



Interaction of borate and phenylboronate with the cross-linked dextran gel matrix

Yoshinobu Miyazaki^{a,*}, Shiro Matsuoka^b, Kei Asada^a, Yuma Kawasaki^a, Kazuhisa Yoshimura^c

^a Department of Chemistry, Fukuoka University of Education, Akamabunkyo-machi, Munakata, Fukuoka 811-4192, Japan

^b Department of Environmental Science, Faculty of Science, Niigata University, Ikarashi, Niigata 950-2181, Japan

^c Department of Chemistry, Faculty of Sciences, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

ARTICLE INFO

Article history:

Received 9 April 2018

Accepted 18 May 2018

Available online 29 May 2018

Keywords:

Cross-linked dextran gel

Binding sites

Adsorbed boron species

Boron adsorption property

¹¹B NMR

ABSTRACT

The interaction of borate and phenylboronate with dextran gels having different degrees of cross-linking was investigated to clarify the structures of the adsorbed boron species, binding sites of the gel matrix, and the adsorption properties. The main adsorbed species of the phenylboronate was the five-membered mono-chelate complex. In addition to this, the five-membered bis-chelate complex, and the five- and six-membered bis-chelate complex were also the main species for the borate. The boron adsorption was not produced by the glucopyranoside units that were the major constituents of the dextran gel, but by the gluconate residues and various forms of the glycerol residues, which had been generated during the cross-linking process of the dextran. The adsorption behavior was reproduced by the calculation taking the complexation of boron with the gel matrix and the Gibbs–Donnan relation into consideration.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Increasing attention has been paid to the environmental toxicity of boron in water [1,2]. Boron is a micronutrient for plants and animals, but the range between its deficiency and excess is narrow. Boron has a toxic effect on crops when it exists in a high concentration in irrigation water. It is also harmful to humans causing abdominal pain, diarrhea, nausea and vomiting. Boron compounds are commonly utilized in various industries [3], including the production of glasses, ceramics, detergents, etc., which leads to an increase in the concentration of boron in wastewater. The World Health Organization (WHO) set a health-based guideline value of 2.4 mg/L for the concentration of boron in drinking water [2]. According to the domestic regulations in Japan, the environmental water-quality standard for boron is set at 1.0 mg/L and its concentration in discharge water should be reduced to less than 10 mg/L for public water and 230 mg/L for the sea area. Boron is also used as a dopant for P-type semiconductors. Because the presence of boron could significantly influence the characteristics of semiconductors, ultra-trace amounts of boron should be eliminated from the cleaning water used in the manufacturing. The effective removal of boron from various types

of water has been highly demanded. Several polymer-based boron-selective adsorbents having polyhydroxy moieties, such as *N*-methyl-D-glucamine [4–7], saccharides [8–13], 2-(hydroxymethyl)-1,3-propanediol [14] and pyrocatechols [15], have been investigated. The *N*-methyl-D-glucamine resin with a strong boron adsorption was used for the removal of boron from irrigation water. Besides the removal of boron, the separation of boron isotopes is also an interesting research area. Boron naturally exists as ¹⁰B and ¹¹B isotopes, the latter of which accounts for about 80% of natural boron. The ¹⁰B isotope has been used as a neutron absorber material, and the enrichment of ¹⁰B is highly required for the development of drugs used in boron neutron capture therapy (BNCT) [16]. The *N*-methyl-D-glucamine type resin [17] and the pyrocatechol-modified resins [15] were evaluated for the separation of boron isotopes.

Boric acid and boronic acid behave as Lewis acids to produce the borate ion or boronate ion, the structures of which around the boron change from trigonal planar to tetrahedral. The acid dissociation constants of the boric acid and phenylboronic acid are $pK_a = 9.05$ [6] and 8.77 [18] ($I = 0.1$, 295 K), respectively. The boron binds with polyols to form complexes with five- and/or six-membered chelate rings [18–25]. During the 1:1 complexation step, neutral polyols, such as ethylene glycol and glycerol, react with the tetrahedral borate ion and phenylboronate ion, whereas acidic polyols, such as α -hydroxy carboxylic acid, react with the trigonal boric

* Corresponding author. Fax: +81 940 35 1711.

E-mail address: miyazaky@fukuoka-edu.ac.jp (Y. Miyazaki).

acid and phenylboronic acid. The 1:1 complexes of the boric acid/borate ion can then react with another neutral polyol to form 1:2 complexes. All of these reactions produce tetrahedral anionic complexes. In order to develop boron-selective adsorbents suitable for a variety of purposes, comprehensive knowledge about the solution chemistry of boron is required.

Sephadex, which is a polysaccharide gel produced by the cross-linking of dextran with epichlorohydrin, has been widely used as a medium for gel chromatography. The dextran elaborated by a lactic acid bacterium termed *Leuconostoc mesenteroides* NRRL B-512 (F) consists of an α -(1,6)-linked glucan as the main chain with 4.1% α -(1,6)-linked glucan side-chains attached by α -(1,3) branch linkages to the backbone glucose units [26]. Sephadex with the appropriate cross-linking degree can be prepared by changing the molecular weight of dextran, the concentration of dextran and the amount of epichlorohydrin. Holmberg studied the structure of Sephadex G-25 and reported the following characteristics [27]: only 4% of the glucose units are cross-linked and 80% of the Sephadex beads consist of dextran, and eight different structural elements were identified, including several glyceryl ethers of glucose and cyclic structures containing 1,4-dioxan rings. The cross-linked dextran gel has many hydroxy groups in the matrix, thus the gel exhibits an adsorption for boron without introducing any specific functional groups. Boric acid/borate ion is adsorbed onto the polysaccharide gel from an alkaline medium and reversibly desorbed into an acidic medium [8]. The pH dependent boron adsorption increases with the decreasing concentration of boron, while it decreases in a higher pH range. The ^{11}B NMR spectra for the dextran gel equilibrated with a boric acid/borate ion solution clearly showed that the adsorption was a consequence of the complex formation between the borate ion and the gel matrix [11–13]. We revealed that a five- and six-membered bis-chelate complex in addition to the five-membered mono- and bis-chelate complexes and the six-membered mono-chelate complex were formed as the adsorbed boron species. We also reported that the boron-binding site was the glucopyranoside unit, which was the major constituent of the cross-linked dextran. However, it is unclear as for the reason why the boron adsorption depends on the concentration of boron, and decreases in the higher pH range. In this study, we have reexamined the binding sites of the dextran gels and the structures of the adsorbed species to elucidate the boron adsorption properties. To be specific, we have investigated the interaction of the phenylboronic acid/phenylboronate ion as well as the boric acid/borate ion with dextran gels having different degrees of cross-linking by equilibrium distribution measurements, NMR spectroscopy and DFT calculations. The ionic strength was maintained constant at 0.1 (NaCl) as in our previous research. The knowledge acquired in this study will be useful to establish a new guiding principle to develop boron-selective adsorbents suitable for various purposes.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used as received. Dextran gels with different degrees of cross-linking, Sephadex G-10, G-15, G-25, G-50 and G-75, were purchased from GE Healthcare Bio-Sciences AB (Uppsala, Sweden). These gels were treated with a 0.1 mol dm^{-3} NaCl solution, fully washed with water, then stored under an air-dried condition. Azomethine H and phenylboronic acid were purchased from Dojindo Laboratories (Kumamoto, Japan) and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), respectively. All other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

2.2. Gel parameters

The Sephadex gel bed can be simply divided into the following three regions: the gel internal solution, the gel skeleton, and the interstitial space between the gel beads. The volume of the gel internal solution was determined as follows. An appropriate amount of dried gel was swollen in a 0.1 mol dm^{-3} NaCl solution, then packed into a column (1.5 cm id, 11.5 cm length). A sufficient quantity of a 0.1 mol dm^{-3} NaCl solution was added to flow through the column. The NaCl solution in the interstitial space was filtered off with suction and the column was weighed. It was then dried in a thermostatically controlled oven at 90°C for 2 days. The dried column was cooled in a desiccator and weighed. The volume of the gel internal solution (imbibed water) was estimated by the decrease in weight, and was taken as the gel phase volume, V_g , expressed in cm^3/g dried gel.

The concentration of the glucopyranoside unit in the Sephadex, C_{glu} , was calculated in mmol dm^{-3} , assuming that the chemical formula could be expressed as $\text{C}_6\text{H}_{10}\text{O}_5$, and the concentration of the moieties participating in the cross-linking was ignored.

The quantities of carboxylate (gluconate) in the Sephadex G-10, G-15 and G-25 were determined by acid–base titrations. An appropriate amount of Sephadex was placed in a column, a sufficient quantity of a 0.01 mol dm^{-3} HCl solution was passed through it, then the gel in the column was thoroughly washed with water. The treated Sephadex was titrated with a 0.01 mol dm^{-3} NaOH solution using an automatic AT-510 titrator (Kyoto Electronics) in a state of being suspended in distilled water under an atmosphere of nitrogen gas. The concentration of carboxylate (gluconate) in the Sephadex, C_{GA} , was expressed in mmol dm^{-3} .

2.3. Distribution measurements

To investigate the adsorption behavior of boron onto the Sephadex, the distribution coefficient, K_d , was determined by a batch technique. When m g of the gel is added to $V \text{ cm}^3$ of a solution containing boron, K_d is expressed as

$$K_d = \left(C_B^{\text{int}} - C_B^{\text{eq}} \right) \cdot V / \left(C_B^{\text{eq}} \cdot m \cdot V_g \right) \quad (1)$$

where C_B^{int} is the initial concentration of boron, and C_B^{eq} is the concentration of boron in the equilibrium solution. The volume of the solution absorbed by the gel was ignored.

The effects of the pH and boron concentration on the boron adsorption were determined as follows. To 20 cm^3 of a boron solution ($I = 0.1$, NaCl), whose pH had been adjusted with a slight amount of HCl or NaOH solution, was added 0.5 g of Sephadex. The mixture was mechanically stirred for 24 h at 25°C until equilibrium was reached. The pH of the equilibrium solution was measured by a Horiba F-52 pH meter. The boron concentration in the equilibrated solution was determined using an Agilent 8453 UV–Vis spectrophotometer with Azomethine H as the coloring reagent [28]. The temperature dependence of the boron adsorption was also evaluated. Sephadex G-25 (0.5 g) was equilibrated with 250 cm^3 of a solution ($I = 0.1$, NaCl– Na_2CO_3 –NaOH, pH 11) containing $9.25 \times 10^{-4} \text{ mol dm}^{-3}$ or $7.40 \times 10^{-6} \text{ mol dm}^{-3}$ borate ion over the temperature range from 0 to 45°C . The boron concentration in the equilibrated solution was then measured by the spectrophotometric method using Azomethine H.

2.4. NMR measurements

The ^{11}B and ^{13}C NMR spectra were recorded by a JEOL JNM-ECX400 spectrometer at 128.3 MHz and 100.5 MHz, respectively. The field frequency lock was achieved with the deuterium resonance of D_2O in a concentric capillary tube. Sample tubes made

Download English Version:

<https://daneshyari.com/en/article/7762549>

Download Persian Version:

<https://daneshyari.com/article/7762549>

[Daneshyari.com](https://daneshyari.com)