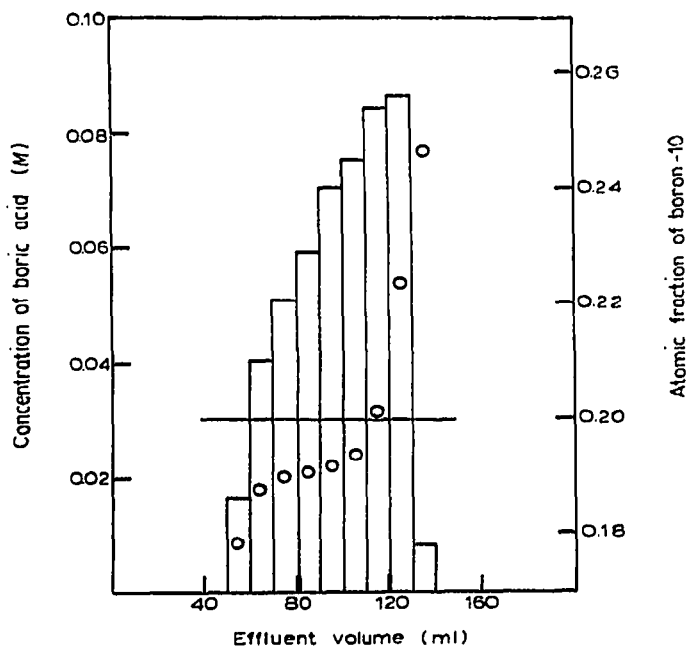


Fig. 2. Results obtained using a column of Diaion WA-21, 100-200 mesh, with a load of 10 ml of 0.497 *M* boric acid at a temperature of 40°C, flow-rate 19 ml/h·cm² and water as eluting agent. □, Concentration of boric acid; ○, atomic fraction of boron-10; —, atomic fraction of boron-10 in natural sample.

with a certain acid and regenerate it so as to prepare the column in the free base form. On the other hand, if we use a weakly basic anion-exchange resin column, the cycle is much simpler: We start from the free base form, prepare a boric acid band and elute the band with water, so that simultaneously the column is converted into the free base form.

Some results obtained on a small column of diameter 1 cm and about 50 cm long are shown in Figs. 1 and 2. The separation is so good and the procedure is so simple that it can be concluded that the system is particularly useful for the separation of boron isotopes.

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