Fundamental Studies on the Ion-Exchange Separation of Boron Isotopes

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The single-stage separation factors for boron isotopes between an ion-exchange resin and an external solution were determined, using an ion-exchange breakthrough operation. The lighter isotope boron-10 was considerably enriched in the anion-exchange resin phase. The separation factor was very much influenced by the boric acid concentration in the external solution, but not as much influenced by the kind of the anion exchange resin used and operation temperature. The separation factor increased with a decrease in the boric acid concentration of external solution from 1.008 (0.501 mol/l)to 1.016 (0.010 mol/l). The value of the separation factors obtained experimentally were compared with those estimated on the basis of the theory of the two-phase distribution of isotopes.

Naturally occurring boron contains 19.8% boron-10 and 80.2% boron-11. The absorption cross section of natural boron for thermal neutrons is 752 barns; for pure boron-10 and boron-11, the corresponding values are 3837 and 0.005 barns, respectively.[1] This means that isotopically pure boron-10 is five times more effective as a neutron shield than natural boron. The large cross section of boron-10 for thermal neutrons and the α particle emission subsequent to neutron capture have suggested the possible use of boron compounds (enriched in boron-10) for neutron therapy of malignant tissue. This kind of nuclear approach is being actively pursued in the world, especially for treatment of brain tumors[2] and melanotic cancer.[3] In view of this characteristic of boron-10, it is not surprising that a demand for the separation of boron isotopes arose in very early stage of the nuclear era.

The first experiment on ion-exchange separation of boron isotopes had been done by Makishima and coworkers in 1959.[4] In this experiment, boric acid solution was passed through a column packed with a strong-base anion exchange resin (Amberlite CG-400-I) in hydroxide form. The boric acid concentration and the atomic fraction of boron-10 in each fraction of the effluent were measured. It was found that the lighter isotope boron-10 was enriched in the resin phase. and that the values of the single-stage separation factors were 1.010 for aqueous 0.03 mol/l boric acid, and 1.016 for 0.1 mol/l boric acid in 8% glycerol–water solution. Large-scale experiments stimulated by Makishima's work were carried out in France[5] and Spain.[6] Nowadays, at the Isobor company in France isotopically pure boron-10 and 11 are being produced from natural boron by means of ion-exchange chromatography, using a strong-base anion exchange resin.

The present authors have pointed out that this process can be greatly improved by using a weak-base resin in free-base form or a strong-base resin in fluoride form, and thus dispensing with regeneration of the resin in the column.[7–9] In these experiments, a high porosity type weak-base anion exchange resin (Diaion WA 21) in the free-base form, and a gel type strong-base anion exchange resin (Diaion SA 20A) in the fluoride form were used. An aqueous solution containing 5 mmol of boric acid was passed through columns packed with these resins, and the borate band formed in the column was eluted with pure water. It was found that:

(1) Boron-10 was considerably enriched in the rear part of the band, and depleted in the frontal part.

(2) The boric acid charged to the column was completely eluted with pure water.

The remarkable feature of this separation system is that it is scarcely necessary to regenerate the resin in the column. Recently, one of the authors has discussed the further possibility of ion-exchange separation of isotopes, giving the case of boron isotopes as an example.[10]

The purpose of the present research is to determine the effects of temperature, the concentration of boric acid charged to the column, and the kind of resin used, on the single-stage separation factor of boron isotopes between the resin and the external solution phases.

Experimental

The ion-exchange resins used were Diaion WA 21, WA 30, WA 10, PA 312, SA 20A, and PK 224. Diaion WA 21 is a high porosity type weak-base anion exchange resin with primary and secondary amine groups. Diaion WA 30 is a high porosity type weak-base anion exchange resin with tertiary amine groups. Diaion WA 10 is a gel type weak-base anion exchange resin with tertiary amine groups. Diaion PA-312 is a porous type strong-base anion exchange resin with quaternary amine groups. Diaion SA 20A is a gel type strong-base anion exchange resin with quaternary amine groups. Diaion PK 224 is a porous type strong-acid cation exchange resin with sulfonic groups. It is known that the increasing order of resin-basicity is as follows:

Diaion WA 21 < Diaion WA 10 < Diaion WA 30
< Diaion SA 20A < Diaion PA 312

The boric acid used in these experiments was recrystallized twice from aqueous solution. The other chemicals were analytical grade materials used without further purification.

Equilibrium Experiment. The columns used were about 20 cm in length and 1 cm in diameter, surrounded by a jacket through which water from a thermostat was circulated so that the columns were maintained at constant temperature within ±0.2 °C. The resins described above were packed in the columns, and subjected to chloride–hydroxide or sodium–hydrogen cycles in a usual manner to ensure regeneration and uniform packing. The columns were thoroughly washed with distilled water after converting the resins into the hydroxide or the hydrogen forms. A boric acid solution was placed in a reservoir above the columns which was connected to the columns with a polyolefin tube. In order to establish isotopic equilibrium between the resin in the column and the boric acid solution, the amount of boric acid charged to the column was more than 50 times the total exchange capacity of the column. The flow rate of the boric acid solution was controlled with a screw cock at the bottom of the column.

After equilibrium was established between the resin and the external solution phases, some samples of the resin in the column were extracted with a pipette, filtered through a sintered glass disk with suction for 10 min, and weighed. Then the boric acid absorbed by the resin was eluted with pure water or other suitable eluting agents, and the concentration of boric acid in the effluent was measured with a Varian Tectron Model 1100 flame photometer and the amount of boric acid absorbed by the resin was calculated. The resin was weighed after being dried in an air bath with autometic controller at 50—60 °C for about 48 h and kept in a desiccator (with silica gel as a drying agent) for 24 h.

The isotopic analysis of boric acid absorbed by the resin was carried out using a Varian Mat CH 5 mass spectrometer by means of the surface ionization method.[11] The mass peaks used were those at *m/e* 88 ($Na_2{}^{10}BO_2{}^+$) and 89 ($Na_2{}^{11}BO_2{}^+$). This mass region was repeatedly scanned about 40 times for each sample, and the ratio of peak heights at *m/e* 88 to *m/e* 89 was calculated as an average of these scans. The atomic fraction of boron-10 was determined from the ratio of the peak-heights. The standard deviation of the isotopic analysis of boron-10 was less than ±0.0002 in every case. Some other samples of the resin in the column, in equilibrium with the external solution of boric acid, were pipetted together with the external solution into eight test tubes. A few drops of an indicator were added to each of these test tubes. The indicators used were methyl red, phenol red, thymol blue, phenolphthalein, cresolphthalein, thynolphthalein, alizarin yellow R. and the Kolthoff's universal indicator. The pH of the resin phase was roughly estimated by comparing the color of the resin with that of standard buffer solutions.

Breakthrough Experiment. A boric acid solution was passed through the same column as used in the equilibrium experiment. The superficial velocity of the boric acid solution was 13 ml h^{-1} cm^{-2}. A number of 20 ml fractions of the effluent were successively collected in 20 ml measuring flasks, and the boric acid concentration and the atomic fraction of boron-10 in these fractions were determined by the methods used in the equilibrium experiment.

Results and Discussion

The results obtained from the equilibrium and breakthrough experiments are summarized in Table 1 along with the experimental conditions. Some examples of the elution graphs obtained from the breakthrough experiment are shown in Figs. 1 through 4. The ${}^{10}_{11}S$ shown in Table 1 is the single-stage separation factor for boron isotopes between the resin and the external solution phases, defined in the following equation:

$$ {}^{10}_{11}S = \frac{\text{Total amount of boron-10 in the resin phase}}{\text{Total amount of boron-11 in the resin phase}} \times \frac{\text{Total amount of boron-11 in the external solution phase}}{\text{Total amount of boron-10 in the external solution phase}} \qquad (1) $$

In the case of the equilibrium experiment, the first term of the right hand side of Eq. 1 is the value of isotope ratio measured for the boric acid absorbed by the resin at the equilibrium, and the second term is that of the external solution which is simply the natural isotope ratio. In the case of the breakthrough experiment, ${}^{10}_{11}S$ can be calculated from the experimental data by means of the following equation,[12]

$$ {}^{10}_{11}S = 1 + \frac{1}{Q}\cdot\frac{1}{R_0(1-R_0)}\cdot(R_0-R_i)\cdot f_i \qquad (2) $$

where Q is the total amount of boron in the resin phase (mmol), R_0 the atomic fraction of boron-10 in the feed solution, R_i the atomic fraction of boron-10 in fraction i of the effluent, and f_i the total amount of boron

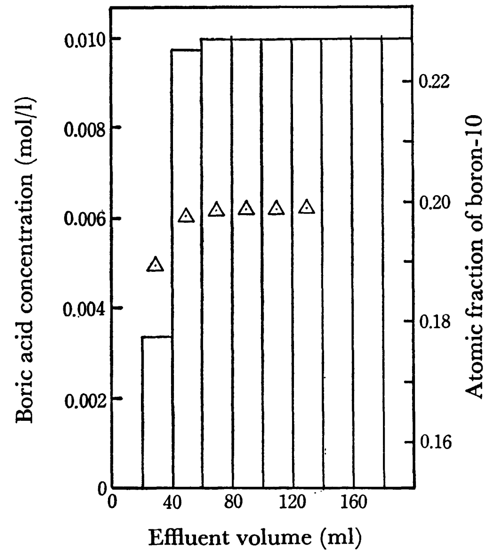


Fig. 1. Breakthrough graph.
Column: Diaion WA 21, free-base form, 20—50 mesh, 1 cm × 10 cm bed.
Load: 0.00999 mol/l boric acid.
Temperature: 25 °C.
Flow rate: 13 ml h^{-1} cm^{-1}.
□: Boric acid concentration in each effluent fraction (mol/l).
△: Atomic fraction of boron-10 in each effluent fraction.

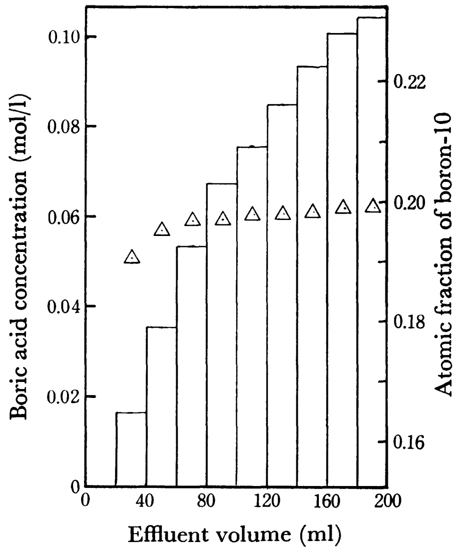


Fig. 2. Breakthrough graph.
Column, temperature, flow rate, □, and △: same as shown in Fig. 1.
Load: 0.105 mol/l boric acid.

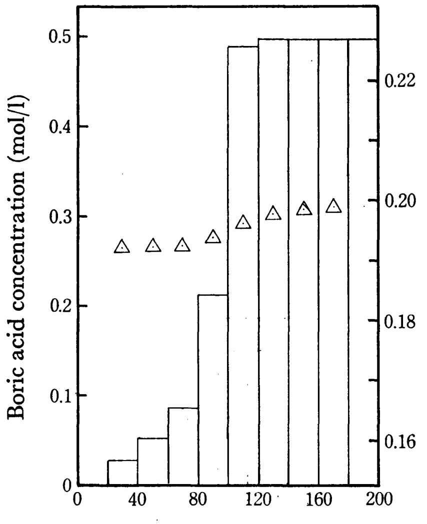


Fig. 3. Breakthrough graph.
Column, temperature, flow rate, ▭, and △: same as shown in Fig. 1.
Load: 0.496 mol/l boric acid.

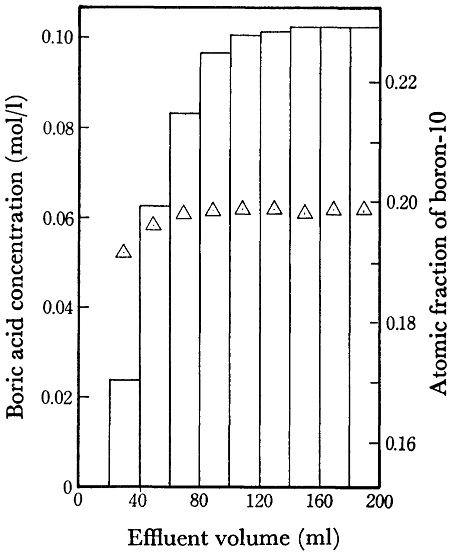


Fig. 4. Breakthrough graph.
Column, flow rate, ▭, and △: same as shown in Fig. 1.
Temperature: 40 °C
Load: 0.102 mol/l boric acid.

isotopes in fraction i (mmol). In some cases of Diaion WA 21 and Diaion WA 10, both equilibrium and breakthrough experiments were carried out. The values of ${}^{10}_{11}S$ obtained from the equilibrium experiment agreed well with those obtained from the breakthrough experiment. The values of ${}^{10}_{11}S$ shown in Table 1 are average values of ${}^{10}_{11}S$ obtained from both experiments. In other

TABLE 1. EXPERIMENTAL RESULTS AND CONDITIONS
T: Temperature, ${}^{10}_{11}S$: single-stage separation factor, q: amount of boron absorbed in resin phase, W: weight fraction of water in resin phase, M: boric acid concentration in resin phase.

Run	Resin	T (°C)	Load $B(OH)_3$ (mol/l)	${}^{10}_{11}S$ Experimental value	${}^{10}_{11}S$ Calculated value (pH)	q (mmol/g-dry resin)	W	M (mol/l)	pH of resin phase
1	Diaion WA 21	40	0.00945	1.014	1.0184(11.0), 1.0185(11.5)	0.03	0.39	0.05	11—11.5
2			0.102	1.011	1.0126(10.0)	0.69	0.43	0.91	10
3			0.494	1.008	1.0073 (8.5), 1.0080 (9.0)	8.3	0.49	8.6	8.5—9
4		25	0.0107	1.017	1.0192(11.0)	0.06	0.40	0.09	11
5			0.102	1.013	1.0094 (9.5), 1.0122(10.0)	1.6	0.43	2.1	9.5—10
6			0.518	1.011	1.0061 (8.0), 1.0065 (8.5)	10.0	0.47	11.0	8—8.5
7		5	0.0104	1.023		0.08	0.47	0.09	10.5—11
8			0.106	1.014		3.4	0.47	3.8	9.5
9			0.511	1.011		11.0	0.49	11.0	8
10	Diaion WA 10	40	0.00945	1.014	1.0185(11.5), 1.0186(12.0)	0.10	0.66	0.05	11.5—12
11			0.105	1.011	1.0132(10.0), 1.0161(10.5)	1.6	0.69	0.72	10—10.5
12			0.496	1.008	1.0080 (9.0)	17.0	0.69	7.6	9
13		25	0.0101	1.016	1.0192(11.0), 1.0193(11.5)	0.08	0.63	0.05	11—11.5
14			0.0991	1.013	1.0131(10.0)	2.5	0.68	1.2	10
15			0.501	1.009	1.0065 (8.5), 1.0072 (9.0)	19.0	0.69	8.5	8.5—9
16		5	0.511	1.013		20.0	0.70	8.6	8.5
17	Diaion WA 30	25	0.00999	1.017	1.0193(11.5)	0.20	0.50	0.20	11.5
18			0.493	1.009	1.0072 (9.0)	7.8	0.56	6.1	9
19	Diaion PA 312	25	0.0104	1.019	1.0176(12.0), 1.0190(13.0)	5.7	0.57	4.3	>12
20			0.109	1.010	1.0107(10.0)	9.9	0.51	9.5	10
21			0.501	1.007	1.0062 (8.0), 1.0065 (8.5)	13.0	0.48	14.0	8—8.5
22	Diaion SA 20A	25	0.106	1.011	1.0177(12.0), 1.0190(13.0)	7.1	0.64	4.0	12
23			0.511	1.010	1.0107(10.0)	16.0	0.65	8.6	10
24	Diaion PK224	25	0.106	1.000	1.000 (3.0), 1.000 (4.0)	0.05	0.45	0.06	<4
25			0.498	1.000	1.000 (3.0), 1.000 (4.0)	0.25	0.43	0.33	<4

cases using Diaion WA 21, Diaion WA 10, and other resins, the values of $^{10}_{11}S$ were determined from the equilibrium experiment only. Of the other symbols in Table 1, q is the mass concentration of boron absorbed in the resin phase (mmol/g-dry resin), and W is the weight fraction of water in the resin phase, defined as

$$W = \frac{W_w}{W_r + W_w} \tag{3}$$

where W_r is the weight of the dry resin, and W_w the weight of water in the resin. M is the molar concentration of boric acid in the resin phase, which can be calculated by means of the following equation:

$$M = \frac{1-W}{W} \times q \tag{4}$$

The following can be seen from Table 1 and Figs. 1—4 under the present experimental conditions:

(1) The lighter isotope boron-10 is considerably enriched in the anion exchange resin phase, while in the case of the cation exchange resin no isotope effect is found within our limits of experimental accuracy.

(2) The separation factor is very much influenced by the boric acid concentration in the external solution, but not so much influenced by the kind of anion exchange resins used nor by the operating temperature. The separation factor increases with a decrease in the boric acid concentration.

(3) The amount of boron absorbed in the weak-base anion exchange resins (Diaion WA 21 and 10) increases with a decrease in temperature at a certain concentration of boric acid in the external solution.

(4) The amount of boron absorbed in the weak-base anion exchange resins (Diaion WA 21, 10, and 30) increases remarkably with an increase of the boric acid concentration in the external solution, while in the case of the strong-base anion exchange resins (Diaion PA 312 and SA 20A) it reaches the maximum value at the relatively low concentration of boric acid.

(5) The boric acid concentration in the anion exchange resin phase is very high; that is, at an operating temperature of 25 °C, when the boric acid concentration in external solution is 0.5 mol/l its value reaches about 10 mol/l in the resin.

(6) The pH of the anion exchange resin phase in equilibrium with the external solution shows a considerably higher value (8—12) than that of boric acid solutions; 4.9 at 0.01 mol/l, 4.7 at 0.1 mol/l, 4.3 at 0.5 mol/l.

(7) The breakthrough graph is influenced effectively by the boric acid concentration of the external solution and operating temperature: Its features become sharper with a decrease in the boric acid concentration of the external solution and with an increase in the operating temperature.

The values of the separation factor obtained from the present research agree closely with those obtained for a strong-base anion exchange resin by Rosset and coworkers[5]: 1.018 at 0.0098 mol/l; 1.014 at 0.103 mol/l; 1.011 at 0.249 mol/l; 1.009 at 0.555 mol/l boric acid. This would seem to confirm the correctness of the present results.

The boron-isotope exchange reaction,

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- = {}^{11}B(OH)_3 + {}^{10}B(OH)_4^-, \tag{5}$$

occurs in aqueous solutions of boric acid. The isotope effect between a trigonal planar structure ($B(OH)_3$) and a tetrahedral structure[13,14] ($B(OH)_4^-$) as calculated from spectroscopic data on molecular vibrations, based on statistical mechanics with quantum corrections, is remarkable.[7,15,16]

The value of equilibrium constant is 1.0194 at 298.1 K as shown in Table 2. This means that boron-10 is enriched in the anionic species $B(OH)_4^-$.

It has been reported by Ingri[17] that the main species formed in aqueous solutions of boric acid are $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$. That is, the following equilibria exist in the solutions:

$$B(OH)_3 + OH^- \overset{K_1}{=} B(OH)_4^- \tag{6}$$

$$3B(OH)_3 + OH^- \overset{K_2}{=} B_3O_3(OH)_4^- + 3H_2O \tag{7}$$

$$3B(OH)_3 + 2OH^- \overset{K_3}{=} B_3O_3(OH)_5^{2-} + 3H_2O \tag{8}$$

where K_1, K_2, and K_3 are the stability constants; the respective values at 25 °C are $\log K_1 = 5.27$, $\log K_2 = 7.41$, and $\log K_3 = 11.67$. The distribution of the hydrolyzed

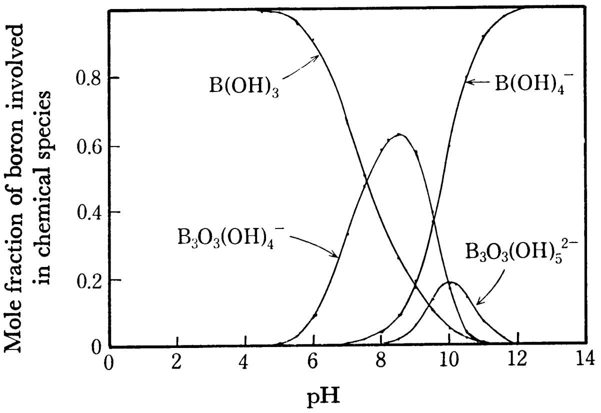


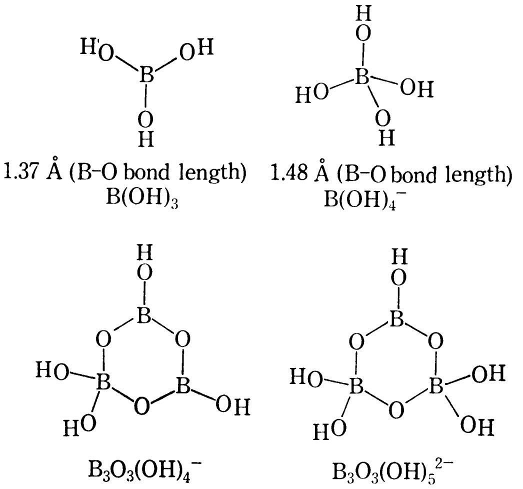
Fig. 5. The calculated distribution of the hydrolyzed species in aqueous solution of boric acid.
Total boron concentration: 0.5 mol/l.
Temperature: 25 °C.

TABLE 2. CALCULATED REDUCED PARTITION FUNCTION RATIOS FOR $B(^{16}OH)_3$ AND $B(^{16}OH)_4^-$, AND EQUILIBRIUM CONSTANTS FOR BORON ISOTOPE EXCHANGE REACTION BETWEEN $B(^{16}OH)_3$ AND $B(^{16}OH)_4^-$

$f_{B(^{16}OH)_3}$: Reduced partition function ratio for $B(^{16}OH)_3$.
$f_{B(^{16}OH)_4}$: Reduced partition function ratio for $B(^{16}OH)_4$.
$^{10}_{11}K$: Equilibrium constant for boron isotope exchange reaction between $B(^{16}OH)_3$ and $B(^{16}OH)_4^-$.

Temperature (K)	$f_{B(^{16}OH)_3}$	$f_{B(^{16}OH)_4^-}$	$^{10}_{11}K$
273.1	1.2315	1.2066	1.0206
278.1	1.2248	1.2003	1.0204
288.1	1.2123	1.1887	1.0199
298.1	1.2008	1.1780	1.0194
313.1	1.1852	1.1635	1.0187
323.1	1.1758	1.1549	1.0181
333.1	1.1671	1.1468	1.0177

species in the boric acid solution, calculated at the total boron concentration of 0.5 mol/l from the values of the stability constants described above, is represented graphically in Fig. 5. Figure 5 shows that the main species are $B(OH)_3$ at pH less than 6, $B(OH)_3$ and $B_3O_3(OH)_4^-$ in the pH range 7—8, $B(OH)_3$, $B_3O_3(OH)_4^-$, and $B(OH)_4^-$ in the pH range 8—9, $B(OH)_3$, $B_3O_3(OH)_4^-$, $B(OH)_4^-$, $B_3O_3(OH)_5^{2-}$ in the pH range 9—10, and $B(OH)_4^-$ at pH greater than 10. As mentioned above, in aqueous solution $B(OH)_3$ has a trigonal planar structure and $B(OH)_4^-$ has a tetrahedral structure. It has been also reported[18)] that polyborate ions, $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$, have both trigonal planar and tetrahedral structure: $B_3O_3(OH)_4^-$ is composed of two triangular groups and a tetrahedral group joined by three common oxygen atoms; $B_3O_3(OH)_5^{2-}$ is composed of a triangular group and two tetrahedral groups joined by three common oxygen atoms (Fig. 6).



1.37 Å (B-O bond length) $B(OH)_3$

1.48 Å (B-O bond length) $B(OH)_4^-$

$B_3O_3(OH)_4^-$

$B_3O_3(OH)_5^{2-}$

Fig. 6. Structure of boron species.

From the facts mentioned above, the main species present in the anion exchange resin phase in equilibrium with the external solution, could be $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_3O_3(OH)_5^{2-}$, while the main species in the external solution phase is $B(OH)_3$ only. Consequently, the high value of the separation factor for boron isotopes between the two phases is caused by the structure change between boron species existing in the two phases: from trigonal planar structure to tetrahedral structure. The high concentration of boric acid in the resin phase may be caused by the formation of polyborate anions. In the case of the cation exchange resin, the only species present in the two phases is $B(OH)_3$, and therefore, the value of the separation factor is approximately unity.

The separation factor (${}^{10}_{11}S$) for boron isotopes between the anion exchange resin and the external solution phases can be estimated on the basis of the theory of the two phase distribution of isotopes proposed by Kakihana,[19,20)] that is, expressed by the following equation,[7)]

$$\begin{aligned}{}^{10}_{11}S = \{&({}^{10}\overline{[B(OH)_3]} + {}^{10}\overline{[B(OH)_4^-]} + {}^{10}\overline{[B_3O_3(OH)_4^-]}\\ &+ {}^{10}\overline{[B_3O_3(OH)_5^{2-}]})/({}^{11}\overline{[B(OH)_3]} + {}^{11}\overline{[B(OH)_4^-]}\\ &+ {}^{11}\overline{[B_3O_3(OH)_4^-]} + {}^{11}\overline{[B_3O_3(OH)_5^{2-}]})\}\\ &\times ({}^{11}[B(OH)_3]/{}^{10}[B(OH)_3]) \qquad (9)\end{aligned}$$

$$\begin{aligned}= [&\bar{X}_{{}^{11}B(OH)_3} + \bar{f}_{B(OH)_3}\cdot\bar{f}^{-1}_{B(OH)_4^-}\cdot\bar{X}_{{}^{11}B(OH)_4^-}\\ &+\bar{f}_{B(OH)_3}\cdot\bar{F}^{-1}_{B_3O_3(OH)_4^-}\cdot\bar{X}_{{}^{11}B_3O_3(OH)_4^-}\\ &+\bar{f}_{B(OH)_3}\cdot\bar{F}^{-1}_{B_3O_3(OH)_5^{2-}}\cdot\bar{X}_{{}^{11}B_3O_3(OH)_5^{2-}}]\\ &\times f^{-1}_{B(OH)_3}\cdot f_{B(OH)_3} \qquad (10)\end{aligned}$$

where the bracket [ ] denotes the molar concentration of boron isotopes involved in the corresponding species, the symbol — the resin phase, X the atomic fraction of a given boron isotope in the form of the specified chemical species, f the reduced partition function ratio, and F the reduced partition function ratio of polyborate anion. Since the difference of the reduced partition function ratios of the same chemical species between the resin and the external solution phase is very small, we can make the approximations $\bar{f}_{B(OH)_3}=f_{B(OH)_3}$, $\bar{f}_{B(OH)_4^-}=f_{B(OH)_4^-}$, $\bar{F}_{B_3O_3(OH)_4^-}=F_{B_3O_3(OH)_4^-}$, $\bar{F}_{B_3O_3(OH)_5^{2-}}=F_{B_3O_3(OH)_5^{2-}}$.

The atomic fraction of boron isotope in a chemical species can be approximated by the mole fraction of the corresponding chemical species.[21)] As mentioned above, $B_3O_3(OH)_4^-$ is composed of two triangular groups and a tetrahedral group joined by three common oxygen atoms, while $B_3O_3(OH)_5^{2-}$ a triangular group and two tetrahedral groups joined by three common oxygen atoms. Therefore, the reduced partition function ratios can be approximated by the following equations,

$$F_{B_3O_3(OH)_4^-} = \frac{2f_{B(OH)_3}+f_{B(OH)_4^-}}{3} \qquad (11)$$

$$F_{B_3O_3(OH)_5^{2-}} = \frac{f_{B(OH)_3}+2f_{B(OH)_4^-}}{3} \qquad (12)$$

Equation 10 is reduced to

$$\begin{aligned}{}^{10}_{11}S = &\bar{X}_{B(OH)_3} + f_{B(OH)_3}\cdot f^{-1}_{B(OH)_4^-}\cdot\bar{X}_{B(OH)_4^-}\\ &+f_{B(OH)_3}\cdot\left\{\frac{2f_{B(OH)_3}+f_{B(OH)_4^-}}{3}\right\}^{-1}\cdot\bar{X}_{B_3O_3(OH)_4^-}\\ &+f_{B(OH)_3}\cdot\left\{\frac{f_{B(OH)_3}+2f_{B(OH)_4^-}}{3}\right\}^{-1}\cdot\bar{X}_{B_3O_3(OH)_5^{2-}} \qquad (13)\end{aligned}$$

Thus, ${}^{10}_{11}S$ is calculated as a function of pH and boric acid concentration in the resin phase from Eq. 13, using the stability constants of boron species determined by Ingri and the calculated reduced partition function ratios for $B(OH)_3$ and $B(OH)_4^-$ (Fig. 7 and Table 1). It is apparent from Fig. 7 and the calculated values of ${}^{10}_{11}S$ in Table 1 *i.e.*:

(1) The calculated separation factor increases with an increase of the boric acid concentration in the resin at pH below 8.7, but has the contrary tendency at pH above 8.7, and is independent of the boric acid concentration in the resin at pH 8.7. The formation of polyborate anions containing the tetrahedral groups may contribute to the high values of the separation factor at pH below 8.7.

(2) The calculated separation factors show roughly agreement with those obtained experimentally. The discrepancy between the calculated values and the

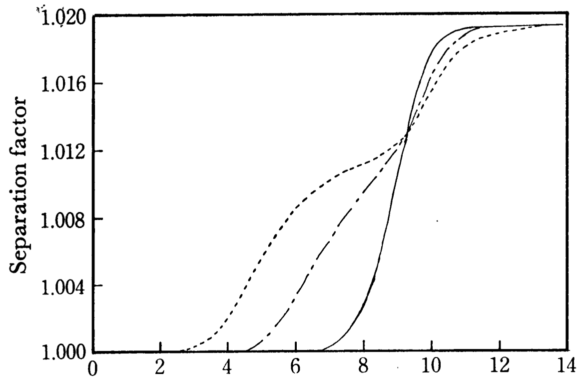


Fig. 7. Separation factor of boron isotopes calculated as a function of pH and boric acid concentration in resin phase at 25 °C.
——: The total boron concentration of 0.05 mol/l.
-·-·-: The total boron concentration of 1.20 mol/l.
------: The total boron concentration of 8.50 mol/l.

experimental values may be caused mainly by the insufficient accuracy of the resin-phase pH measurement and the use of the stability constants in such a high concentration range (up to 10 molarity), and subsidiarily by the use of the approximate values of the reduced partition function ratio for the polyborate ion. ${}^{10}_{11}S$ was also calculated at 40 °C by the use of the stability constants of boron species determined by Mesmer[22] (Table 1), and the values had a same tendency as these of ${}^{10}_{11}S$ at 25 °C.

The separation system of boron isotopes by means of weak-base anion exchange resins such as Diaion WA 21 may indeed be one of the best separation systems, because the separation factor is as high as that for the system using a strong-base anion exchange resin, the boric acid charged to the column is absorbed in the resin to a high concentration, and it can be completely eluted with pure water. The advantages of the boric acid charged to the column being easily eluted with pure water are that it is scarcely necessary to regenerate the resin in the column, and that the boric acid is free from contamination by any other chemicals.

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