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Boron Isotope Fractionation in Liquid Chromatography with Boron-Specific Resins as Column Packing Material

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ABSTRACT

Boron-specific resins with *n*-methyl glucamine as the functional group were used as column packing material of liquid chromatography for boron isotope separation. The shapes of chromatograms in reverse breakthrough experiments were heavily dependent on the pH of the eluents, and there existed a pH value at which a chromatogram of the displacement type was realized nearly ideally. The value of the single-stage separation factor for the boron isotopes varied between 1.010 and 1.022, depending on the temperature and the form of the resins. The existence of the three-coordinate boron species in addition to the four-coordinate species in the resin phase is suggested.

INTRODUCTION

Boron-10 is one of the most important nuclides in nuclear-related fields due to its large thermal neutron absorption cross-section; it is used for reactor control in nuclear fission reactors and neutron capture therapy of melanotic cancers and brain tumors. Various methods of separating ^{10}B from its heavier isotope, ^{11}B, have been investigated and developed. Liq-

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uid chromatography with anion exchangers as the column packing materials is one of them. A variety of studies on chromatographic separation of boron isotopes have been carried out, not only to investigate the feasibility of a practical separation process but also to acquire knowledge on fundamental boron isotope effects.

The first application of liquid chromatography using anion exchangers to boron isotope separation was performed by Yoneda et al. (1) in 1959. The resin they used was a strongly basic anion-exchange resin. The dependence of the single-stage $^{11}B/^{10}B$ separation factor (S) on the resin form was investigated in one of our previous papers (2). A weakly basic anion-exchange resin in the free base form was first applied to boron isotope separation by Kotaka et al. (3). Based on this fundamental study, Aida et al. (4) succeeded in obtaining a product with over 98% ^{10}B on a laboratory scale, starting with boron of the natural isotopic composition ($^{10}B \doteqdot 20\%$). The value of S achieved with weakly basic resins is relatively small, around 1.01.

Boron-specific ion-exchange resins which, as their names show, have specific affinity toward boric acids (strictly speaking, toward borate ions), could be alternatives to common strongly and weakly basic organic ion-exchange resins. In a study using a resin of this type, Itagaki et al. (5) reported S values as high as 1.02 even at 80°C. Stimulated by their work, we carried out a series of experiments on the chromatographic separation of boron isotopes using boron-specific resins. In this paper we report the results of such experiments. The aim of the present study is twofold. One is to investigate the dependence of the S value on the forms of boron-specific resins (free base vs sulfate) and on temperature (25 and 50°C). The other is to examine, using the breakthrough and reverse breakthrough techniques, the conditions of realizing a boron chromatogram of the displacement type, regarded as the most appropriate shape for isotope separation among various shapes of chromatograms.

EXPERIMENTAL

Resins and Chemicals

The resins used were boron-specific ion-exchange resins, Diaion CRB02 resin and Amberlite IRA743 resin. They were originally developed and utilized for the recovery of boron from natural waters like seawater and for the removal of boron from wastewater (6). Both resins have the same structure (cf. Fig. 1); the skeleton is the stylene–divinylbenzene copolymer, and *n*-methyl glucamine was introduced as the functional group. As can be understood from the structure, the nitrogen atom of the *n*-methyl

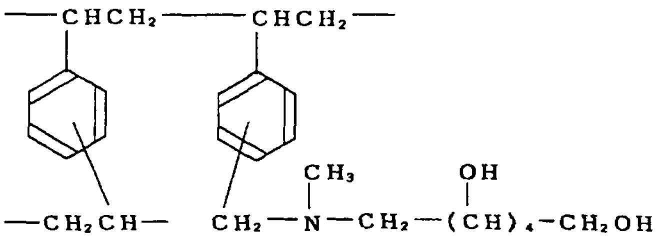
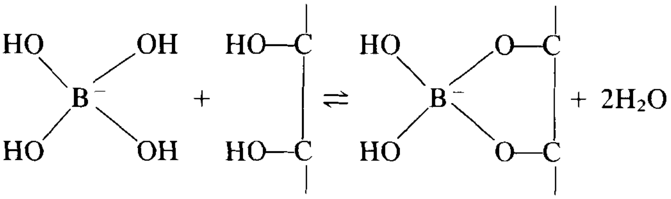


FIG. 1 The structure of Diaion CRB02 and Amberlite IRA743 resins in the free base form.

glucamine part can work as an anion-exchange site. The CRB02 and IRA743 resins can thus be regarded as weakly basic anion-exchange resins. Boron is considered to be adsorbed into the resins through the esterification of borate ions with the polyol parts of the resins (7):



(1)

The free base and sulfate forms of the resins were investigated in the present work. The adsorption isotherms obtained with aqueous boric acid solutions as external solutions are depicted in Fig. 2. A characteristic of the resins is that they can adsorb rather large amounts of boron even at very low boron concentrations in external solutions. Comparison at a given boron concentration in the external solution phase and a given temperature shows that the resin in the free base form has a larger boron uptake than the resin in the sulfate form. This is probably attributable to the difference in pH in the resin phase between the free base and sulfate forms; the pH value in the resin phase is expected to be higher for the free base form resin than for the sulfate form resin, and it is well known that esterification of the borate ion with a polyol is in general promoted at a high pH value (8, 9). For the given resin in the given form, a lower temperature results in a larger amount of boron adsorbed per 1 g of resin, although this trend is not clear for the IRA743 resin.

The reagents used were all Wako's special-grade chemicals and were used without further purification. The pure water used was once-distilled water.

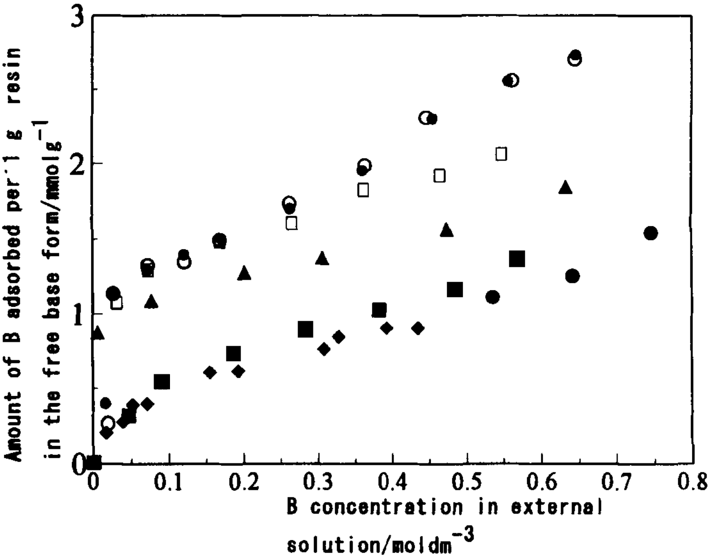


FIG. 2 Adsorption isotherms. The external solutions are aqueous boric acid solutions. (■) Resin, Diaion CRB02 in the sulfate form; temperature, 25°C. (◆) CRB02 in the sulfate form, 50°C. (□) CRB02 in the free base form, 25°C. (▲) CRB02 in the free base form, 50°C. (●) IRA743 in the free base form, 25°C. (○) IRA743 in the free base form, 50°C.

Chromatographic Process

Chromatographic experiments were carried out in the breakthrough and reverse breakthrough manners. In breakthrough experiments the resin was packed in a chromatographic column of Pyrex glass (150 cm × 1 cm I.D. or 100 cm × 1 cm I.D.) and was converted to the free base or sulfate form by the usual method. A 1 mol/dm^3 sodium hydroxide solution and 1 mol/dm^3 sulfuric acid were used as conditioning agents. After washing out the conditioning agent with pure water, an aqueous boric acid solution was fed to the column at a constant flow rate. The effluent from the column was collected and divided into fractions. In reverse breakthrough experiments an aqueous boric acid solution was fed to a chromatographic column packed with the resin in the desired form until the boron concentration of the effluent became nearly equal to that of the feed solution. Boron adsorbed on the resin was then eluted by an eluent at a constant flow rate. The effluent was collected and divided into fractions as in the case of breakthrough experiments.

TABLE 1
Experimental Conditions

Experiment	Resin: Name	Resin: Form	Operating manner[a]	Temperature (°C)	Resin bed height (cm)	Flow rate ($cm^3 \cdot cm^{-2} \cdot h^{-1}$)	Boron concentration in feed ($mol \cdot dm^{-3}$)	Eluent: Acid	Eluent: pH	Figure
B-1	Diaion CRB02	Free base	b	25	140.0	21.9	0.100	—		3
B-2	Diaion CRB02	Free base	b	50	122.0	21.8	0.102	—		5
B-3a	Diaion CRB02	Free base	rb	25	135.7	20.0	0.103	HCl	0.76	
B-3b	Diaion CRB02	Free base	rb	25	130.9	20.0	0.102	HCl	0.81	7
B-4a	Diaion CRB02	Free base	rb	50	125.5	20.0	0.101	HCl	0.64	
B-4b	Diaion CRB02	Free base	rb	50	130.0	20.0	0.103	HCl	0.75	7
B-4c	Diaion CRB02	Free base	rb	50	130.5	20.0	0.101	HCl	0.94	
B-5	Diaion CRB02	Sulfate	b	25	141.1	21.8	0.100	—		4
B-6	Diaion CRB02	Sulfate	b	50	136.4	21.8	0.100	—		
B-7a	Diaion CRB02	Sulfate	rb	50	138.0	21.8	0.100	H_2SO_4	1.12	6
B-7b	Diaion CRB02	Sulfate	rb	50	136.1	21.8	0.100	H_2SO_4	1.18	6
B-7c	Diaion CRB02	Sulfate	rb	50	138.0	21.8	0.100	H_2SO_4	1.21	6
B-7d	Diaion CRB02	Sulfate	rb	50	138.5	21.8	0.100	H_2SO_4	1.34	6
B-8	Amberlite IRA743	Free base	b	25	94.0	12.1	0.100	—		
B-9	Amberlite IRA743	Free base	b	50	129.6	20.0	0.103	—		
B-10	Amberlite IRA743	Free base	rb	25	138.0	20.0	0.101	HCl	0.83	
B-11a	Amberlite IRA743	Free base	rb	50	123.6	20.0	0.103	HCl	0.75	
B-11b	Amberlite IRA743	Free base	rb	50	133.4	20.0	0.101	HCl	0.77	
B-11c	Amberlite IRA743	Free base	rb	50	147.8	20.0	0.101	HCl	0.83	
B-11d	Amberlite IRA743	Free base	rb	50	135.7	20.0	0.101	HCl	0.88	

[a] b = breakthrough; rb = reverse breakthrough.

The column temperature was kept constant throughout a chromatographic experiment by circulating thermostatted water through a jacket surrounding the column.

Experimental conditions are summarized in Table 1. Shapes of chromatograms in reverse breakthrough experiments are heavily dependent on the pH of the eluents (vide infra). A couple of experiments with eluents of slightly different pH values, i.e., Experiments B-3a, 3b; B-4a ~ B-4c; B-7a ~ B-7d; B-11a ~ B-11d, were hence carried out in the reverse breakthrough manner in order to determine the pH value of the eluent at which the chromatogram of the displacement type could be obtained.

Analysis

The boron concentration of each fraction from each experiment was determined by neutralization titration (2). The boron isotopic ratios, $^{10}B/^{11}B$, of selected fractions were measured by the surface ionization method with a Finnigan MAT 261 or a Varian MAT CH-5 mass spectrometer. The relative standard deviation of the isotopic ratio measurements was typically 0.07% (10).

RESULTS AND DISCUSSION

Examples of chromatograms and ^{10}B isotopic mole fractions obtained are shown in Figs. 3–7. In Figs. 3–6 the step-like lines in the lower parts of the figures represent the boron concentration profiles and the filled circles in the upper parts denote the ^{10}B mole fractions. Only the isotopic data are depicted in Fig. 7. The "original" lines show the value of the ^{10}B mole fraction in boron feed solutions (= 0.1983).

Various Factors Affecting Shapes of Chromatograms and Boron Isotope Accumulation Curves

A comparison of the results of Experiments B-1 (Fig. 3) and B-5 (Fig. 4) clarifies the effect of the form of resin (free base vs sulfate) in breakthrough experiments at 25°C. The breakthrough point is much larger for the resin in the free base form than in the sulfate form. This is a consequence of the difference in the adsorption isotherm between the two forms (cf. Fig. 2); compared with the boron concentration of 0.10 mol-dm^{-3} of the external solution, the amount of boron adsorbed per 1 g of resin is much larger for the resin in the free base form than in the sulfate form. As for the chromatograms, we also see that in the case of the resin in the free base form, the boron concentration in the effluent very quickly becomes equal to that of the feed solution after the breakthrough point, while in the case of the resin in the sulfate form, it gradually approaches the boron

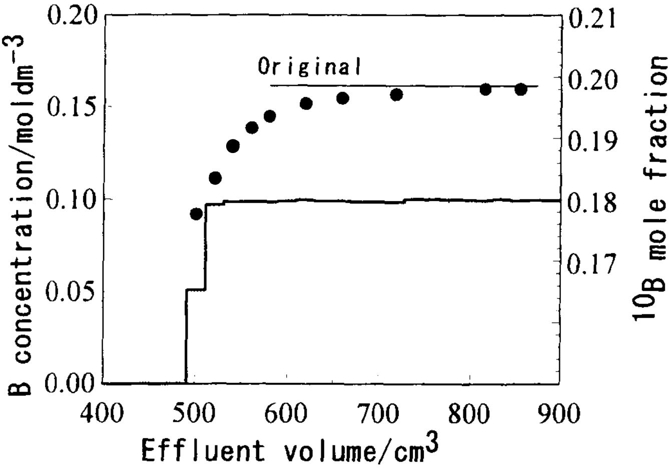


FIG. 3 The boron concentration profile and the ^{10}B isotopic mole fractions obtained in a breakthrough experiment [Experiment B-1 (cf. Table 1)]. The experimental conditions are: resin, Diaion CRB02 in the free base form; temperature, 25°C; boron concentration in the feed solution, 0.100 mol·dm^{-3}.

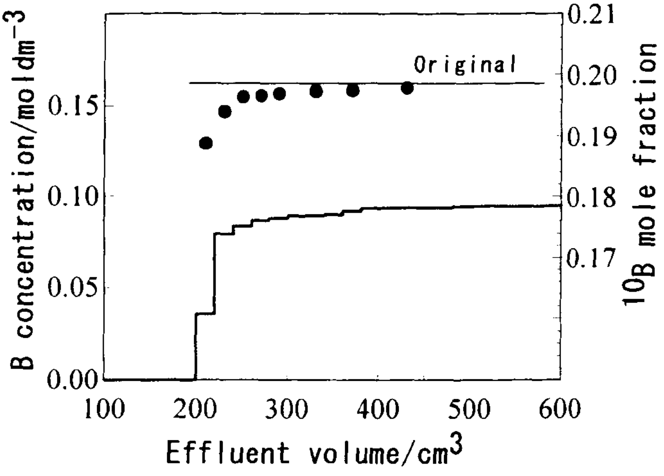


FIG. 4 The boron concentration profile and the ^{10}B isotopic mole fractions obtained in a breakthrough experiment [Experiment B-5 (cf. Table 1)]. The experimental conditions are: resin, Diaion CRB02 in the sulfate form; temperature, 25°C; boron concentration in the feed solution, 0.100 mol·dm^{-3}.

concentration of the feed and even at an effluent volume of 600 cm^3 it still does not become equal to that concentration (Fig. 4). The free base form thus seems superior to the sulfate form for obtaining a chromatogram of the displacement type. Regarding boron isotope accumulation, the lighter isotope, ^{10}B, is depleted in the front parts of the chromatograms in both the cases. The maximum degree of ^{10}B depletion achieved in the front-most fraction is higher for the resin in the free base form than in the sulfate form, which indicates that the resin in the free base form has a higher capability for separating boron isotopes than the resin in the sulfate form. A similar effect of the form of resin in breakthrough experiments was observed between Experiments B-2 and B-5 at 50°C.

By comparing the results of Experiments B-1 (Fig. 3) and B-2 (Fig. 5), we can examine the effect of temperature in breakthrough experiments (25 vs 50°C) for Diaion CRB02 resin in the free base form. The difference in the shape of chromatograms is insubstantial, which shows the temperature dependence of the chromatogram is small within the experimental conditions examined. As for boron isotope accumulation, a higher temperature yields a higher degree of ^{10}B depletion in the front-most fraction and seems to result in a steeper accumulation curve than a lower temperature. Similar observations were made between Experiments B-5 and B-6 for Diaion CRB02 in the sulfate form and between B-8 and B-9 for Amberlite IRA743 in the free base form.

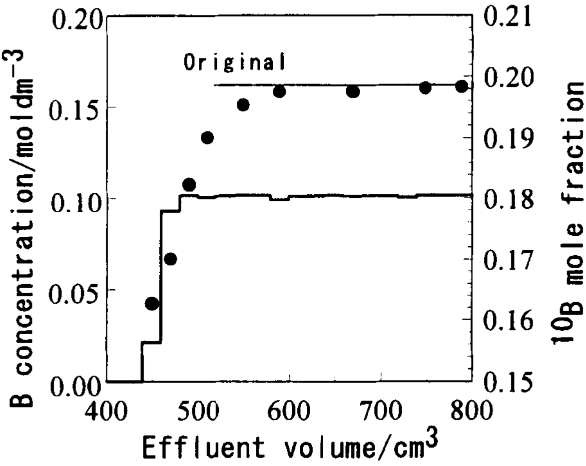


FIG. 5 The boron concentration profile and the ^{10}B isotopic mole fractions obtained in a breakthrough experiment [Experiment B-2 (cf. Table 1)]. The experimental conditions are: resin, Diaion CRB02 in the free base form; temperature, 50°C; boron concentration in the feed solution, 0.102 mol·dm^{-3}.

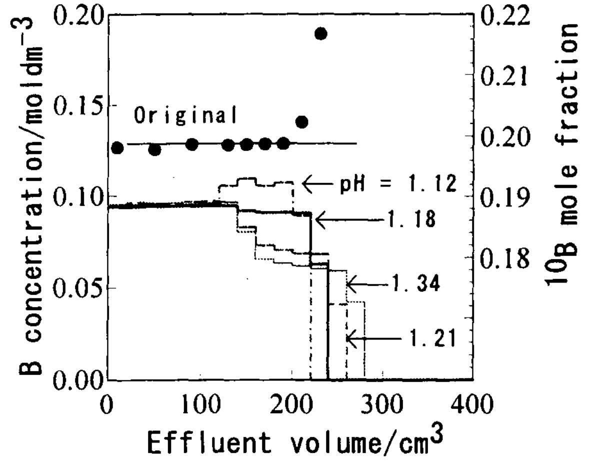


FIG. 6 The boron concentration profiles and the ^{10}B isotopic mole fractions obtained in a reverse breakthrough experiment [Experiments B-7a–B-7d (cf. Table 1)]. The experimental conditions are; resin, Diaion CRB02 in the sulfate form; temperature, 25°C; the boron concentration in the feed solutions, 0.100 mol·dm^{-3}; eluents, H_2SO_4 solutions with pH 1.12 (B-7a), 1.18 (B-7b), 1.21 (B-7c), and 1.34 (B-7d). The ^{10}B isotopic mole fractions shown are those of Experiment B-7b.

Figure 6 shows the results of a series of reverse breakthrough experiments (Experiments B-7a to B-7d) in which we varied the pH values of the eluents slightly while keeping other experimental conditions practically constant. Illustrated is the effect of the pH of eluent on the boron concentration profiles in reverse breakthrough experiments. As can be seen, the chromatogram is, in principle, of the two-step shape and the boron concentration of the latter (second) part is heavily dependent on the pH of the eluent. At a lower pH (= 1.12), the boron concentration in the effluent becomes higher than that of the feed solution after being nearly equal to that of the feed solution for a while. Contrary to this, at a higher pH (= 1.21 and 1.34) it becomes lower than that of the feed. And a pH value (= 1.18 in this case) exists that causes the boron concentration in the effluent to be equal to that of the feed solution throughout the whole boron chromatogram without the chromatogram having the two-step shape. At this pH value no serious tailing phenomenon is observed and a chromatogram of the displacement type is realized nearly ideally. Similar pH values also exist for the other series of reverse breakthrough experiments (B-3a, B-3b; B-4a to B-4c; B-11a to B-11d), and they are summarized as the "optimum" pH values in Table 2.

TABLE 2

Optimum pH Values of the Eluents and the Separation Factor Values Obtained

Resin	Resin form	Temperature (°C)	Optimum pH of eluent[a]	S^b
Diaion CRB02	Free base	25	0.81	1.021
Diaion CRB02	Free base	50	0.75	1.021
Diaion CRB02	Sulfate	25	—	1.018
Diaion CRB02	Sulfate	50	1.18	1.010
Amberlite IRA743	Free base	25	0.83	1.022
Amberlite IRA743	Free base	50	0.83	1.020

[a] The pH value at which the boron concentration in the effluent is the same as that of the feed solution throughout the whole boron chromatogram.

[b] Calculated from the data in reverse breakthrough experiments whenever available.

The strong dependence of the shape of chromatograms on the eluent pH is ascribable to the nature of the esterification reaction (Eq. 1) occurring in the resin phase. This reaction is reversible and is very sensitive to pH. At a low pH of the solution phase, which means that the pH of the resin phase is accordingly low, borate ions in Eq. (1) are interconverted into neutral molecular boric acids and the backward reaction of Eq. (1) (i.e., hydrolysis) proceeds. This results in a high boron concentration in the solution phase (i.e., high boron concentration in effluents in chromatographic experiments). On the contrary, at a high pH of the solution phase, the forward reaction of Eq. (1) is promoted and more boron is taken up by the resin, resulting in a low boron concentration in the external solution phase.

Figure 7 compares boron isotope accumulation curves in reverse breakthrough experiments at 25°C (Experiment B-3b) and 50°C (Experiment B-4b) for Diaion CRB02 in the free base form. A sharper curve is obtained at a higher temperature, which is consistent with the results observed in breakthrough experiments and indicates that a high temperature is kinetically preferable.

Boron Isotope Separation Factors

The single-stage separation factor, S, for the boron isotopes is defined as

$$S = ([^{11}\mathrm{B}]_{\mathrm{solution}}/[^{10}\mathrm{B}]_{\mathrm{solution}})/([^{11}\mathrm{B}]_{\mathrm{resin}}/[^{10}\mathrm{B}]_{\mathrm{resin}}) \tag{2}$$

where $[\mathrm{A}]_\mathrm{D}$ denotes the mole fraction of A in phase D. The value of S can be calculated from the chromatographic data using the equation of

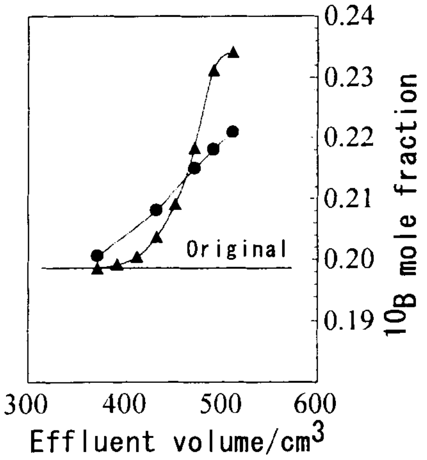


FIG. 7 The ^{10}B isotopic mole fractions obtained in reverse breakthrough experiments [Experiments B-3b and B-4b (cf. Table 1)] (●) Experiment B-3; resin, Diaion CRB02 in the free base form; temperature, 25°C; eluent, HCl with pH 0.81. (▲) Experiment B-4; resin, Diaion CRB02 in the free base form; 25°C; HCl with pH 0.85.

Kakihana and Kanzaki (11):

$$S = 1 + \sum |R_i - R_0| f_i / [QR_0(1 - R_0)] \tag{3}$$

where R_i is the ^{10}B isotopic mole fraction in the ith fraction, R_0 is that in the feed solution, f_i is the amount of boron in the ith fraction, Q is the total exchange capacity of the resin bed, and the summation is taken over all the fractions where isotope fractionation occurs. By definition, S is larger than unity when ^{10}B is preferentially fractionated into the resin phase. The magnitude of the deviation of the S value from unity shows the magnitude of the boron isotope fractionation effect under given experimental conditions. The results of the calculations are listed in Table 2. When the S value is estimated both from breakthrough and reverse breakthrough experiments that of the reverse breakthrough experiment is shown. The results of Table 2 can be summarized as follows.

(a) The S values are 1.018–1.022 at 25°C. They are generally larger than those obtained with common strongly and weakly basic anion exchangers (12). The maximum S value of 1.022 is nearly equivalent to that reported by Itagaki et al. (5). From the standpoint of the separation factor, the present boron-specific resins are better column packing materials than are common anion exchangers for the chromatographic separation of boron isotopes. The main boron isotope exchange reaction for systems with common anion exchangers is expressed as (12)

$$ {}^{10}B(OH)_3 + \overline{{}^{11}B(OH)_4^-} = {}^{11}B(OH)_3 + \overline{{}^{10}B(OH)_4^-} \qquad (4)$$

where the species with overbars exist in the resin phase and those without overbars are in the solution phase. This reaction is very similar to the reaction expected for the present systems (cf. Eq. 5 below), and the equilibrium constants values of Eqs. (4) and (5) should thus be similar to each other. Kakihana et al. (12) showed that polyborates such as $B_2O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$ are formed in the resin phase of systems with common anion exchangers, and their formations made the *S* value decrease. This suggests that the amounts of polyborates in the resin phase of the present system are insubstantial, if any.

(b) A lower temperature tends to yield a larger *S* value. This is consistent with the theory of equilibrium isotope effects. Considering the temperature dependence of the chromatographic accumulation behaviors of the boron isotopes, the effect of temperature on boron isotope separation is thus twofold. A higher temperature results in a smaller *S* value, which is its drawback, while it yields a steeper boron isotope accumulation curve, which is its advantage. In other words, a lower temperature is thermodynamically favorable while a higher temperature favors kinetics. In a practical boron isotope separation system, the operating temperature has to be determined by considering these two consequences.

(c) At a given temperature, the *S* value is larger for a resin in the free base form than in the sulfate form. This, coupled with the fact that a resin in the free base form realized chromatograms of the displacement type more ideally than that in the sulfate form, shows that the free base form is more preferable for boron isotope separation than is the sulfate form.

We feel some consideration is needed for item (c) above. That is, why is the *S* value larger for the resin in the free base form than for the resin in the sulfate form? According to a solution chemical study of boron (13), boric acid, $B(OH)_3$, is practically the only viable boron species in the solution phase of the present systems. The main boron species in the resin phase is considered to be $B(OH)_2(OC-)_2^-$ (the first species on the right-hand side of Eq. 1). As mentioned earlier, boron is considered to be adsorbed through the esterification of borate ions with the polyol parts of the resins (7), and consequently, in the discussion below, we will ignore the possibility that boron may be adsorbed as an anionic species at the ion-exchange sites of the resins. The main boron isotope exchange reaction which gives rise to the boron isotope fractionation observed in the present study is then expressed as

$$^{10}B(OH)_3 + {}^{11}B(OH)_2(OC\text{-})_2^- = {}^{11}B(OH)_3 + {}^{10}B(OH)_2(OC\text{-})_2^- \quad (5)$$

Since ^{10}B is preferentially fractionated into the resin phase, the value of the equilibrium constant of this reaction is larger than unity. If $B(OH)_2(OC\text{-})_2^-$ is the only boron species in the resin phase, the *S* value should be nearly independent of the resin form. The resin-form dependence of the *S* value strongly indicates the existence of boron species other than $B(OH)_2(OC\text{-})_2^-$ in the resin phase. The most conceivable species is the neutral three-coordinate species, $B(OH)(OC\text{-})_2$. This three-coordinate species is not identified inside the present boron-specific resins. However, a ^{11}B NMR spectroscopic study suggested its existence in aqueous solutions containing boric acid and a polyol (14). This species starts to appear at a pH lower than the pH at which the four-coordinate species, $B(OH)_2(OC\text{-})_2^-$, does. If part of the boron in the resin phase exists as the three-coordinate species, then the *S* value of that system would be smaller than the *S* value of the system where all the boron in the resin phase exists as the four-coordinate species. This is because the equilibrium constant of the boron isotope exchange reaction between boric acid in the solution phase and the three-coordinate boron species in the resin phase is expected to be much closer to unity than that between boric acid and the four-coordinate species due to the fact that the coordination number of boron in boric acid is also three and the sum of forces acting on boron atoms is hence expected to be similar to each other in $B(OH)_3$ and $B(OH)(OC\text{-})_2^-$. The pH value in the resin phase is considered to be lower for the resin in the sulfate form than in the free base form. The proportion of three-coordinate boron species is then expected higher in the resin in the sulfate form than in the free base form. This leads to the conclusion that the *S* value should be larger for the resin in the free base form than for the resin in the sulfate form, and this is consistent with the present experimental results.

CONCLUSION

Major findings of the present study, in which boron-specific resins having *n*-methyl glucamine as the functional group were applied for the chromatographic separation of boron isotopes, are summarized as follows.

(1) The shape of the chromatogram in a reverse breakthrough experiment is strongly dependent on the pH of the eluent. A higher pH results in a lower boron concentration in the effluent, and a lower pH yields a higher concentration. There exists an intermediate pH value at which a chromatogram of the displacement type can be realized nearly ideally.

(2) The value of the separation factor depends on the form of the resin, and the maximum *S* value obtained is 1.022. This resin-form dependence of the *S* value is qualitatively explainable by assuming the existence of a three-coordinate boron species, $B(OH)(OC-)_2$, in the resin phase in addition to a four-coordinate species, $B(OH)_2(OC-)_2^-$.

(3) The resin in the free base form shows a better boron isotope separation performance than the resin in the sulfate form; the former gives a larger *S* value at given conditions and can realize a chromatogram of the displacement type more ideally than the latter.

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