

Complexation of Borate with Cross-Linked Polysaccharide Anion Exchanger: ^{11}B NMR and Adsorption Properties Studies

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ABSTRACT: Boron adsorption behavior on cross-linked polysaccharide anion exchangers, QAE-Sephadex and QA cellulose, was examined in detail by ^{11}B NMR measurements and distribution studies. For the QAE-Sephadex system, two signals of 1:1 borate complexes with α,β - and α,γ -diol moieties of the glucopyranoside residues were observed, showing identical chemical shift values with those for the Sephadex gel system. Only the 1:1 complex of borate with α,β -diol moiety of the gel matrix was formed for QA cellulose. The formation constants of the borate complexes, estimated by the signal intensities of ^{11}B NMR, were almost the same in the anion exchangers and Sephadex gel. The adsorbability of boric acid/borate was not enhanced as much by the presence of charged functional groups, because both the ion-exchange selectivity toward borate and formation constants of borate complexes with the gel matrix are not so high. The pH in the anion exchanger phase is higher than that in the external equilibrated solution, however, is slightly lower than the value expected from the Donnan relation, as a result of the fixation of anionic borate onto the gel matrix by the complexation: $-\log[\text{H}^+] = -a \log[\text{H}^+] + b$ ($a \leq 1$ and $b > 0$). Boron adsorption behaviors on the polysaccharide anion exchangers, such as pH dependence, boron concentration dependence, and background electrolyte effect, can be explained satisfactorily on the basis of such properties.

Introduction

There exist a large number of reports on the hydrogel formation of polyhydroxyl compounds such as poly(vinyl alcohol),^{1–9} poly(glyceryl methacrylate),^{10,11} and polysaccharide^{12–17} in the presence of borate. The characteristic properties of the polymer–borate mixtures, such as gelation and rheological behavior, are controlled by the complex formation of borate. It has been confirmed by NMR spectroscopy that borate reacts with ligands containing diol or triol to form stable complexes with 1:1 and 1:2 stoichiometries.^{18–26} In the sol–gel transition, intermolecular complexes between borate and polyhydroxyl groups on the polymer chains work as cross-links. Most of the studies on the transient reversible gels focused on the gelation mechanism and rheological properties; however, effects of borate complexation upon solid-phase inner solution properties in permanent gels have never been studied.

We are interested in boron adsorption behavior on polymers with polyhydroxyl groups as well as their reaction mechanism to develop boron-selective adsorbents for the concentration and recovery of boron, purification of materials from boron, and the isotope separation. Previously, we clarified that the interaction of boric acid/borate with linear and cross-linked polysaccharides is a consequence of complex formation between borate and diol moieties of glucopyranoside residues by ^{11}B NMR studies.²⁷ It was also revealed that hydrodynamic and steric hindrance due to rigid structures of

the polymer ligands are important factors for the complexation. On the basis of the property that boron adsorbability onto Sephadex gel (dextran cross-linked by epichlorohydrin) is dependent on pH of the equilibrated solution, the gel has been used to concentrate boron in natural water and rocks.²⁸

In this paper, boron adsorption behavior on QAE-Sephadex gel, which is an anion-exchange Sephadex containing diethyl(2-hydroxypropyl) quaternary amino groups (Figure 1), was examined in detail by using distribution studies and ^{11}B NMR measurements. The adsorption of boron onto QA cellulose anion exchange gel having a structure (Figure 1) similar to that of QAE-Sephadex was also investigated. The main objective of this work is to clarify the reaction mechanism of boric acid/borate with the anion-exchange gels and the effects of borate complexation on the gel phase properties. A comparison between boron adsorption behaviors for Sephadex gel and those for two kinds of anion-exchange gels provides useful information about the influences of cationic functional groups introduced into polysaccharide gels on the adsorption.

Experimental Section

Chemicals. All chemicals were of analytical grade. Deionized water prepared with a Milli-Q SP system (Millipore) was used throughout. QAE-Sephadex A-25 (Pharmacia) and QA-52 cellulose (Whatman) in the chloride forms were used. The gels were regenerated by using a 0.1 mol dm⁻³ NaCl solution and then washed fully with water. After the solution was filtered off with suction, the wet gels were stored in polyethylene containers.

Gel Parameters. The anion exchanger gel phase was simply divided into three regions as Sephadex G-25 gel.²⁷ The volume of gel internal solution, v_i (cm³ g⁻¹), was determined as follows: a 0.1 mol dm⁻³ NaCl solution containing 1.0 mmol

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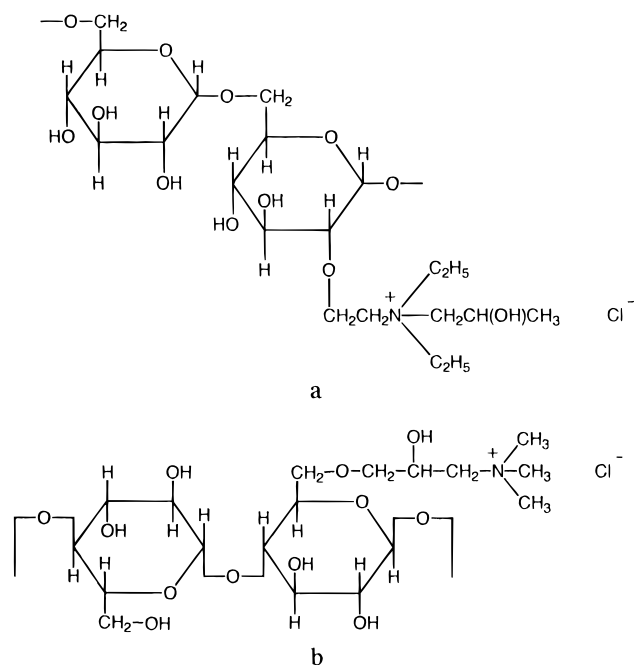


Figure 1. Functional groups of anion exchanger QAE-Sephadex A-25 (a) and QA-52 cellulose (b).

dm^{-3} $MgCl_2$ was mixed with 1.00 g of QAE-Sephadex A-25 or QA-52 cellulose gel which had been dried at $110^\circ C$ for 24 h before use, and the mixture was stirred mechanically at $25^\circ C$ for 3 h. After the supernatant solution was filtered through a $0.45\ \mu m$ cellulose nitrate membrane filter (Advantec), the concentration of Mg^{2+} in the solution was determined by atomic absorption spectrophotometry with a Nippon Jarrell-Ash apparatus, model AA-8500. The unit inner volume v_i was calculated by the increase in the concentration of Mg^{2+} in the equilibrated solution, since Mg^{2+} is excluded from the anion exchanger phase.

Similarly, the volume of interstitial space between the gel beads, v_0 , was determined. An appropriate amount of solution containing $0.1\ mol\ dm^{-3}$ NaCl and $1.0\ mmol\ dm^{-3}$ $MgCl_2$ was made to flow through a column (16 mm i.d., 100 mm long) containing 1.00 g of QAE-Sephadex A-25 or QA-52 cellulose swollen in water. After having passed through the column, the solution in interstitial space of the gel was eluted with water. The interstitial space volume v_0 was estimated from the concentration of Mg^{2+} in the eluate determined by the foregoing method.

The total gel bed volume v_t was obtained by measuring the volume of a known amount of dried gel equilibrated with a sufficient amount of a $0.1\ mol\ dm^{-3}$ NaCl solution with a volumetric cylinder. The volume of the gel skeleton (v_g) was calculated from the relation: $v_g = v_t - v_0 - v_i$.

The ion-exchange capacities of the two kinds of anion exchangers were determined by the following method. A $0.1\ mol\ dm^{-3}$ $NaNO_3$ solution was slowly passed through the column packed with a known amount of each anion exchanger in the chloride form, and then, the amount of Cl^- in the effluent was determined by Fajans' argentometry. The concentrations of the glucopyranoside residues in the gel phase were estimated as reported previously.²⁷ These gel characteristic parameters are listed in Table 1.

Distribution Measurements. To investigate the adsorption behavior of boric acid/borate on QAE-Sephadex gel, the distribution coefficient K_d was determined by the batch technique. When a mass m of the gel is added to a volume v of a solution containing boron, K_d is expressed as

$$K_d = (C_{int} - C_{eq}) v / (C_{eq} m v_i) \quad (1)$$

where C_{int} is the initial concentration of boron and C_{eq} the concentration of boron in the equilibrated solution.

The effect of pH of the equilibrated solution on the adsorption of boric acid/borate was examined as follows. To $25\ cm^3$ of a $1.0\ mmol\ dm^{-3}$ boric acid solution ($I = 0.1$, NaCl), in which pH was adjusted with a little amount of acetate, phosphate, or ammonia buffer, or NaOH solution, was added 2.00 g of QAE-Sephadex A-25. The mixture was stirred mechanically for 3 h at $25^\circ C$ until equilibrium was reached. Then, the equilibrium solution was filtered through a $0.45\ \mu m$ cellulose nitrate membrane filter, and the pH of the solution was measured with a Horiba pH meter, model F-22. The boron concentration in the equilibrated solution was determined using a JASCO U-best 35 UV/vis spectrophotometer with Azomethine-H as a coloring reagent.²⁹

The variation of adsorbability of boric acid/borate onto QAE-Sephadex gel with the concentration of boron in the equilibrated solution (pH 10.3 and $I = 0.1$) was investigated in the same way as mentioned above. In the case that the total concentration of boron in the equilibrated solution was lower than $10^{-5}\ mol\ dm^{-3}$, $1000\ cm^3$ of the sample, with the pH of the solution adjusted to 10.3 with ammonia buffer solution and the ion strength to $I = 0.1$, was made to pass through the column containing 2.00 g of QAE-Sephadex A-25 which had been conditioned with a dilute ammonia solution (pH 10). After the solution in the interstitial space of gel beads was removed with suction, the boron was desorbed with $0.1\ mol\ dm^{-3}$ HCl solution. The boron concentration in the effluent was determined by the above method.

To clarify the ion-exchange behavior of ions, we investigated the selectivity coefficients of HCO_3^- , Br^- , NO_3^- , ClO_4^- , and $B(OH)_4^-$ ions for QAE-Sephadex gel as well as for QA cellulose gel in the chloride form. The selectivity coefficient has been evaluated as follows. To every $10\ cm^3$ of $1.0\ mmol\ dm^{-3}$ of HCO_3^- , Br^- , NO_3^- , or ClO_4^- solution, 0.200 g of QAE-Sephadex A-25 or QA-52 cellulose in the chloride form was added. After being mechanically stirred for 3 h, the mixtures were filtered and the concentrations of Cl^- in the equilibrated solutions were measured by ion chromatography with an apparatus set up by our laboratory. In the case of $B(OH)_4^-$, 0.200 g of QAE-Sephadex or QA cellulose in the chloride form was added to $10\ cm^3$ of $2.0\ mmol\ dm^{-3}$ Borax solution whose pH was adjusted at 9.3 with ammonia buffer under nitrogen gas. After equilibration, the concentration of boron in the equilibrated solution was determined spectrophotometrically by the Azomethine-H method and that of Cl^- by ion chromatography.

NMR Measurements. ^{11}B NMR measurements were performed on a JEOL JNM-GSX 500 spectrometer at a resonance frequency of 160.0 MHz with a 10 mm multinuclear probe at $24 \pm 1^\circ C$. The boric acid/borate solutions ($I = 0.1$, NaCl/ NH_4Cl) containing a known amount of QAE-Sephadex A-25 or QA-52 cellulose gel were prepared. To avoid the formation of polyborate,³⁰ the total concentrations of boric acid/borate were controlled below $0.025\ mol\ dm^{-3}$. The pH of the solution was adjusted with a small amount of HCl, NaOH, or NH_3-NH_4Cl buffer solution. After equilibration, the mixtures were used for the NMR measurements. The standard NMR parameters were as follows: the flip angle was ca. 90° (36 μs), the pulse repetition time was 1 s, and the spectral width was 31 kHz. The chemical shifts were reported with respect to a $0.1\ mol\ dm^{-3}$ boric acid as an external reference. Overlapping NMR signals were resolved into individual peaks by Lorentzian curve-fitting method.

Results

^{11}B NMR Studies. Figures 2 and 3 show the ^{11}B NMR spectra for QAE-Sephadex A-25 and QA-52 cellulose gels equilibrated with solutions ($I = 0.1$, NaCl/ NH_4Cl) containing boric acid/borate at different pH values, respectively. Since the complexation between boric acid/borate and diol sites is slow relative to the ^{11}B NMR time scale, signals due to the complexes are observed separately from those of free boric acid/borate. The signals whose chemical shifts change with pH in the equilibrated solution should be ascribed to the free

Table 1. Characteristic Parameters for Polysaccharide Gels^a

	volume/cm ³ g ⁻¹			
	V_t	V_i	V_0	V_g
QAE-Sephadex A-25	5.97	2.92 ± 0.36	2.27 ± 0.01	0.78 ± 0.12
QA-52 cellulose	6.29	1.49 ± 0.13	3.13 ± 0.09	1.67 ± 0.09

	concentration/monomol dm ⁻³		
	C_G	C_{ex}	C_{GLC}
QAE-Sephadex A-25	1.41 ± 0.01	0.640 ± 0.002	0.773 ± 0.002
QA-52 cellulose	1.70 ± 0.05	0.274 ± 0.002	1.70 ± 0.05

^a C_G : total concentration of glucopyranoside residues in the unit gel phase ($V_i + V_g$). C_{ex} : concentration of the glucopyranoside residues with the functional groups in the unit gel phase. C_{GLC} : concentration of the glucopyranoside residues participating in complex formation in the unit gel phase.

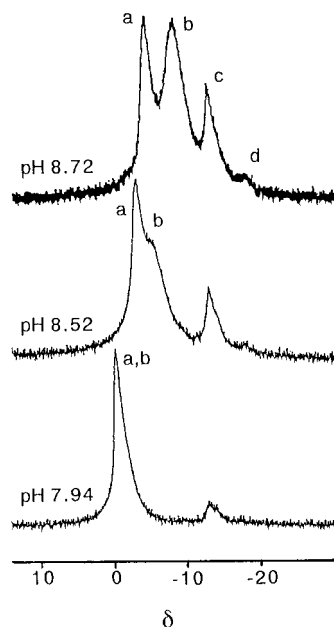


Figure 2. ¹¹B NMR spectra for the mixtures of boric acid/borate solution and QAE-Sephadex gel at different pH. Solution: 0.02 mol dm⁻³ boric acid/borate ($I = 0.1$, NaCl), 100 cm³. Ion exchanger: QAE-Sephadex A-25, 5.00 g. Key: (a) free boric acid/borate in the equilibrated solution; (b) free boric acid/borate in QAE-Sephadex gel phase; (c) 1:1 complex (α,β); (d) 1:1 complex (α,γ).

boric acid/borate in the anion exchanger and/or the external solution, the others to the complexes formed in the gel phase.

If glucopyranoside residues of QAE-Sephadex A-25 and QA-52 cellulose serve as O,O-bidentate ligands to combine with borate, the chemical shift values of the complexes should be the same as those of linear or cross-linked polysaccharides.²⁷ As shown in Figure 2, the complexes formed for the QAE-Sephadex system have shown completely identical chemical shift values with those for the Sephadex gel system. The signal at -13.4 ppm is due to the 1:1 complex with an α,β -diol moiety of the glucopyranoside residue, where hydroxyl groups are on adjacent carbon atoms, and that at around -18 ppm should be due to the 1:1 and/or 1:2 complexes with α,γ -diol moieties (hydroxyl groups on alternate carbon atoms). Since the cellulose gel is 1,4-linked polymer of the glucopyranoside residues, only the 1:1 complex of borate with the α,β -diol moiety of the glucopyranoside residue having a chemical shift of -13.4 ppm is observed (Figure 3). All of the chemical shift values are in good accordance with those of borate complexes with polyhydroxy compounds reported by van Duin et al.²⁰

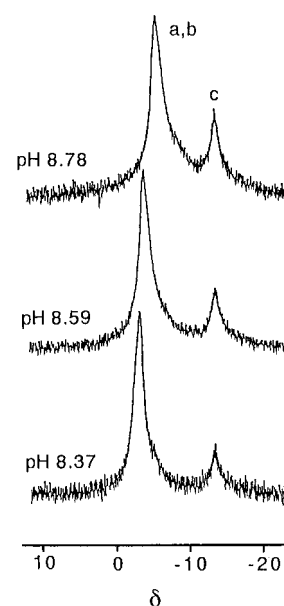


Figure 3. ¹¹B NMR spectra for the mixtures of boric acid/borate solution and QA cellulose gel at different pH. Solution: 0.02 mol dm⁻³ boric acid/borate ($I = 0.1$, NH₄Cl), 100 cm³. Ion exchanger: QA-52 cellulose, 5.00 g. Key: (a) free boric acid/borate in the equilibrated solution; (b) free boric acid/borate in QA cellulose gel phase; (c) 1:1 complex (α,β).

The signal intensities of these complexes increase with an increase in pH of the external solution, i.e. with an increase in the mole fraction of B(OH)₄⁻. It is desirable to measure the NMR spectra at pH > 10, since the active species is the borate anion. However, it was fairly hard to get detailed information about the complex formation under such a condition because the signals ascribed to the complexes and the free boric acid/borate overlapped each other for the QAE-Sephadex system. Therefore, the measurements were carried out in a pH range of 8–9. Under our experimental conditions, the signal belonging to the borate complex with diols of 1:2 stoichiometry was not observed.

It is notable that the signal belonging to free boric acid/borate in the QAE-Sephadex system was gradually separated into two peaks with the increase in pH of the equilibrated solution (Figure 2). Similarly, the spectra for QA cellulose system (Figure 3) showed that the peak due to free boric acid/borate was gradually broadened with the increase in pH of the equilibrated solution. The overlapping signal could be resolved into two individual peaks using the Lorentzian curve-fitting method. In comparison with the solution spectra without the gels, the signals appearing at the lower magnetic field were ascribed to boric acid/borate in the equilibrated solutions and the others at the higher magnetic field to those in

Table 2. Formation Constants of Borate Complexes with Glucopyranoside Residues

	$K_1(\alpha, \beta)$	$K_1(\alpha, \gamma)$
Sephadex G-25 ^a	0.94	0.09
QAE-Sephadex A-25	0.96 ± 0.10	0.14 ± 0.02
QA-52 cellulose	0.95 ± 0.41	

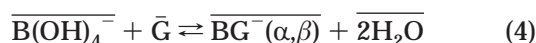
^a Data from ref 27.

the gel phases. These phenomena mean that (1) the exchange rate of the chemical species between the gel phase and the external solution was sufficiently low on the NMR time scale, and (2) the pH in the anion exchanger phase is different from that in the equilibrated solution.

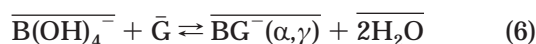
For the cross-linked polysaccharide anion exchanger system, the complexation equilibria of borate can be represented by the following equations:



$$K_a = [\text{B(OH)}_4^-][\text{H}^+]/[\text{B(OH)}_3] = 10^{-9.05} \quad (3)$$



$$\bar{K}_1(\alpha, \beta) = [\overline{\text{BG}^-(\alpha, \beta)}]/([\text{B(OH)}_4^-][\bar{\text{G}}]) \quad (5)$$



$$\bar{K}_1(\alpha, \gamma) = [\overline{\text{BG}^-(\alpha, \gamma)}]/([\text{B(OH)}_4^-][\bar{\text{G}}]) \quad (7)$$

Here, G denotes the glucopyranoside residue, BG^- the 1:1 complex of borate with one G, and K_1 the formation constant of the 1:1 complex, and the binding sites are indicated in parentheses. The barred symbols refer to the species in the exchanger phase and the others to those in the solution, respectively. These formation constants were estimated based on the peak intensities of ^{11}B NMR signals. The mole fraction of borate anion to the total uncomplexed boron species in the anion exchanger phase was estimated from ^{11}B NMR chemical shifts of boric acid/borate by using the following equation:

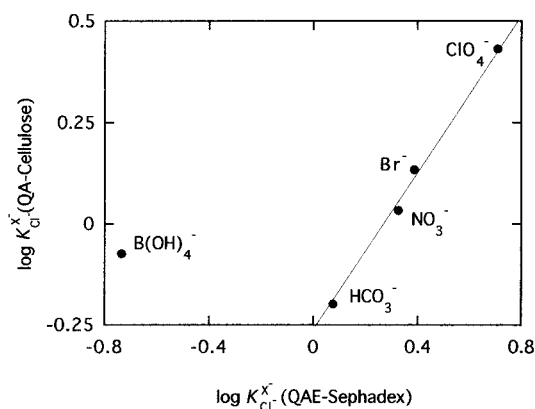
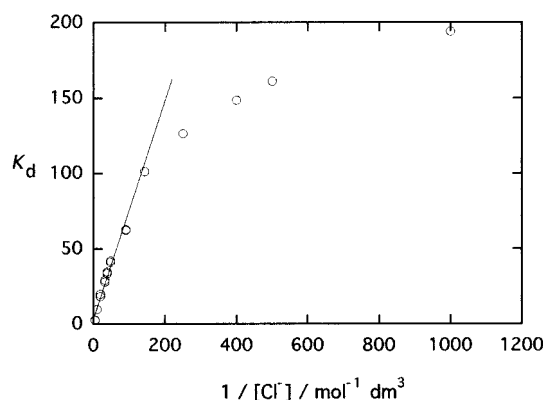
$$\bar{\delta}_{\text{obs}} = \bar{\chi}_{\text{B(OH)}_3} \bar{\delta}_{\text{B(OH)}_3} + \bar{\chi}_{\text{B(OH)}_4^-} \bar{\delta}_{\text{B(OH)}_4^-} \quad (8)$$

Here, $\bar{\delta}_{\text{obs}}$ is the ^{11}B chemical shift observed, $\bar{\delta}_{\text{B(OH)}_3}$ (= 0 ppm) and $\bar{\delta}_{\text{B(OH)}_4^-}$ (= -17.7 ppm) are the characteristic chemical shifts of B(OH)_3 and B(OH)_4^- , and $\bar{\chi}_{\text{B(OH)}_3}$ and $\bar{\chi}_{\text{B(OH)}_4^-}$ are the mole fractions of B(OH)_3 and B(OH)_4^- , respectively. The formation constants evaluated are summarized in Table 2 together with the results for Sephadex G-25. The constants for the 1:1 complexes with α, β -diol appeared to be almost the same in the three kinds of cross-linked polysaccharide gels. The complexibility of either anion exchanger was not enhanced by the presence of attached cationic functional groups.

Ion-Exchange Behavior. Figure 4 shows the relationship of the selectivity coefficients of HCO_3^- , Br^- , NO_3^- , ClO_4^- , and B(OH)_4^- toward Cl^- between QAE-Sephadex and QA cellulose gels. When the ion-exchange equilibrium has been reached, the selectivity coefficient $K_{\text{Cl}^-}^{\text{X}^-}$ can be expressed as

$$\text{RCl} + \text{X}^- \rightleftharpoons \text{RX} + \text{Cl}^- \quad (9)$$

$$K_{\text{Cl}^-}^{\text{X}^-} = [\text{Cl}^-][\bar{\text{X}}^-]/([\bar{\text{Cl}}^-][\text{X}^-]) \quad (10)$$

**Figure 4.** Relationship between selectivity coefficients for QAE-Sephadex gel and for QA cellulose gel.**Figure 5.** Variation of distribution coefficient of boric acid/borate onto QAE-Sephadex gel with the inverse of $[\text{Cl}^-]$ in the equilibrated solution at pH 10.3.

The selectivity coefficients for both anion exchangers gave an order of $\text{ClO}_4^- > \text{Br}^- > \text{NO}_3^- > \text{HCO}_3^-$, B(OH)_4^- and showed a linear free energy relationship except for B(OH)_4^- , indicating that the ion-exchange behavior for these anions can be correlated with the differences in their hydrated ionic radii and hydrophobicities. In addition, the selectivity coefficients for QAE-Sephadex were larger than those for QA cellulose in the case of HCO_3^- , Br^- , NO_3^- , and ClO_4^- ions, which is probably due to the difference in charged functional groups of the two gels (Figure 1).

Adsorption Behavior. (1) Background Electrolyte Effect. The presence of sodium chloride affected the adsorption of boron significantly (Figure 5). At a higher Cl^- concentration range, the boron adsorbability on QAE-Sephadex increased linearly with $1/[\text{Cl}^-]$. However, with the decrease of the Cl^- concentration, the distribution coefficient K_d observed gave a lower value than expected.

(2) pH Effect. Figure 6 shows the pH dependence of boron adsorbability on QAE-Sephadex. Above pH 7, the boron adsorbability increased with an increase in pH of the equilibrated solution, which is identical with the NMR results (Figure 2). After giving a maximum at about pH 10.8, the distribution ratio decreased.

(3) Borate Concentration Effect. An increase in the concentration of boron in the equilibrated solution at pH 10.5 and $I = 0.1$ (Figure 7) resulted in a decrease in the adsorbability of boron onto QAE-Sephadex. The similar phenomenon had also been observed for PVA by Pezron et al.⁵ as well as for Sephadex gel in our previous work.²⁸

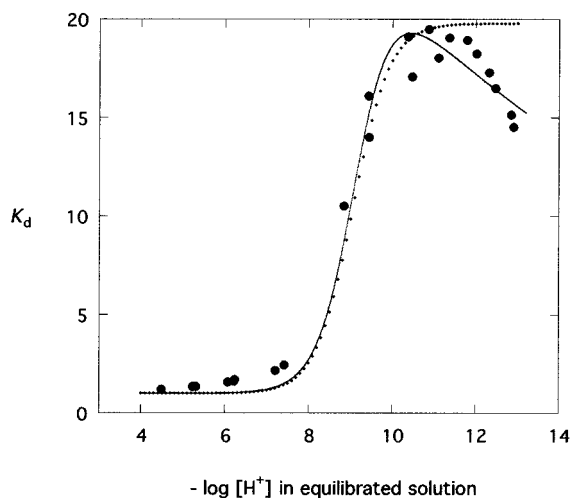


Figure 6. Variation of distribution coefficient K_d of boric acid/borate onto QAE-Sephadex gel with $-\log[H^+]$ in the equilibrated solution. Points refer to the experimental results; while the dotted line is calculated using eqs 14 and 15, the solid line is calculated using eqs 14 and 19 ($a = 0.956$ and $b = 1.49$), respectively.

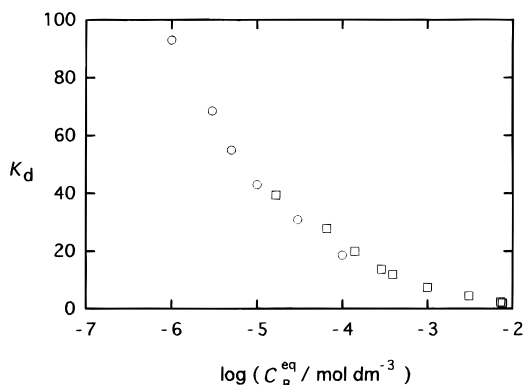


Figure 7. Variation of distribution coefficient of boric acid/borate onto QAE-Sephadex gel with the concentration of boron in the equilibrated solution C_B^{eq} at pH 10.5 and $I = 0.1$. Key: (○) column method; (□) batch method.

Discussion

It has been revealed from ^{11}B NMR results that borate binds with glucopyranoside residues of QAE-Sephadex and QA cellulose gels instead of the anion-exchange functional groups. Contrary to linear and cross-linked dextran systems,²⁷ the 1:2 complexes with diol moieties were not formed for QAE-Sephadex A-25 and QA-52 cellulose, even if 1:1 complexibility was almost the same in either anion exchanger or Sephadex gel. This should be due to the rigid chain structures of cross-linked dextran and cellulose skeletons extended in ion exchanger phase solutions owing to the repulsion among fixed cationic functional groups, so that intra- and intermolecular 1:2 complexes cannot be formed.^{15,17} According to the literature,^{31–33} the pH value in an anion exchanger phase is usually higher than that in the external solution in the equilibrium state. Now it has been fully proved by the NMR measurements for QAE-Sephadex A-25 and QA-52 cellulose as shown in the Results.

Figure 4 also shows a different ion-exchange behavior for $\text{B}(\text{OH})_4^-$ as a result of the complexation: The selectivity coefficients of $\text{B}(\text{OH})_4^-$ for both anion exchangers deviated from the linear free energy relationship. The selectivity coefficient for QA cellulose was

larger than that for QAE-Sephadex although their formation constants of the complexes were almost the same (Table 2). This should be due to the higher concentration of glucopyranoside residues available for the complex formation in cellulose ion exchanger than that in QAE-Sephadex (Table 1).

In the system of the anion exchanger equilibrated with a boric acid/borate solution, there exist two equilibria simultaneously, i.e., complexation and ion-exchange equilibria. Therefore, the adsorption behavior will be discussed on the basis of these two equilibria.

The dependence of K_d of boron on the concentration of supporting electrolyte (NaCl) for the anion exchanger can be examined by the following equations:

$$K_d = \frac{[\overline{\text{B}(\text{OH})_3}] + [\overline{\text{B}(\text{OH})_4^-}] + [\overline{\text{BG}^-(\alpha, \beta)}] + [\overline{\text{BG}^-(\alpha, \gamma)}]}{[\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-]} \\ = K_{\text{Cl}^-}^{\text{B}(\text{OH})_4^-} \times \frac{[\overline{\text{Cl}^-}] ([\overline{\text{H}^+}] + \bar{K}_a + \bar{K}_a (\bar{K}_1(\alpha, \beta) + \bar{K}_1(\alpha, \gamma)) [\bar{\text{G}}])}{[\text{Cl}^-] ([\text{H}^+] + K_a)} \quad (11)$$

Here, $K_{\text{Cl}^-}^{\text{B}(\text{OH})_4^-}$ is the selectivity coefficient between $\text{B}(\text{OH})_4^-$ and Cl^- . $[\overline{\text{Cl}^-}]$ and $[\bar{\text{G}}]$ were constants under the experimental condition that the total amount of borate was $1/40$ th of the ion-exchange capacity. There should be a linear relationship between distribution coefficient K_d and $1/[\text{Cl}^-]$ if $\bar{K}_a = K_a$ was assumed and the concentration of hydrogen ion in each phase was kept constant

$$K_d = K'/[\text{Cl}^-] \quad (K': \text{constant at a fixed pH}) \quad (12)$$

where

$$K' = K_{\text{Cl}^-}^{\text{B}(\text{OH})_4^-} \times \frac{[\overline{\text{Cl}^-}] ([\overline{\text{H}^+}] + \bar{K}_a + \bar{K}_a (\bar{K}_1(\alpha, \beta) + \bar{K}_1(\alpha, \gamma)) [\bar{\text{G}}])}{[\text{H}^+] + K_a} \quad (13)$$

As shown in Figure 5, the variation of K_d with $1/[\text{Cl}^-]$ for the QAE-Sephadex system at pH 10.3 of the external solution showed a linear relationship in a Cl^- concentration range of 0.007 – 0.2 mol dm^{-3} .³⁴ This indicates that the effect of background electrolyte on the boron adsorption is mainly due to an ion-exchange process even if the complexation takes part in the adsorption.

The pH dependence of K_d for the QAE-Sephadex system can be calculated by the following equation:

$$K_d = \frac{[\overline{\text{B}(\text{OH})_3}] [\overline{\text{H}^+}] [\overline{\text{H}^+}] + \bar{K}_a + \bar{K}_a (\bar{K}_1(\alpha, \beta) + \bar{K}_1(\alpha, \gamma)) [\bar{\text{G}}]}{[\overline{\text{B}(\text{OH})_3}] [\overline{\text{H}^+}] [\overline{\text{H}^+}] + K_a} \quad (14)$$

In the case of a low degree of boron adsorption, $[\bar{\text{G}}]$ can be taken as the total concentration of the glucopyranoside residues participating in complex formation in the anion exchanger phase (\bar{C}_{GLC} , mol dm^{-3}). The value of $[\overline{\text{B}(\text{OH})_3}]/[\text{B}(\text{OH})_3]$ in eq 14 was assumed to be 1 on the basis of the experimental results for the Sephadex gel system,²⁷ and $\bar{K}_a = K_a$ was also assumed. As shown in Results section, the pH values in anion exchangers are higher than those in the equilibrated solutions, thus the

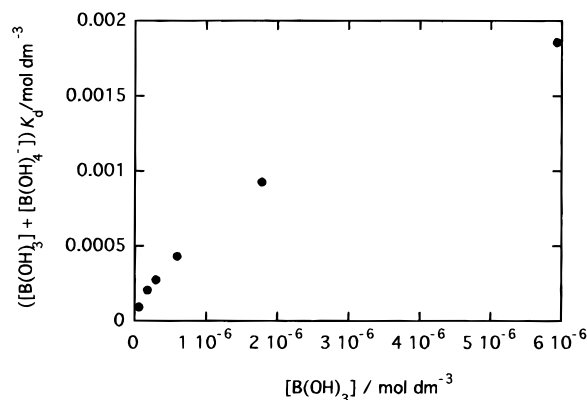


Figure 8. Relationship between $([B(OH)_3] + [B(OH)_4^-])K_d$ and $[B(OH)_3]$ at pH 10.5 and $I = 0.1$.

concentration of hydrogen ion in the ion exchanger phase can be given by the Donnan relation as follows:

$$-\log[\bar{H}^+] = -\log[H^+] + b \quad (b: \text{constant}) \quad (15)$$

The pH dependence of boron distribution coefficient calculated by using eqs 14 and 15 is shown in Figure 6, where b was selected to give a maximum distribution ratio similar to that of the experimental result. It is obvious that the calculated curve (dotted line) was quite different from the result of the distribution measurements: at a pH range higher than 10.8, the calculated distribution coefficient shows a constant maximum value, whereas the experimental value decreases. One possible reason for this disagreement is that the $-\log[\bar{H}^+]$ in the anion exchanger phase may be influenced by the formation of anionic charge fixed on the gel matrix, and eq 15 cannot be valid for this system.

The boron concentration dependence of K_d for QAE-Sephadex gel (Figure 7) can be examined by the following equations:

$$K_d = \frac{[B(OH)_3](1 + \bar{K}_a/[\bar{H}^+] + \bar{K}_a(\bar{K}_1(\alpha, \beta) + \bar{K}_1(\alpha, \gamma))[\bar{G}]/[\bar{H}^+])}{[B(OH)_3] + [B(OH)_4^-]} \quad (16)$$

$$([B(OH)_3] + [B(OH)_4^-]) K_d = \left(1 + \frac{\bar{K}_a}{[\bar{H}^+]} + \frac{\bar{K}_a(\bar{K}_1(\alpha, \beta) + \bar{K}_1(\alpha, \gamma))[\bar{G}]}{[\bar{H}^+]} \right) [B(OH)_3] \quad (17)$$

Here $[B(OH)_3] = [B(OH)_3]$ was assumed. If the pH of the equilibrated solution is kept constant and $[\bar{G}]$ is also constant, $(1 + \bar{K}_a/[\bar{H}^+] + \bar{K}_a(\bar{K}_1(\alpha, \beta) + \bar{K}_1(\alpha, \gamma))[\bar{G}]/[\bar{H}^+])$ should be a constant value and a linear relationship between $([B(OH)_3] + [B(OH)_4^-])K_d$ and $[B(OH)_3]$ can be obtained according to eq 17. However, Figure 8 shows that the plots obtained from the experimental results did not give a linear relationship; that is, the distribution ratio decreased with the increase in the boric acid/borate concentration. This means that the concentration of hydrogen ion in the gel phase increased with the increase in the concentration of boron, in other words, increased with the increase in the concentration of anionic complexes fixed onto the gel matrix, even if the pH of the external solution is maintained constant. We can deduce from these facts that the anion exchanger

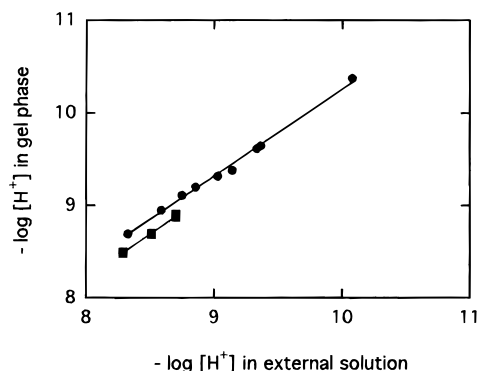


Figure 9. Relationship between $-\log[\bar{H}^+]$ in the anion exchangers and $-\log[H^+]$ in the external solution. Key: (●) QAE-Sephadex A-25; (■) QA-52 cellulose.

emerges a kind of cation-exchange function as a result of the fixation of anionic charge formed by the complexation.

The hydrogen ion concentration in the anion exchanger could be estimated from ^{11}B NMR chemical shift of boric acid/borate sorbed into the gel phase by using following equation:

$$[\bar{H}^+] = K_a((\bar{\delta}_{B(OH)_4^-} / \bar{\delta}_{\text{obs}}) - 1) \quad (18)$$

Here, $\bar{K}_a = K_a$ was assumed. Figure 9 shows the relationships between $-\log[\bar{H}^+]$ in the anion exchanger phase and $-\log[H^+]$ in the bulk solution for QAE-Sephadex and QA cellulose systems. The $-\log[\bar{H}^+]$ values in both of the anion exchanger phases were kept higher than those in the external equilibrated solutions and the slope of each plot was slightly lower than 1. Therefore, we may apply the following relation for these systems:

$$-\log[\bar{H}^+] = -a \log[H^+] + b \quad (a, b: \text{constants}) \quad (19)$$

Here, $a \leq 1$ and $b > 0$.

Now, we calculated the pH-dependent K_d for the QAE-Sephadex system with a and b values estimated by a least-squares fitting to the experimental points using eqs 14 and 19. As shown in Figure 6 (solid line), the pH dependence of boron adsorption calculated for QAE-Sephadex agreed well with the experimental results with respect to the $-\log[\bar{H}^+]$ values in the gel phase evaluated by eq 19 with $a = 0.956$ and $b = 1.49$. The difference between $-\log[\bar{H}^+]$ in QAE-Sephadex gel phase and $-\log[H^+]$ in the bulk solution was over 1, which is larger than the difference (ca. 0.3) obtained by the NMR results in Figure 9, but might be reasonable at low loadings of borate under the pH dependence measurement conditions.

Above all, the unexpected low selectivity toward borate was shown mainly due to the poor ion-exchange selectivity and low stability of borate complexes with the gel matrix. A kind of cation-exchange property can be revealed for the cross-linked polysaccharide anion exchanger as a result of the fixation of anionic borate onto the gel matrix by the complexation and can influence the concentration of hydrogen ion in the anion exchanger. The pH in the anion exchanger phase is higher than that in the external equilibrated solution; however, it is slightly lower than the value expected from the Donnan relation. The adsorbability of borate

onto the polysaccharide anion exchangers could be well understood on the basis of such properties.

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