Fractionation of Boron Isotopes to Bis(2-hydroxyalkyl)amine Borate and Boric Acid in Aqueous Solutions

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^{10}B is more fractionated to B(OH)L {H_2L: a ligand having a bis(2-hydroxyalkyl)amino group (alkyl: ethyl and propyl)} with a tetrahedral coordination mode than to $B(OH)_3$ with a planar triangular coordination mode in aqueous solutions, exhibiting an isotope separation factor of 1.027 at 25 °C, which is greater than the upper limit of anion exchangers.

The separation of boron isotopes using anion exchange resins has been explored based on the fractionation of ^{10}B to anionic $B(OH)_4^-$ according to the following isotope exchange equilibrium:[1]

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- \rightleftharpoons {}^{11}B(OH)_3 + {}^{10}B(OH)_4^- ; \quad K{=}1.019 \text{ at } 27\ °C \qquad (1)$$

and the boron-isotope separation factor is restricted to the upper limit of 1.019 (27 °C).[1,2] However, no research on boron-isotope separation chelating agents other than anion exchange resins has been undertaken, probably because of the lack of a design concept of chelating ligands effective in the separation of boron isotopes in aqueous solutions.

The difference in fractionation of isotopes between two chemical species is principally due to a difference in the intramolecular forces of the species acting on the isotopic atom.[3] Thus, we evaluated the fractionation of boron isotopes in isotopic exchange reactions with BX_3 (D_{3h} symmetry) and BX_4^- (T_d symmetry) (X: halogens) from quantum-chemical calculations, and demonstrated that ^{10}B is more fractionated to BX_4^- (tetrahedral) than to BX_3 (planar trigonal) under the same coordination atom and also to the molecules with X in the order of F<Cl<Br<I under the same coordination mode.[4] This strongly suggests that the fractionation of boron isotopes may be due to a change in the coordination geometry of complexing and in the coordination atom. From this theoretical consideration, we have found out a marked difference in fractionation of boron isotopes to bis(2-hydroxyalkyl)amine borate with a tetrahedral coordination geometry and boric acid in aqueous solutions.

The complexation equilibrium of boric acid with benzyl-bis(2-hydroxyethyl)amine (BBHEA) and benzyl-bis(2-hydroxypropyl)amine (BBHPA; an equimolar mixture of diastereomers) in aqueous solutions was examined in terms of coordination mode around the boron by ^{11}B-NMR spectroscopy,[5] and the results are shown in Figure 1. The signal, the chemical shift value of which changes with an increase in the molar ratio of diolamine (N) to boron (B), is ascribed to boric acid/ borate ions, and the signal which is unchanged with the N/B ratio is ascribed to the boron complex. The latter peak appears at the chemical shift of –9.4 ppm for BBHEA and –9.7 ppm for BBHPA. We confirmed no formation of polynuclear boron complexes[6] in the present conditions. The complex formed under the present conditions is almost certainly a 1:1 bicyclo-type complex with an η^3-NO_2-η^1-O coordination mode (Figure 2), because the bicyclo-type and tricyclo-type complexes of boron with tris(2-hydroxyethyl)amine (THEA) appear at –9.5 ppm and at –5.8 ppm, respectively.[7] For the 1:1 complex, there is a possibility of several types of coordination: η^1-O coordination (acyclic η^1-O coordination), η^2-NO coordination resulting in 5-membered monocyclization (monocyclic η^2-NO coordination), and η^2-O_2 coordination resulting in 8-membered monocyclization (monocyclic η^2-O_2 coordination). However, the formation of acyclic η^1-O coordination- and monocyclic η^2-NO coordination-type complexes is not feasible, because it was revealed from ^{11}B-NMR spectroscopy that benzyl-2-hydroxyethylamine forms no boron complex. The monocyclic η^2-O_2 coordination-type

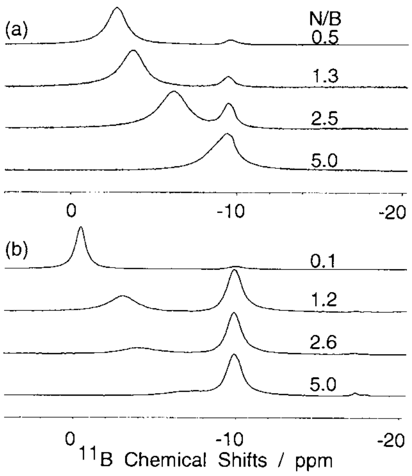

Figure 1. ^{11}B-NMR spectra of D_2O solutions containing 50 mmol dm^{-3} boric acid and BBHEA (a) and BBHPA (b) with various N/B ratios.

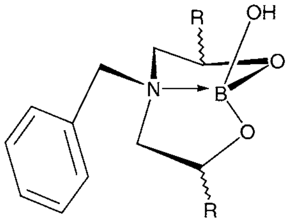

Figure 2. The proposed structure of boron complexes with benzyl-bis(2-hydroxyalkyl)amine (R: H and CH_3) based on NMR spectroscopy.

Table 1 Boron-isotope separation factors of boron-chelating ligands with bis(2-hydroxyalkyl)amino groups at 25 °C

Polymer	Polymer weight/ g	Solution volume/ cm^3	B concentration in solution/ mmol dm^{-3}		$^{10}B/^{11}B$ Ratio in solution		pH	S^a
			C_0	C_s	α_0	α_s		
1	1.7117	10	9.25	6.48	0.25254	0.25049	6.13	1.027 (0.001)
2	1.9379	10	9.25	5.71	0.25254	0.24996	6.00	1.027 (0.001)

[a] The numbers in parentheses denote the standard deviation σ (the number of samples n=15).

complex is not likely to be formed, because, to the best of our knowledge, an 8-membered cyclic boroester has not been reported so far. The 8-membered cyclic complex would show a ^{11}B-NMR signal at a chemical shift value near –18 ppm, which is very far from the value given in Figure 1, because 1:1 boron complexes with 1,2- and 1,3-diols have ^{11}B-NMR signals around –12.6 to –14.9 ppm and –17.9 to –18.5 ppm, respectively.[8] We can conclude from these considerations that the complex observed in the ^{11}B-NMR spectra of Figure 1 is the 1:1 bicyclo-type complex with an η^3-NO_2-η^1-O coordination mode as shown in Figure 2. The formation of this boron complex is supported by ^{13}C-NMR spectroscopy.[9] The boron complexes with bis(2-hydroxyalkyl)amine have a tetrahedral coordination geometry around the boron atom through the coordination of heteroatoms. The complexes are expected to form in a pH range of 6-11, from the result of pH dependence in the formation of a 1:1 bicyclo-type boron complex with THEA.[7]

The fractionation of boron isotopes by chelating ligands with bis(2-hydroxyalkyl)amino groups was investigated by using chelating polymers possessing the relevant ligands. Chloromethylated polystyrene (the content of chloromethyl groups: 3.6 mmol g^{-1}) was obtained by the usual chloromethylation[10] of styrene-divinylbenzene copolymer beads (Amberlite XAD-4). It was reacted with bis(2-hydroxyethyl)amine and bis(2-hydroxypropyl)amine (an equimolar mixture of diastereomers) in dimethylformamide at 100 °C for 4 h to obtain chelating polymers with bis(2-hydroxyethyl)amino (**1**) and bis(2-hydroxypropyl)amino groups (**2**), respectively {N contents: 1.51 (**1**) and 1.16 mmol g^{-1} (**2**); H^+ uptakes: 1.3 (**1**) and 1.0 mmol g^{-1} (**2**)}.

The isotopic separation equilibrium was examined batchwise by shaking the chelating polymer beads in a 100 mg dm^{-3} boric acid solution (Merck, suprapur) at 25 °C for 7days. The boron concentrations in the solution before and after adsorption (C_0 and C_s) were determined by ICP emission spectroscopy. The $^{10}B/^{11}B$ ratios in the solution before and after adsorption (α_0 and α_s) were determined by negative thermal ionization mass spectrometry with a VG Sector54 type mass spectrometer (Fisons Insts.), measuring the beam strengths of the mass numbers 42 and 43 with respect to negative BO_2^- (the precision is < 0.002 % for the internal error and < 0.05 % for the external error). The isotope separation factor (S) is defined as $S=(^{10}B/^{11}B)_{polymer}/(^{10}B/^{11}B)_{solution}$ and its value can be determined from the values of C_0, C_s, α_0, and α_s.

The exchange equilibrium of boron isotopes on the chelating polymer H_2L (**1** and **2**) from a boric acid solution with a pH value < 7 is expressed by eq 2,

$$^{10}B(OH)_3 + {}^{11}B(OH)L \rightleftharpoons {}^{11}B(OH)_3 + {}^{10}B(OH)L \qquad (2)$$

where B(OH)L denotes the boron complex in the polymer phase, which has a distorted tetrahedral coordination geometry around the central boron atom with an η^3-NO_2-η^1-O coordination mode.

The results of isotope separation factors are summarized in Table 1. The isotope separation factors of chelating polymers **1** and **2** are 1.027, demonstrating that ^{10}B is bound on the tetrahedral species B(OH)L more selectively than on the planar triangular species $B(OH)_3$. It is noteworthy that the isotope separation factors of chelating polymers **1** and **2** are greater than the upper limit (1.019) of the anion exchangers. The marked increase in the isotope separation may be due to the distortion of the regular tetrahedral coordination geometry around the central boron atom through the coordination of heteroatoms with an η^3-NO_2-η^1-O chelation mode.

In conclusion, ^{10}B is more fractionated to bis(2-hydroxyalkyl)amine borate with a tetrahedral coordination mode than to boric acid with a planar triangular coordination geometry in aqueous solutions, exhibiting an isotope separation factor of 1.027 which is larger than the upper limit of anion-exchangers. The concept of tetrahedral coordination around the boron atom through heteroatoms will be very useful in the design of novel ligands for the separation of boron isotopes in aqueous solutions.

References and Notes

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9 ^{13}C-NMR [100.53 MHz, a D_2O solution of 0.5 mol dm^{-3} boric acid and 0.5 mol dm^{-3} BBHEA, 0 °C, relative to sodium 2,2-dimethyl-2-silapenta-5-sulfonate as an internal standard]: δ 57.5 (N-$\underline{C}H_2$-CH_2-OB), 62.5 (N-CH_2-$\underline{C}H_2$-OB), and 61.6 (Ph-$\underline{C}H_2$-N) due to the complex, accompanied by 57.5 (N-$\underline{C}H_2$-CH_2-OH), 60.7 (N-CH_2-$\underline{C}H_2$-OH), and 60.9 (Ph-$\underline{C}H_2$-N) due to the free ligand.

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