Bull. Chem. Soc. Jpn., 73, 1131—1133 (2000)

pH-Dependence of the Fractionation of Boron Isotopes with *N*-Methyl- D-Glucamine Resin in Aqueous Solution Systems

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(Received November 4, 1999)

We have found a unique pH dependence of the fractionation of boron isotopes with *N*-methyl-D-glucamine resin in aqueous solution systems. The fractionation is due to the adsorption of ^{10}B isotopes from the solution phase to the resin phase. For pH values less than 7, the boron-isotope separation factors are 1.027, indicating that ^{10}B isotopes are concentrated in the resin more selectively than ^{11}B isotopes. On the other hand, for the pH values greater than 11, the factors are 0.998, revealing no fractionation of boron isotopes. In the intermediate pH range, the factors are decreased significantly with an increase in pH. This finding confirms that ^{10}B is fractionated as boron complexes with a tetrahedral coordination geometry in resin phase more selectively than as those with a planar trigonal coordination geometry in solution phase, while ^{11}B exhibits the opposite relation. This finding will provide a very important basis for separation of boron isotopes with novel chelating resins in aqueous solution systems.

We are interested in the molecular design of novel chelating polymers for separation of boron isotopes with a boron-isotope separation factor greater than those of anion exchangers.[1—3] Our design for such chelating polymers is based on the concept that the fractionation of boron isotopes is primarily due to a change in coordination geometry, that is, ^{10}B is fractionated more to boron complexes with a tetrahedral coordination structure than to those with a planar triangular coordination structure.[4] We have already found a markedly more selective fractionation of ^{10}B isotopes to bis(2-hydroxyalkyl)amine borate with a tetrahedral coordination structure than to boric acid with a planar trigonal coordination structure in aqueous solution systems.[4—6] It is well known that an *N*-methyl-D-glucamine type resin[7] (MGR), which has 1-deoxy-1-(methylamino)-D-glucitol groups (H_5L) as a functional group, shows a high amount of boron adsorbed in aqueous solution systems.[8—12] Recently, Yoshimura et al. reported that the resin forms a 1 : 1 tetradentate boron complex, $B^-(H_2L)^+$, with a tetrahedral coordination geometry.[13] In this study, we demonstrate for the first time that pH dependence of the fractionation of boron isotopes with MGR in aqueous solution systems is due to the adsorption of ^{10}B isotopes from the solution phase to the resin phase.

Experimental

Chemicals. **Chloromethylated Polystyrene Type Resin.** Commercially available poly(styrene-*co*-divinylbenzene) beads, Amberlite XAD-4 (Rohm and Haas), were washed with acetonitrile. The beads were dried at reduced pressure (50 °C, < 133 Pa) and the fraction between the 60 and 30 mesh sieve (250—500 µm) was collected. The dried beads (94.6 g) were put in a flat-bottom separable flask substituted in nitrogen gas. The beads were swelled in the poured 1,1,1,3-tetrachloroethane (100 g). After addition of chloromethyl methyl ether (500 g), the flask was cooled in an ice water bath. After addition of aluminum chloride (94.5 g) as catalyst using forceps for about 1 h, they were reacted at room temperature for 19 h. The reactants were poured into ice water to stop the reaction and the chloromethylated resin was collected by filtration. The resin was washed with water until the solution was neutral and with acetone until the solution was colorless. We obtained 125 g of chloromethylated polystyrene type resin after drying at reduced pressure. The existence of chloromethyl group was confirmed by the peak at 1271 cm^{-1} on infrared spectra analysis. The content of introduced chloromethyl group was 3.6 mmol/g-resin by elemental analysis of chlorine.

***N*-Methyl-D-glucamine Type Resin (MGR).** The dried chloromethylated polystyrene type resin (20.80 g) was put into a flat-bottom separable flask and swelled with *N*,*N*-dimethylformamide (DMF) (100 cm^3). 22.29 g of *N*-methyl-D-glucamine, which was suspended in DMF, was added into the reactor, and heated in an oil bath at 100 °C. The *N*-methyl-D-glucamine was soluble in the solution by heating. After 4 h, the reaction was quenched by addition of water; the resin was collected by filtration. The resin was washed with hot water and deionized water until the solution was neutral and with acetone until the solution was colorless. We obtained 24.02 g of MGR as a boron adsorbent after drying at reduced pressure. The contents of introduced 1-deoxy-1-(methylamino)-D-glucitol group were 1.26 mmol/g-resin by elemental analysis of nitrogen.

Boron Adsorption. The isotopic separation study was carried out batchwise by shaking MGR (0.2 g) and 20 cm^3 of 100 ppm boric acid solutions (Merck, suprapur) with different pH values containing 0.1 M KCl (1 M = 1 mol dm^{-3}) at 10 or 30 °C for one week. All 100 ppm boric acid aqueous solutions with different pH values were prepared by dilution in 100 cm^3 volumetric flasks which had contained a 25 cm^3 of 400 ppm boric acid, a 10 cm^3 of 1 M KCl, and a fixed hydrochloric acid or sodium hydroxide solution. After adsorption equilibrium, MGRs were filtered out. The boron concentrations of filtrates were measured with an inductively coupled plasma-atomic emission spectrometer (SPS 1500, Seiko Instruments Inc.). Amounts of boron adsorbed per 1 g dry resin were calculated from the difference of boron concentration in the solution by the adsorption.

Measurements of Boron Isotope Ratio. The $^{10}B/^{11}B$ ratios in the solution were determined with a thermal ionization mass spectrometer (Sector 54, Fisons Inst.) in negative ion mode using single rhenium filament unit, which was prepared by loading in the following order—calcium nitrate, sodium hydroxide, and sample of boron solution. The measurements detected the beam strengths of the mass numbers 42 and 43 with respect to BO_2^- using two Faraday cups at the same time. One measurement was accumulated for 10 s; a set of 10 measurements is called a block that is measured almost under the same apparatus conditions. The average isotope ratios in each block were changed by time, but relatively stabilized at 3—5 h after warming the filament unit. The isotope ratio in each filament is obtained as an average value in 30 stable blocks. The relative internal standard deviation (1σ) was 0.0040% within the same filament for 30 blocks and the external value was 0.05% for 15 independent measurements. The boron-isotope separation factor (S) is defined in Eq. 1,

$$S = (^{10}B/^{11}B)\mathrm{resin}/(^{10}B/^{11}B)\mathrm{solution}$$
$$= [\alpha_0(1+\alpha_s)C_0 - \alpha_s(1+\alpha_0)C_s]/[\alpha_s(1+\alpha_s)C_0 - \alpha_s(1+\alpha_0)C_s], \quad (1)$$

where C_0 and C_s are the boron concentrations and α_0 and α_s are $^{10}B/^{11}B$ ratios in solution phase before and after adsorption, respectively.

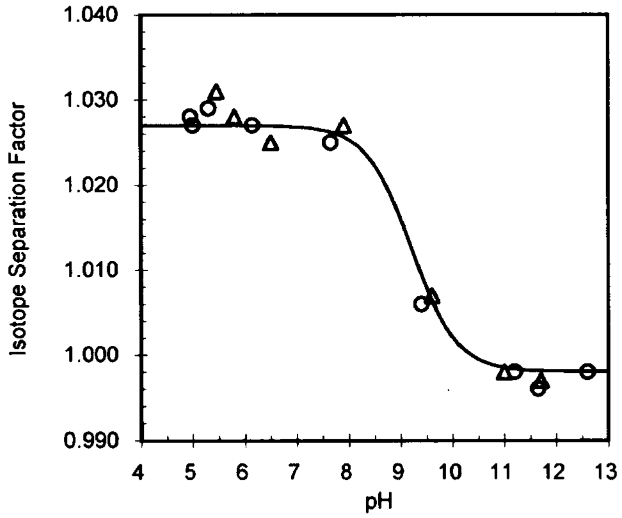

Fig. 2. pH dependence of the fractionation of boron isotopes with *N*-methyl-D-glucamine type resin in a boric acid solution at 10 °C (△) and 30 °C (○). The solid line represents the theoretical estimation by Eq. 5 using $S_1 = 1.027$, $S_0 = 1.029$ under an assumption of $pK_{11} = pK_a$ (= 9.22) (see text).

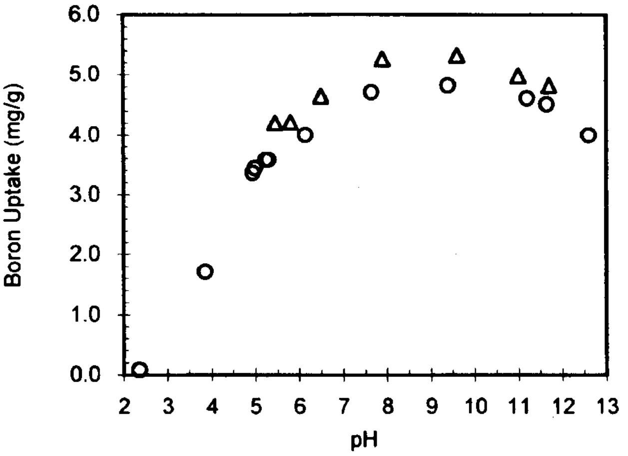

Fig. 1. pH dependence of the boron uptake on *N*-methyl-D-glucamine type resin at 10 °C (△) and 30 °C (○).

Results and Discussion

The adsorption of boron on MGR is given as a function of pH in Fig. 1. The amount of boron adsorbed of MGR increases with an increase of the pH value larger than 2, attaining a maximum around pH 9. Further increase in pH results in a decrease of the amount of boron adsorbed. Figure 1 shows also that MGR exhibits a higher amount of boron adsorbed at the lower temperature. These characteristics are in good accordance with previously reported results on MGR.[8—12] The fractionation of boron isotopes with MGR exhibits a unique dependence on the pH value of the boric acid solution (Fig. 2). For pH values less than 7, S values are 1.027, indicating that ^{10}B isotopes are concentrated on MGR more selectively than ^{11}B isotopes. On the other hand, for the pH values greater than 11, the S values are 0.998, revealing no fractionation of boron isotopes. In the intermediate pH range, S decreases significantly with an increase in pH. S hardly varies with a change of temperature from 30 to 10 °C, as shown in Fig. 2. The pH dependence of S appears similar to the distribution curve of $B(OH)_3$ in a boric acid solution. What determines the pH dependence of the fractionation of boron isotopes with MGR, as shown in Fig. 2? In order to understand this phenomenon, we consider $B(OH)_3$ and $B(OH)_4^-$ as boron species in solution phase, because of no formation of polynuclear boron complexes in the present boron concentrations, as is also supported by the literature,[14] and a tetradentate complex, $B^-(H_2L)^+$,[13] between boron and *N*-methyl-D-glucamine groups (H_5L), as a boron species in the resin phase. The 1 : 1 complex, $B^-(H_2L)^+$, has a tetrahedral coordination geometry.[13] The hydrolysis equilibrium of boric acid is shown in Eq. 2:

$$B(OH)_3 + H_2O \rightleftarrows B(OH)_4^- + H^+$$
$$K_a = [B(OH)_4^-][H^+]/[B(OH)_3], \quad (2)$$

where K_a is the equilibrium constant and $pK_a = 9.22$.[15] Furthermore, the boron-isotope exchange equilibrium between $B(OH)_3$ and $B(OH)_4^-$ is shown in Eq. 3:

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- \rightleftarrows {}^{11}B(OH)_3 + {}^{10}B(OH)_4^-$$
$$S_0 = [^{11}B(OH)_3][^{10}B(OH)_4^-]/[^{10}B(OH)_3][^{11}B(OH)_4^-], \quad (3)$$

where S_0 is the isotope separation factor. It is noted that $S_0 = K_{10}/K_{11}$, where K_{10} and K_{11} are the equilibrium constants of Eq. 2 holding for ^{10}B and ^{11}B, respectively. Generally, both $B(OH)_3$ and $B(OH)_4^-$ exist in the solution phase, so the isotope separation factor S is expressed by the following Eq. 4:

$$S=\frac{[\overline{{}^{10}\mathrm{B}^-(\mathrm{H_2L^+})}]/[\overline{{}^{11}\mathrm{B}^-(\mathrm{H_2L^+})}]}{\{[{}^{10}\mathrm{B(OH)_3}]+[{}^{10}\mathrm{B(OH)_4}^-]\}/\{[{}^{11}\mathrm{B(OH)_3}]+[{}^{11}\mathrm{B(OH)_4}^-]\}}, \tag{4}$$

where upper lines denote a species in the resin phase. Based on the equilibrium in Eqs. 2 and 3, Eq. 4 is written into Eq. 5.

$$\begin{aligned} S &= S_1\times\frac{[\mathrm{H^+}]+K_{11}}{[\mathrm{H^+}]+K_{10}} \\ &= S_1\times\frac{[\mathrm{H^+}]+K_{11}}{[\mathrm{H^+}]+S_0K_{11}}, \end{aligned} \tag{5}$$

where

$$S_1=\frac{[\overline{{}^{10}\mathrm{B}^-(\mathrm{H_2L^+})}]/[\overline{{}^{11}\mathrm{B}^-(\mathrm{H_2L^+})}]}{[{}^{10}\mathrm{B(OH)_3}]/[{}^{11}\mathrm{B(OH)_3}]}. \tag{6}$$

The boron-isotope separation factor S_1 is related to the equilibrium between $\mathrm{B(OH)_3}$ and $\overline{\mathrm{B^-(H_2L)^+}}$ as in Eq. 7:

$${}^{10}\mathrm{B(OH)_3}+\overline{{}^{11}\mathrm{B^-(H_2L)^+}} \rightleftarrows {}^{11}\mathrm{B(OH)_3}+{}^{11}\mathrm{B(OH)_3}. \tag{7}$$

If $[\mathrm{H^+}] \gg K_{11} \approx K_{10}$, $S \approx S_1$. From the results in Fig. 2, the S_1 value is equal to 1.027. On the other hand, if $[\mathrm{H^+}] \ll K_{11} \approx K_{10}$, $S \approx S_1/S_0$.

$$\frac{S_1}{S_0}=\frac{[\overline{{}^{10}\mathrm{B}^-(\mathrm{H_2L^+})}]/[\overline{{}^{11}\mathrm{B}^-(\mathrm{H_2L^+})}]}{[{}^{10}\mathrm{B(OH)_4}^-]/[{}^{11}\mathrm{B(OH)_4}^-]}. \tag{8}$$

The S_1/S_0 is related to the equilibrium between $\mathrm{B(OH)_4}^-$ and $\overline{\mathrm{B^-(H_2L)^+}}$ as in Eq. 9:

$${}^{10}\mathrm{B(OH)_4}^- + \overline{{}^{11}\mathrm{B^-(H_2L)^+}} \rightleftarrows {}^{11}\mathrm{B(OH)_4}^- + \overline{{}^{10}\mathrm{B^-(H_2L)^+}}. \tag{9}$$

Thus, Fig. 2 shows clearly that the S_1/S_0 value is equal to 0.998. When we assumed $K_{11}=K_a=10^{-9.22}$, $S_1=1.027$ and $S_0=1.029$ in Eq. 5, the theoritical curve could be shown by the solid line in Fig. 2. The line is in good agreement with the plotted experimental data. This experimental S_0 value (1.029) is close to the theoretical one (1.025) by Hirotsu et al. using density functional theory methods,[16] but slightly greater than that (1.019) reported by Kakihana et al.[3] The Formula of S in Eq. 5 demonstrates that ${}^{10}\mathrm{B}$ isotopes are more fractionated to $\mathrm{B(OH)_4}^-$ and $\overline{\mathrm{B^-(H_2L)^+}}$, although ${}^{11}\mathrm{B}$ isotopes are more fractionated to $\mathrm{B(OH)_3}$. With an increase of pH, the adsorption of ${}^{10}\mathrm{B}$ isotopes is more significant due to an increase in the mole fraction of $\mathrm{B(OH)_4}^-$ in solution phase, and results in no fractionation of boron isotopes with MGR in the pH value greater than 11, because of $S_1 \approx S_0$. This finding confirms that ${}^{10}\mathrm{B}$ is fractionated in boron complexes with a tetrahedral coordination geometry more selectively than in those with a planar trigonal coordination geometry, while ${}^{11}\mathrm{B}$ exhibits the opposite relation, leading to our concept for design of chelating resins for separation of boron isotopes. We have already found a higher affinity of ${}^{10}\mathrm{B}$ isotopes to a tetrahedral coordination than to a planar trigonal one in bis(2-hydroxyalkyl)amine borate.[4—6] Bigeleisen and Mayer[17] have shown that a change in coordination geometry of complexing does not necessarily lead to a useful isotope fractionation by indicating the large cancellation of the fractionation of ${}^{118}\mathrm{Sn}$ and ${}^{120}\mathrm{Sn}$ between $\mathrm{SnCl_4}$ and $\mathrm{SnCl_6}^{2-}$ as an example. The successful fractionation in the case of boron isotopes is probably due to both a larger mass ratio between boron isotopes and a larger intramolecular force field around the boron atom through the higher stability of a boron complex with a planar trigonal geometry, as pointed out by Palko and Drury.[18] Furthermore, the expression in Eq. 5 indicates strongly that fractionation of ${}^{10}\mathrm{B}$ isotopes has to be considered in the separation of boron isotopes with a chelating resin having ligand groups which form tetrahedral complexes with boron in an aqueous boron solution.

In conclusion, we have found a pH,dependence of the fractionation of boron isotopes with *N*-methyl-D-glucamine resin, $\mathrm{H_5L}$, in aqueous solution systems which can be expressed by Eq. 5. The pH dependence is due to the adsorption of ${}^{10}\mathrm{B}$ from the solution phase to the resin phase. This finding will provide a very important basis for separation of boron isotopes with novel chelating resins in aqueous solution systems.

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