Speciation of Boron Species Adsorbed onto Polysaccharide Gel by $^{11}$B NMR Spectroscopy

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Abstract
Boron species adsorbed onto polysaccharide gels, cellulose (Cellulofine GC), cellulose cross-linked with epichlorohydrin (Cellulofine GCL) and dextran cross-linked with epichlorohydrin (Sephadex G), were characterized by $^{11}$B NMR spectroscopy. Borate ion reacts with Cellulofine GCL-25 to form both (α,β)-monochelate and (α,β)(α,β)-bischelate complexes. In the case of Cellulofine GC-100, however, hydrogen bonds among the cellulose chains to hold the gel structure prevent the complexation with borate. For Sephadex G-25 the formation of (α,β)(α,γ)-bischelate complex was revealed in addition to (α,β)-monochelate, (α,β)(α,β)-bischelate and (α,γ)-monochelate complexes similarly to the borate-dextran system. Formation constants of borate complexes with Cellulofine GCL and Sephadex G are reported.

1 Introduction
Tetrahedral borate ion reacts with polyhydroxy compounds to form anionic complexes of both 1:1 and 1:2 stoichiometries. This characteristic of borate has been applied to the selective separation and concentration of boron [1] and polyols [2] by a chromatographic method using an adsorbent with low boron adsorbability like polysaccharide gels. The elucidation of the nature of the interaction of boric acid/borate with the polysaccharide gel should give important information for such practical purpose as boron isotope separation. Previously our group revealed by applying $^{11}$B NMR spectroscopy to characterize boron species adsorbed onto the polysaccharide gels that borate is selectively adsorbed onto Sephadex gels (cross-linked dextran gel) is as a consequence of complex formation of borate with glucopyranoside residues of the gel matrix.[3,4] The formation of (α,β)-monochelate, (α,β)(α,β)-bischelate and (α,γ)-monochelate complexes was confirmed for Sephadex with low cross-linking degrees like G-100, G-75 and G-50.[3] As a part of our further investigation boron species adsorbed onto cross-linked polysaccharide gels, cellulose (Cellulofine GC), cellulose cross-linked by epichlorohydrin (Cellulofine GCL) and dextran cross-linked by epichlorohydrin (Sephadex G) with a higher cross-linking degree, were characterized by the $^{11}$B NMR method in this work.
2 Experimental

2.1 Chemicals and Gels

All chemicals were of analytical grade and used without further purification. Sephadex G-25 (Pharmacia Biotech, Sweden) and Cellulofine GCL-25, GCL-90, GCL-300 and GC-100 (Seikagaku Co., Japan) were treated with a 0.1 mol dm\(^{-3}\) NaCl solution, washed fully with water, and then stored in air-dried form.

2.2 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 298 °K. 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. Quartz glass tubes (10 mm outer diameter) were employed for the measurements. The equilibrium mixtures of 0.02 mol dm\(^{-3}\) boric acid/borate solutions (I = 0.1, NaCl) and a known amount of Sephadex or Cellulofine gel were used as NMR samples.

2.3 Distribution Measurements

The adsorption behavior of boric acid/borate was examined as follows: To 20 cm\(^3\) of a 10\(^{-3}\) mol dm\(^{-3}\) boric acid solution (I = 0.1, NaCl), in which pH was adjusted with a little amount of HCl or NaOH solution, an appropriate amount of the gel was added. The mixture was stirred mechanically for 24 h at 25°C until the equilibrium was reached, and then, pH of the equilibrated solution was measured. The boron concentration in the equilibrated solution was determined spectrophotometrically with Azomethine-H as a coloring reagent. The distribution coefficient \(K_d\) is expressed as: \(K_d = (C_{\text{int}} - C_{\text{equiv}})v/(C_{\text{equiv}}m)\), where \(C_{\text{int}}\) is the initial concentration of boron, \(C_{\text{equiv}}\) the concentration of boron in the equilibrated solution, \(m\) the mass of the gel, and \(v\) the volume of the solution.

3 Results and discussion

Since the complexation between borate and the diols is slow relative to the \(^{11}\)B NMR time-scale, new NMR signals due to the complexes are observed besides the signal of free boric acid/borate. Each complex has a characteristic chemical shift, so that one can determine binding structures of the borate complexes on the basis of their shift values. Recently we clarified that the formation of (α,β)(α,γ)-bischelate complex for the borate-dextran system in addition to (α,β)-momochelate, (α,β)(α,β)-bischelate and (α,γ)-monochelate complexes.[5] Sephadex is a dextran gel covalently cross-linked with epichlorohydrin and has three hydroxyl groups at C-2, C-3 and C-4 in the glucopyranoside residues. Fig. 1 shows \(^{11}\)B NMR spectra for Sephadex G-25 equilibrated with solutions (I = 0.1, NaCl) containing 0.02 mol dm\(^{-3}\) boric acid/borate at pH 8.5. In the same way as that for dextran the signal of (α,β)(α,γ)-bischelate complex is distinctly observed at -14 ppm besides those of (α,β)-momochelate, (α,β)(α,β)-bischelate and (α,γ)-monochelate complexes at -13, -9 and -17 ppm, respectively.

Cellulofine GCL is a cellulose gel covalently cross-linked with epichlorohydrin and has three hydroxyl groups at C-2, C-3 and C-6 in the glucopyranoside residues, which will serve as O,O bidentate ligands to bind with borate as in the case of Sephadex. In Fig. 2 the \(^{11}\)B NMR spectrum for Cellulofine GCL-90 equilibrated with a solution (I = 0.1, NaCl) containing 0.02 mol dm\(^{-3}\) boric acid/borate at pH 11.3 is shown. The signal at -13 ppm is ascribed to the (α,β)-monochelate complex formed in the gel phase. None of the signals due to (α,γ)
solution, and then, decreased after a maximum around pH 10. The adsorbability for Cellulofine GCL-25 is lower than Sephadex G-25, however, the behavior is identical with Sephadex.

Cellulofine GC is a cellulose gel without cross-linking by epichlorohydrin. None of the signals was observed except free boric acid/borate (Fig. 2), which means that hydroxyl groups of Cellulose are not available for the complexation with borate. Because three hydroxyl groups at C-2, C-3 and C-6 of the glucopyranoside residues in a cellulose chain interact with hydrogen atoms at C-2, C-3 and C-5 of those in another chain, respectively, to cross-link each other and form the crystal-like domain. That is, hydrogen bonds among the polysaccharide chains to hold the rather stiff gel structure prevent the complexation with borate, which agrees with the fact that Cellulofine GC-100 shows the lowest boron adsorbability as shown in Fig. 3. For Cellulofine GCL, on the other hand, the hydrogen bonding must be in parts hampered by the complexes can be observed for cellulose gels.

For Cellulofine GCL-25 we can also observe a broad signal around -9 ppm in addition to that of (α,β)-monochelate complex (Fig. 2). The broad one is attributable to the (α,β)(α,β)-bischelate complex. This assignment is confirmed by the fact that the ratio of NMR signal intensities of -9 ppm to -13 ppm, that is, the concentration ration of (α,β)(α,β)-bischelate to (α,β)-monochelate, are almost constant independent of the concentration of borate in the equilibrated solution, where the concentration of glucopyranoside residues is much higher than those of adsorbed boron species. The distribution results for Cellulofine GCL-25 and Sephadex G-25 are shown in Fig. 3. Above pH 7, the $K_d$ value increased with an increase in pH of the equilibrated solution.

![Fig. 1](image1.png)

**Fig. 1** $^{11}$B NMR spectra for the mixtures containing boric acid/borate solution and Sephadex G-25.

![Fig. 2](image2.png)

**Fig. 2** $^{11}$B NMR spectra for mixtures containing boric acid/borate solution and cellulose gels at pH 11-12.
cross-link with epichlorohydrin, so that borate could bind with hydroxyl groups at C-2 and C-3 of the glucopyranosides to form (α,β)-monochelate and (α,β)(α,β)-bischelate complexes as discussed above.

Formation constants of borate complexes with these polysaccharide gels were estimated from the NMR signal intensities (Table 1). In the evaluation the volume of the polysaccharide gel phase was taken as the volume of the gel internal solution and the ligand concentration was expressed by the concentration of the glucopyranoside residues in monomol dm⁻³ [3,4]. As can be expected from the results for boron adsorbability (Fig. 3), the formation constant of (α,β)-monochelate (complex for Sephadex G25 is higher than those for Cellulofine GCL gels. The complexibility is almost the same among Cellulofine GCL gels with different cross-linking degrees. Dehydration of cellulose gel leads the formation of strong hydrogen bonds among the cellulose chains, which would prevent the complexation with borate. Therefore, the adsorbability and complexibility of boron against cellulose gel would be dependent on the dry condition before the experiments.

Table 1  Formation constants of borate complexes with glucopyranoside residues of polysaccharide gels.

<table>
<thead>
<tr>
<th></th>
<th>β₀(α,β) (M⁻¹)</th>
<th>β₀(α,β)(α,β) (M⁻²)</th>
<th>β₀(α,β)(α,β) (M⁻²)</th>
<th>β₀(α,β) (M⁻¹)</th>
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<tbody>
<tr>
<td>Cellulofine GCL-25</td>
<td>0.19</td>
<td>0.05</td>
<td>–</td>
<td>–</td>
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<tr>
<td>GCL-90</td>
<td>0.11</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
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<tr>
<td>GCL-300</td>
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<td>n.d.</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Sephadex G-25</td>
<td>0.60</td>
<td>0.11</td>
<td>0.05</td>
<td>0.28</td>
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</table>

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References