Boron Isotope Effect in Liquid Chromatography with Boron-specific Resins as Packing Material

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Boron isotope separation by liquid chromatography using boron specific resins with *N*-methyl glucamine as the functional group was performed. The single-stage separation factor, *S*, is generally dependent on the resin in the sequence S (free base form resin) $> S(F^-$ form resin) $> S(Cl^-$ form resin) $\geqq S(Br^-$ form resin) for given experimental conditions. This sequence is the same as that of the pH value expected in the resin phase and reasonably understandable by assuming in addition to the predominant four-coordinate species a three-coordinate boron species in the resin phase whose relative abundance increases with decreasing pH. Supporting evidence for three-coordinate species was obtained by ^{11}B NMR measurements of boric acid-glycerol and boric acid-1,3-propanediol solutions.

Key words: Boron isotopes, isotope separation, boron specific resin, liquid chromatography, ^{11}B NMR.

I. Introduction

Naturally occurring boron consists of two stable isotopes, ^{10}B (about 20%) and ^{11}B (about 80%). ^{10}B has important applications in nuclear science and technology due to its large thermal neutron absorption cross-section. It is used in neutron therapy of brain tumors and melanotic cancers and in nuclear fission reactor facilities for reactor control. Methods for separating ^{10}B from its heavier isotope have been studied, among which is liquid chromatography using anion exchangers as column packing materials. Several studies on chromatographic separation of boron isotopes have been carried out; some were designed to acquire knowledge on fundamental boron isotope effects and others were intended to investigate the feasibility of a practical separation process.

In a previous paper [1], we showed that boron-specific ion exchange resins, which have specifically high affinity towards borate ions, could be alternatives to common strongly and weakly basic organic ion exchange resins. Values of the ^{11}B-to-^{10}B single-stage separation factor, *S*, were $1.018 \sim 1.022$ at 25 °C. These values should be compared with $S = 1.010 \sim 1.028$ reported for strongly basic anion exchange resins [2–4] and $S = 1.010 \sim 1.013$ for weakly basic anion exchange resins [4, 5] under similar experimental conditions. The *S* value of the boron-specific resin systems seemed to depend on the form of the resins, which indicates the existence of three-coordinate boron species in addition to four-coordinate ones in the resin phase [1]. To confirm the dependence of *S* on the resin form and to elucidate the cause of it, we performed additional and more systematic experiments on chromatographic separation of boron isotopes and, in addition, ^{11}B NMR studies on aqueous boric acid-polyol solutions to find out evidence for the existence of three-coordinate boron species in the resin phase.

II. Experimental

1) Column Experiments

The resins used were the boron-specific ion exchange resins Diaion CRB02 and Amberlite IRA743. Both resins have the structure shown in Fig. 1; the skeleton is the stylene-divinylbenzene copolymer, and *N*-methyl glucamine, $CH_3NHCH_2[CH(OH)]_4CH_2(OH)$ (**1**), was introduced as the functional group. The nitrogen atom of the *N*-methyl glucamine group can work as an anion exchange site, and thus the resins can be regarded as weakly basic anion exchangers. Boron is

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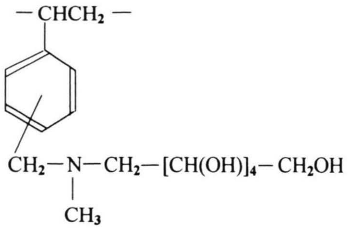
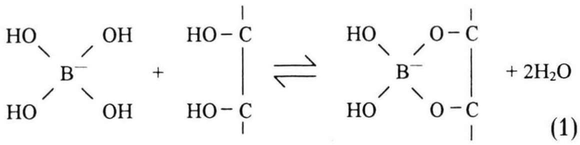


Fig. 1. The structure of the boron specific resins used (free base form).

said to be adsorbed into the resins through the esterification of borate ions with the polyol parts of the resins [6];



(1)

The free base and halide (F^-, Cl^-, Br^-) forms of the resins were investigated in the present work.

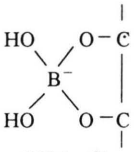
Chromatographic experiments were carried out in the breakthrough and reverse breakthrough manners. In the breakthrough experiments, the resin was packed in a chromatographic column of Pyrex glass (150 cm × 1 cm ∅) and was converted to the desired form by the usual method. After washing out the conditioning agent by pure water, an aqueous boric acid solution with the boron concentration of 0.1 M ($M = mol/dm^3$) 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 with the boron concentration 0.1 M was fed to the chromatographic column packed with the resin in the desired form until the amount of the boron fed became about three times larger than the exchange capacity of the column. 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. The column temperature was kept constant at 25 or 50 °C throughout a chromatographic experiment by circulating thermostated water through a jacket around the column.

The boron concentration in each fraction of the effluent of each experiment was determined by ICP-AES or neutralization titration. The boron isotopic ratio, $^{10}B/^{11}B$, of selected fractions was 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% [7].

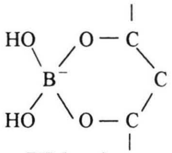
2) ^{11}B NMR Measurements

To cast some light on the nature of complex formations between boron species and *N*-methyl glucamine groups in the resins, ^{11}B NMR measurements of aqueous solutions containing boric acid and a polyol were carried out. The polyols studied were glycerol (1,2,3-propanetriol), $CH_2(OH)CH(OH)CH_2(OH)$ (**2**), and 1,3-propanediol, $CH_2(OH)CH_2CH_2(OH)$ (**3**), in addition to (**1**). (**2**) and (**3**) are chosen as simple model alcohols of the *N*-methyl glucamine group.

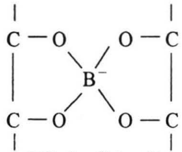
(**1**) is expected to form complexes of 1:1 mole ratio of the borate ion ($\mathbf{B^-}$) and (**1**) with borate ions (α, β)- or (α, γ)-coordinated ($\mathbf{B^-L}(\alpha\,\beta)$ and $\mathbf{B^-L}(\alpha\,\gamma)$) and complexes of 1:2 mole ratio of the borate ion and (**1**) with the borate ions (α, β)-, (α, β)-; (α, γ)-, (α, γ)- or (α, β)-, (α, γ)-coordinated ($\mathbf{B^-L_2}(\alpha\,\beta)(\alpha\,\beta)$, $\mathbf{B^-L_2}(\alpha\,\gamma)(\alpha\,\gamma)$ and $\mathbf{B^-L_2}(\alpha\,\beta)(\alpha\,\gamma)$) [8, 9]:



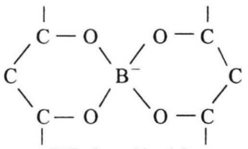
$\mathbf{B^-L}(\alpha\,\beta)$



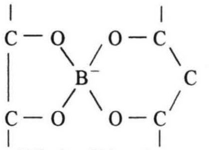
$\mathbf{B^-L}(\alpha\,\gamma)$



$\mathbf{B^-L_2}(\alpha\,\beta)(\alpha\,\beta)$

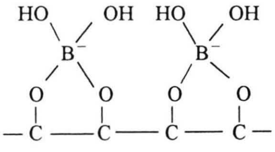


$\mathbf{B^-L_2}(\alpha\,\gamma)(\alpha\,\gamma)$



$\mathbf{B^-L_2}(\alpha\,\beta)(\alpha\,\gamma)$

Furthermore, higher order complexes such as complexes of 2:1 mole ratio of $\mathbf{B^-}$ and (**1**) ($\mathbf{B_2^-L}$) like



$\mathbf{B_2^-L}$

may be formed [9]. (**2**) is expected to form (α, β)- and (α, γ)-complexes ($\mathbf{B^-L}(\alpha\,\beta)$, $\mathbf{B^-L}(\alpha\,\gamma)$, $\mathbf{B^-L_2}(\alpha\,\beta)(\alpha\,\beta)$, $\mathbf{B^-L_2}(\alpha\,\gamma)(\alpha\,\gamma)$ and $\mathbf{B^-L_2}(\alpha\,\beta)(\alpha\,\gamma)$), and (**2**) forms ($\alpha$, γ)- complexes ($\mathbf{B^-L}(\alpha\,\gamma)$ and $\mathbf{B^-L_2}(\alpha\,\gamma)(\alpha\,\gamma)$) only [8].

Various sample solutions containing boric acid and one of the polyols were prepared for the ^{11}B NMR measurements. The pH of each solution was adjusted with sodium hydroxide solution of hydrochloric acid. The ionic strength was kept constant at 3.0 M by adding sodium chloride to each sample.

The NMR spectrometer used was a JEOL JNM-GX270 operated at 86.55 MHz and about 25 °C. The NMR probe unit consisted of a 10 mm o.d. and a 5 mm o.d. quartz probe. Diethyl ether-boron trifluoride (1/1), $(C_2H_5)_2OBF_3$, used as an external reference (chemical shift, $\delta = 0.0$ ppm) and dissolved in $CDCl_3$ used as a lock was placed in the 5 mm o.d. probe. $2 \sim 3\ cm^3$ of a sample solution was placed in the 10 mm o.d. probe. The 5 mm o.d. probe was capped and inserted into the 10 mm o.d. probe and fixed to it with fixing kits.

Details of the ^{11}B NMR measurements are given in [10, 11].

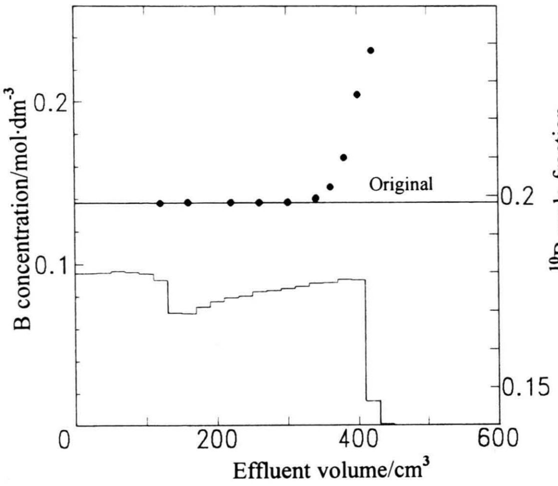


Fig. 2. The boron concentration profile and ^{10}B isotopic mole fractions (full circles) obtained in a reverse breakthrough experiment. Experimental conditions are: the resin, IRA743 resin in the bromide form; the resin bed height, 134.0 cm; flow rate, 23.7 $cm^3\ cm^2\ h^{-1}$; temperature, 25 °C; and eluent, HBr of pH 1.15.

III. Results and Discussion

1) Chromatographic Experiments

As an example of chromatograms and boron isotope accumulation curves obtained, in Fig. 2 the results of an experiment are depicted whose conditions are: resin: IRA743 in the bromide form; resin bed height: 134.0 cm; flow rate: 23.7 $cm^3\ cm^{-2}\ h^{-1}$; temperature: 25 °C; eluent: HBr of pH 1.15; operation manner: reverse breakthrough manner. We note that the shape of chromatograms in the reverse breakthrough experiments is heavily dependent on the pH of eluents and the near displacement-type shape like the one shown in Fig. 2 is obtained only for an eluent with a specific pH value stated in [1].

The results of the estimation of the single-stage separation factor, defined as

$$S = \frac{[\text{amount of } ^{11}\text{B in the solution phase}]}{[\text{amount of } ^{10}\text{B in the solution phase}]} \cdot \frac{[\text{amount of } ^{10}\text{B in the resin phase}]}{[\text{amount of } ^{11}\text{B in the resin phase}]}, \qquad (2)$$

using the chromatographic data, are summarized in Table 1. The S values obtained range from 1.014 to 1.022. A general tendency of S (free base form resin) > $S(F^-) > S(Cl^-) \geqq S(Br^-)$ is observed. This sequence is opposite to the sequence of acidity of hydrogen halides and water in water; acidity(HBr) ≧ acidity(HCl) > acidity(HF) > acidity(H_2O). Thus, the observed decreasing order in S is the same as that of the pH value expected for the resin phase; a higher pH value in the resin phase results in a larger S value.

2) Major Boron Species in the Solution and Resin Phases

To analyze (2) theoretically, it is essentially important to know the boron species and their relative abundances in the solution and resin phases and the values of their reduced partition function ratios (RPFR) [12]. In the experiments listed in Table 1, the solution phase is 0.1 M boric acid. The neutral boric acid molecule, $\mathbf{B}^0$, is the sole boron species practically viable in those solutions.

The kinds of boron species and their relative abundances in the resin phase of the present resins may be affected by various factors such as the relative and absolute concentrations of boron and *N*-methyl glucamine group and the pH in the resin phase. The complex formations in aqueous solutions containing boric acid and (**1**) are very complicated. Figure 3 shows examples of ^{11}B NMR spectra for the solutions with pH 10.55 and 12.02, both containing 0.020 M boric acid and 0.025 M (**1**). Even in these relatively dilute solutions, six distinct signals are observed, showing that at least six different boron species exist in those solutions. Referring to [8–11], the small signal at

Table 1. The values of the separation factors (S)*.

Run No.	Resin	Resin form	Temp/ °C	S	Ref.
1	Diaion CRB02	free base	25	1.021 ± 0.002	[1]
2		Cl^-	25	1.021 ± 0.001	this work
3		free base	50	1.021 ± 0.002	[1]
4		Cl^-	50	1.018 ± 0.001	this work
5	Amberlite IRA743	free base	25	1.022 ± 0.001	[1]
6		F^-	25	1.019 ± 0.002	this work
7		Cl^-	25	1.018 ± 0.001	this work
8		Br^-	25	1.017 ± 0.001	this work
9		free base	50	1.020 ± 0.002	[1]
10		F^-	50	1.017 ± 0.002	this work
11		Cl^-	50	1.014 ± 0.002	this work
12		Br^-	50	1.015 ± 0.002	this work

* When the S value was obtained from both the breakthrough and reverse breakthrough experiments, the value of the reverse breakthrough experiment is listed.

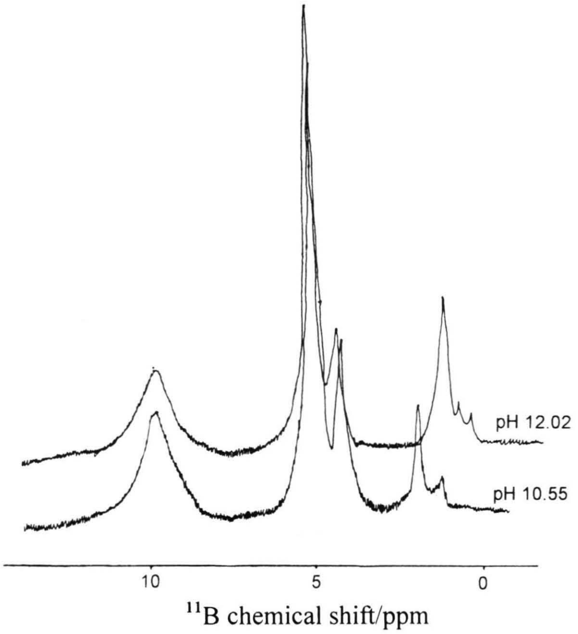


Fig. 3. ^{11}B NMR spectra obtained for aqueous solutions with the ionic strength of 3.0 M containing 0.02 M boric acid and 0.025 M N-methyl glucamine. The assignments of the signals are given in the text.

around $\delta = 0.9$ ppm can be assigned to $\mathbf{B}^-\mathbf{L}_2(\alpha\,\gamma)\,(\alpha\,\gamma)$, the signal at around $\delta = 1.4$ ppm to $\mathbf{B}^-\mathbf{L}(\alpha\,\gamma)$, the signal at around $\delta = 4.5$ ppm to $\mathbf{B}^-\mathbf{L}_2(\alpha\,\beta)\,(\alpha\,\gamma)$, the signal at around $\delta = 5.7$ ppm to $\mathbf{B}^-\mathbf{L}(\alpha\,\beta)$, the signal at around $\delta = 9.7$ ppm to $\mathbf{B}^-\mathbf{L}_2(\alpha\,\beta)\,(\alpha\,\beta)$, and the signal at $\delta = 1.70$ ppm at pH 12.02 and at 2.04 ppm at pH 10.55 to the concentration-weighted average of $\mathbf{B}^0$ and $\mathbf{B}^-$. It is known that the boron exchange between $\mathbf{B}^0$ and $\mathbf{B}^-$ in aqueous solution is fast on the ^{11}B NMR time scale and that the equilibrium between the two boron species yields a single signal whose chemical shift is the average of those of the two species weighted by their respective concentrations ($\mathbf{B}^0$ and $\mathbf{B}^-$ signals are observed at $\delta = 1.6$ ppm and 19.4 ppm, respectively.).

The tentative values of complex formation constants, all in units of $dm^3\,mol^{-1}$, of the $\mathbf{B}^-$-(**1**) complexes obtained from the peak areas in the ^{11}B NMR spectra of various boric acid-(**1**) solutions are:

$K_1(\alpha\,\beta) = 3.2 \times 10^3$,
$K_1(\alpha\,\gamma) = 1.4 \times 10^2$,
$K_2(\alpha\,\beta)\,(\alpha\,\beta) = 6.2 \times 10^2$,
$K_2(\alpha\,\gamma)\,(\alpha\,\gamma) = 4.3 \times 10^3$, and
$K_2(\alpha\,\beta)\,(\alpha\,\gamma) = 3.3 \times 10^2$.

Definitions of these formation constants are as follows:

$$\mathbf{B}^- + (\mathbf{1}) = \mathbf{B}^-\mathbf{L}(\alpha\,\beta) + 2\,H_2O,$$
$$K_1(\alpha\,\beta) = [\mathbf{B}^-\mathbf{L}(\alpha\,\beta)]/([\mathbf{B}^-]\,[(\mathbf{1})]);$$

$$\mathbf{B}^- + (\mathbf{1}) = \mathbf{B}^-\mathbf{L}(\alpha\,\gamma) + 2\,H_2O,$$
$$K_1(\alpha\,\gamma) = [\mathbf{B}^-\mathbf{L}(\alpha\,\gamma)]/([\mathbf{B}^-]\,[(\mathbf{1})]);$$

$$\mathbf{B}^-\mathbf{L}(\alpha\,\beta) + (\mathbf{1}) = \mathbf{B}^-\mathbf{L}_2(\alpha\,\beta)\,(\alpha\,\beta) + 2\,H_2O,$$
$$K_2(\alpha\,\beta)\,(\alpha\,\beta) = [\mathbf{B}^-\mathbf{L}_2(\alpha\,\beta)\,(\alpha\,\beta)]/[(\mathbf{1})]\,[\mathbf{B}^-\mathbf{L}(\alpha\,\beta)]);$$

$$\mathbf{B}^-\mathbf{L}(\alpha\,\gamma) + (\mathbf{1}) = \mathbf{B}^-\mathbf{L}_2(\alpha\,\gamma)\,(\alpha\,\gamma) + 2\,H_2O,$$
$$K_2(\alpha\,\gamma)\,(\alpha\,\gamma) = [\mathbf{B}^-\mathbf{L}_2(\alpha\,\gamma)\,(\alpha\,\gamma)]/[(\mathbf{1})]\,[\mathbf{B}^-\mathbf{L}(\alpha\,\gamma)]);$$

$$\mathbf{B}^-\mathbf{L}(\alpha\,\beta) + \mathbf{B}^-\mathbf{L}(\alpha\,\gamma) + (\mathbf{1}) = \mathbf{B}^-\mathbf{L}_2(\alpha\,\beta)\,(\alpha\,\gamma),$$
$$K_2(\alpha\,\beta)\,(\alpha\,\gamma) = [\mathbf{B}^-\mathbf{L}_2(\alpha\,\beta)\,(\alpha\,\gamma)]/[(\mathbf{1})]\,[\mathbf{B}^-\mathbf{L}(\alpha\,\beta) + \mathbf{B}^-\mathbf{L}(\alpha\,\gamma)]).$$

Here, [A] denotes the concentration of A. The values of the complex formation constants above show that the ($\alpha\,\beta$)-type is preferred over the ($\alpha\,\gamma$)-type for the 1:1 complex in aqueous solutions, while the ($\alpha\,\gamma$)-type is preferred over the ($\alpha\,\beta$)-type for the 1:2 complex.

Speciation in the resin phase is necessarily different from that of aqueous solution. The exchange capacity of the Diaion CRB02 resin as an anion exchanger is 2.2 meq/g. The average distance between the nitrogen atoms of the two adjacent N-methyl glucamine groups is then estimated as about 10 Å. The number of N-methyl glucamine groups required for the formation of one 1:2 complex is two per one $\mathbf{B}^-$, and this distance is too long for the 1:2 complexes to be formed in substantial amounts.

The boron uptake from a nearly saturated boric acid solution by the CRB02 resin is about the same as the exchange capacity at 25 °C. This indicates that the amount of 2:1 complexes of the borate ion and the *N*-methyl glucamine group is insignificant in the resin phase of the CRB02 resin.

The facts in the above two paragraphs indicate that one *N*-methyl glucamine group captures at most one $\mathbf{B}^-$, that is, the 1:1 complexes are by far the predominant species in the resin phase of the CRB02 resin. Furthermore, judging from the complex formation constants $K_1(\alpha\,\beta)=3.2\times10^3$ and $K_1(\alpha\,\gamma)=1.4\times10^2$, the $(\alpha\,\beta)$-type species is the predominant one in the resin phase; $B(OH)(OC-)_2^-$ (the first species on the right hand side of (1)). A similar consideration can be applied for the Amberlite IRA743 resin.

3) Existence of Three-coordinate Boron Species in the Resin Phase and Resin Form Dependence of the Single-stage Separation Factor

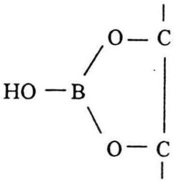
The boron species existing in the present solution phase is boric acid, and the predominant species in the resin phase is $B(OH)_2(OC-)_2^-$. The boron isotope exchange reaction that gives rise to the present boron isotope fractionation is then expressed as

$$^{10}B(OH)_3 + {}^{11}B(OH)_2(OC-)_2^- \overset{K_4}{=} {}^{11}B(OH)_3 + {}^{10}B(OH)_2(OC-)_2^- \qquad (3)$$

If $B(OH)_2(OC-)_2^-$ is the only boron species in the resin phase, the *S* value should be independent of the resin form and equal to the value of the equilibrium constant, K_4, of (3). In reality, it is resin-form dependent, as shown in Table 1. Since the decreasing order of the *S* value coincides with the decreasing order of the pH value expected for the resin phase, the chromatographic results indicate the existence of a second boron species in the resin phase whose relative abundance increases with decreasing pH, and whose RPFR value is closer to that of $B(OH)_3$ than that of $B(OH)_2(OC-)_2^-$. The most probable candidate that satisfies these conditions seems to be a three-coordinate species rather than a four-coordinate species like $B(OH)_2(OC-)_2^-$.

A direct verification of the existence of three-coordinate boron species in the resin phase may be done by ^{11}B NMR measurements. We recorded ^{11}B NMR spectra of boron adsorbed on the present resins with JNM-GX270, but we could not find any signal assignable to the three-coordinate species. Then we decided to find out an evidence for the three-coordinate species in the resin phase using boric acid-polyol solutions. We chose to use simple polyalcohols, **(2)** and **(3)** instead of **(1)**, since ^{11}B NMR spectra of solutions containing boric acid and those polyalcohols are much simpler than those of boric acid and **(1)** and consequently are easy to trace spectral changes.

Figure 4 is an example of an ^{11}B NMR spectrum obtained for boric acid-**(2)** solutions. The concentrations of boric acid, **(2)** and pH are, respectively, 0.1 M, 0.5 M and 7.88. The signal observed at around $\delta=17.3$ ppm is attributable to the average of the signals of $\mathbf{B}^0$ and $\mathbf{B}^-$. The signals at around $\delta=9.8$ ppm and 5.8 ppm can be assigned to $\mathbf{B}^-\mathbf{L}_2(\alpha\,\beta)(\alpha\,\beta)$ and $\mathbf{B}^-\mathbf{L}(\alpha\,\beta)$, respectively. No signals corresponding to $(\alpha\,\gamma)$-complexes are found under the experimental conditions. Figure 5 shows the spectra in the vicinity of $\mathbf{B}^-\mathbf{L}(\alpha\,\beta)$ at various pH values. The peak position of the signal is unchanged at $\delta=5.81$ ppm at pH ≥ 7.56. Below 7.56 the signal shifts downfield and its width becomes broader and broader. This result is best understood by assuming the three-coordinate species



$\mathbf{B}^0\mathbf{L}(\alpha\,\beta)$,

which is formed by the reaction of $\mathbf{B}^0$ and **(2)** with the liberation of two waters, as follows: The signal at $\delta=5.81$ ppm is that of $\mathbf{B}^-\mathbf{L}(\alpha\,\beta)$. $\mathbf{B}^0\mathbf{L}(\alpha\,\beta)$ starts to be formed at around pH = 7.5, and its relative abundance increases with decreasing pH. Analogously to the case

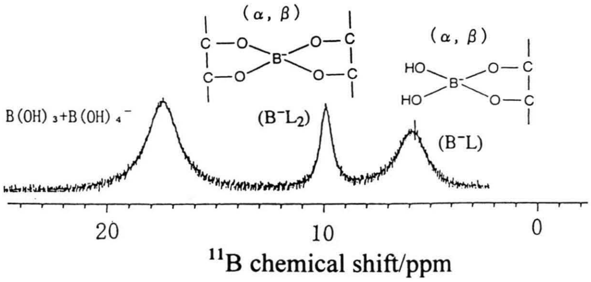


Fig. 4. The ^{11}B NMR spectrum obtained for the aqueous solution with pH of 7.88 and the ionic strength of 3.0 M containing 0.1 M boric acid and 0.5 M glycerol.

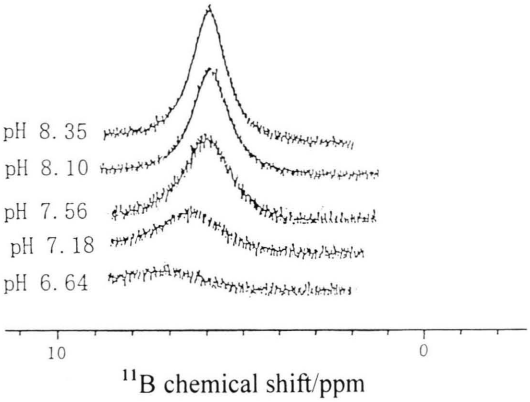


Fig. 5. The ^{11}B NMR spectral change with pH of the signal corresponding to the complex of the 1:1 mole ratio of borate ion and glycerol with borate ions (α, β)-coordinated, observed for solutions with the ionic strength of 3.0 M containing 0.1 M boric acid and 0.5 M glycerol.

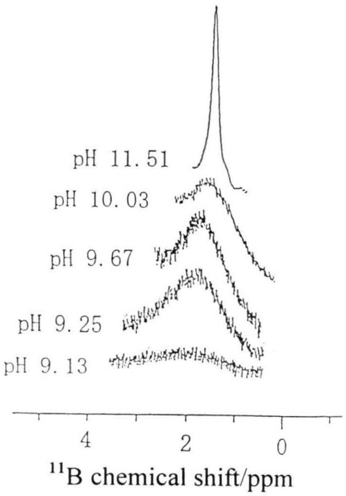


Fig. 6. The ^{11}B NMR spectral change with pH of the signal corresponding to the complex of the 1:1 mole ratio of borate ion and 1,3-propanediol with borate ions (α, γ)-coordinated, observed for solutions with the ionic strength of 3.0 M containing 0.1 M boric acid and 0.5 M 1,3-propanediol.

of $\mathbf{B}^0$ and $\mathbf{B}^-$, the signal of $\mathbf{B}^0\mathbf{L}(\alpha\,\beta)$ is located at much lower field than that of $\mathbf{B}^-\mathbf{L}(\alpha\,\beta)$, and the boron exchange between $\mathbf{B}^0\mathbf{L}(\alpha\,\beta)$ and $\mathbf{B}^-\mathbf{L}(\alpha\,\beta)$ is fast on the ^{11}B NMR time scale. A single signal, whose chemical shift is the weighted average of those of $\mathbf{B}^0\mathbf{L}(\alpha\,\beta)$ and $\mathbf{B}^-\mathbf{L}(\alpha\,\beta)$, is hence observed at pH values below 7.5, and it shows downfield shift with decreasing pH since the relative abundance of $\mathbf{B}^0\mathbf{L}(\alpha\,\beta)$ increases with decreasing pH. At pH values above 7.56, the position of the signal is unchanged because $\mathbf{B}^0\mathbf{L}(\alpha\,\beta)$ does not exist any more in this pH region.

A similar pH dependence of the $\mathbf{B}^-\mathbf{L}$ signal is also observed for the (α γ)-complex, as shown in Fig. 6, although, as mentioned before, the (α γ)-complex is expected to be insignificant in the resin phase of the present resins. The spectral change in Fig. 6, in which only the spectrum in the vicinity of the $\mathbf{B}^-\mathbf{L}(\alpha\,\gamma)$ is depicted, is obtained from solutions containing 0.1 M boric acid and 0.5 M (**3**). The downfield shift of the signal assigned to $\mathbf{B}^-\mathbf{L}(\alpha\,\gamma)$ with decreasing pH indicates the existence of the three-coordinate boron species, $\mathbf{B}^0\mathbf{L}(\alpha\,\gamma)$. Finally, we note that van Haveren et al. [14] also suggested the existence of three-coordinate boron species in boric acid-polyol solution by an ^{11}B NMR spectroscopic study.

Assuming the three coordinate species in the resin phase, S can be expressed as

$$S = K_4\,x + K_3(1-x),$$

where K_4 is the equilibrium constant of reaction (3), K_3 is the equilibrium constant of the reaction

$$^{10}\mathrm{B(OH)_3} + {}^{11}\mathrm{B(OH)(OC-)_2} = {}^{11}\mathrm{B(OH)_3} + {}^{10}\,\mathrm{B(OH)(OC-)_2}, \quad (4)$$

and x is the mole fraction of $\mathrm{B(OH)_2(OC-)_2^-}$ in the resin phase. K_4 is much larger than K_3 and is probably close to 1.022 at 25 °C (close to the S value obtained for the resin in the free base form). K_3 is expected to be very close to unity since it corresponds to the boron isotope effect between two three-coordinate species, both using oxygen atoms as coordination sites, and consequently the RPFR values of the two species are expected to be similar. The pH of the resin phase is pH (free base form resin) > pH ($\mathrm{F^-}$ form resin) > pH ($\mathrm{Cl^-}$ form resin) ≧ pH ($\mathrm{Br^-}$ form resin), and consequently x(free base form resin) > x($\mathrm{F^-}$ form resin) > x($\mathrm{Cl^-}$ form resin) ≧ x($\mathrm{Br^-}$ form resin). This results in the sequence of S(free base form resin) > S($\mathrm{F^-}$ form resin) > S($\mathrm{Cl^-}$ form resin) ≧ S($\mathrm{Br^-}$ form resin).

IV. Conclusion

To summarize, we make the following statements:

(1) In the chromatographic separation of boron isotopes using boron-specific resins as column packing materials, the value of the separation factor, S,

depends on the form of the resin; the general sequence is; S(free base form resin)$>S$(F$^-$ form resin)$>S$(Cl$^-$ form resin)$\geqq S$(Br$^-$ form resin). This resin-form dependence of S is explainable by assuming the existence of a three-coordinate boron species in the resin phase, the relative abundance of which increases with decreasing pH in the resin phase.

(2) The four-coordinate boron species in the resin phase is mostly the complex of the 1:1 mole ratio of the borate ion and the *N*-methyl glucamine group of the resin with borate ions (α, β)-coordinated.

(3) The existence of three-coordinate species in the resin phase is evidenced in solutions containing boric acid and glycerol or boric acid and 1,3-propanediol by ^{11}B NMR measurements of those solutions.

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