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Simple boron removal from seawater by using polyols as complexing agents: A computational mechanistic study

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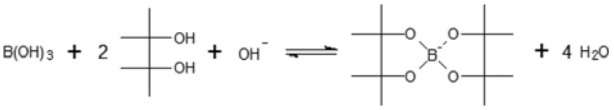
Abstract–The complexation of boric acid ($B(OH)_3$), the primary form of aqueous boron at moderate pH, with polyols is proposed and mechanistically studied as an efficient way to improve membrane processes such as reverse osmosis (RO) for removing boron in seawater by increasing the size of aqueous boron compounds. Computational chemistry based on the density functional theory (DFT) was used to manifest the reaction pathways of the complexation of $B(OH)_3$ with various polyols such as glycerol, xylitol, and mannitol. The reaction energies were calculated as −80.6, −98.1, and −87.2 kcal/mol for glycerol, xylitol, and mannitol, respectively, indicating that xylitol is the most thermodynamically favorable for the complexation with $B(OH)_3$. Moreover, the 1 : 2 molar ratio of $B(OH)_3$ to polyol was found to be more favorable than the ratio of 1 : 1 for the complexation. Meanwhile, latest lab-scale actual RO experiments successfully supported our computational prediction that 2 moles of xylitol are the most effective as the complexing agent for 1 mole of $B(OH)_3$ in aqueous solution.

Keywords: Boron Removal, Boric Acid, Polyol, Complexation, Density Functional Theory, Computational Chemistry

INTRODUCTION

Seawater reverse osmosis (RO) has been verified to be an economical and reliable technology for producing potable water from seawater [1-4]. However, the removal of boron from seawater is still an issue because the rejection of boron in a single-stage RO process is not enough to meet the maximum contaminant level (MCL) set by the World Health Organization (WHO) [5,6]. The approximate amount of boron in seawater is 5 mg/L, and the MCL of boron in potable water is 0.5 mg/L [7], whereas the permeate of a single-stage RO process typically contains one third (~1.5 mg/L) of inlet boron concentration [5,6]. The difficulty of boron removal comes from the size of boric acid ($B(OH)_3$), the primary form of aqueous boron, as small as the nominal pore size of RO membranes [5,6]. Therefore, a 2-pass RO process has been used, where a part of stream is by-passed to increase the efficiency of boron removal by converting $B(OH)_3$ into tetrahydroborate ion ($B(OH)_4^-$) at a high pH [8]. Although $B(OH)_4^-$ is rejected more selectively in the RO membrane, the accompanied basification and neutralization processes render the whole RO process less cost-effective. Moreover, increasing the pH causes scaling problems by the deposition of salt precipitates (insoluble Ca and Mg-based chemical species) on the RO membrane [9].

The complexation of $B(OH)_3$ with polyols was suggested as an effective way to increase the size of aqueous boron compounds for better rejection in RO and even nanofiltration membranes [10,11]. Polyols are compounds containing more than three hydroxyl groups, such as glycerol, xylitol, sorbitol, and mannitol. The complexation of $B(OH)_3$ with polyols follows the reaction (1). The polyols with 1,2-diol react with $B(OH)_3$ to form a stable chelate complex ion having the tetrahedral structure around the boron [12].



(1)

Geffen et al. demonstrated that the complexation of $B(OH)_3$ with mannitol improved the efficiency of boron removal from seawater in desalination membranes [10]. Another study showed an effective way to adsorb $B(OH)_3$ by using polystyrene (PS) resins with functionalized surfaces with hydroxyl groups [13]. Otherwise, ion exchange resins containing amino groups are commercially available as well [14,15].

Mechanistic study on this complexation has not been reported; therefore, we used computational chemistry to calculate the reaction energetics for the complexation of $B(OH)_3$ with various polyols such as glycerol, xylitol, and mannitol. Glycerol (three hydroxyl groups), the smallest polyol, was taken for a comparison with mannitol (six hydroxyl groups), a well-known large size polyol [10]. Xylitol (five hydroxyl groups) is additionally considered owing to its friendly commercial image, "no harm for humans". The calculated reaction energies show the most effective as the complexing agent polyol among all the selected, and the effect of the molar ratio of $B(OH)_3$ to polyols affecting the reaction thermodynamics. Transition complexes are also located to provide the information of the activation energies for the complexation.

COMPUTATIONAL METHOD

All calculations were performed with the Gaussian 09W software (Gaussian Inc., USA) [16], with B3LYP density functional theory (DFT) model chemistry and 6-31G(d) basis set [17-21]. Full

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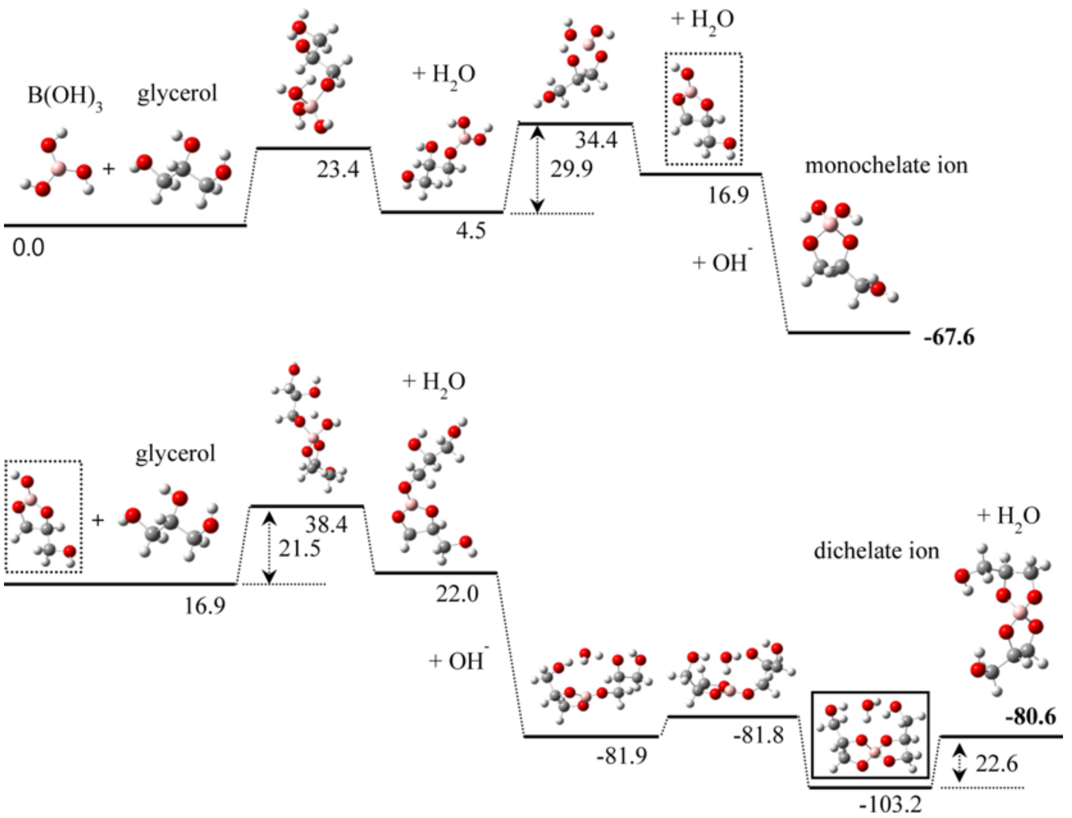

Fig. 1. Calculated energetics for the complexation of $B(OH)_3$ with glycerol. Red, white, gray, and incarnadine balls indicate oxygen, hydrogen, carbon, and boron, respectively. All the energy values are in kcal/mol.

geometry optimization was performed for all the species. The transition state (TS) was optimized using the Berny algorithm [22] as implemented in the GAUSSIAN 09W. The GaussView software (Gaussian Inc., USA) was used for the visualization of the results.

RESULTS AND DISCUSSION

1. Complexation of $B(OH)_3$ with Glycerol

The calculated energetics for the complexation of $B(OH)_3$ with glycerol are shown in Fig. 1. The reaction consists of two parts: the formation of monochelate complex ion (upper in Fig. 1) and dichelate complex ion (lower in Fig. 1). Before reaching the monochelate complex shown in the dotted box in Fig. 1, $B(OH)_3$ and glycerol release two moles of water. Then, the addition of hydroxyl ion (OH^-) stabilizes the whole structure to produce a monochelate complex ion, having oxygen elements positioned in the tetrahedral geometry around the boron. Before being stabilized, the monochelate complex proceeds further to form a dichelate complex ion as shown in the lower energetics of Fig. 1. The pathway seems more complicated, because the addition of hydroxyl ion (OH^-) follows just after the release of one mole of water, and the final release of one mole of water occurs at the end of the whole reaction. The resulting dichelate complex ion also has a stable tetrahedral geometry around the boron similar to that of the monochelate complex ion. The pathway of energetically stable intermediate (denoted by the plain box in Fig. 1) just before the final release of one mole of water is explained following this mechanism, indicating the stabilization of relevant species using water molecules in an aqueous reaction [23]. The dehydration is then driven by the entropy generation. The reaction energies for the formation of monochelate and dichelate complex ions were calculated as −67.6 and −80.6 kcal/mol, respectively. Although the same tetrahedral geometry around the boron stabilizes the whole structure of both complex ions, a 1 : 2 molar ratio of $B(OH)_3$ to glycerol is more favorable than a 1 : 1 ratio from the thermodynamic viewpoint.

Meanwhile, the calculations were based on the gas phase molecules. To consider the solvation effect, a solvation model such as the polarizable continuum model (PCM) [24] was introduced. However, it has been reported that the energy difference between the gas phase and PCM calculations was within 8 kcal/mol even for the reactions involving highly polar molecules [23]. Thus, our results based on the gas phase calculations are still good enough to evaluate the thermodynamic favorableness of the reactions by comparison. The calculated activation barriers for the complexation range from 20-30 kcal/mol, as shown in Fig. 1. Because they are as small as the values for similar aqueous reactions [23,25], the reaction kinetics is favorable. Therefore, we focused on the comparison of thermodynamic favorableness for the complexation with $B(OH)_3$ among the polyols.

2. Complexation of $B(OH)_3$ with Mannitol and Xylitol

For mannitol and xylitol, two types of monochelate complex ion and three types of dichelate complex ion possibly exist according to the position of 1,2-diol participating in the reaction. Figs. 2 and 3 show the calculated energetics for the complexation of $B(OH)_3$

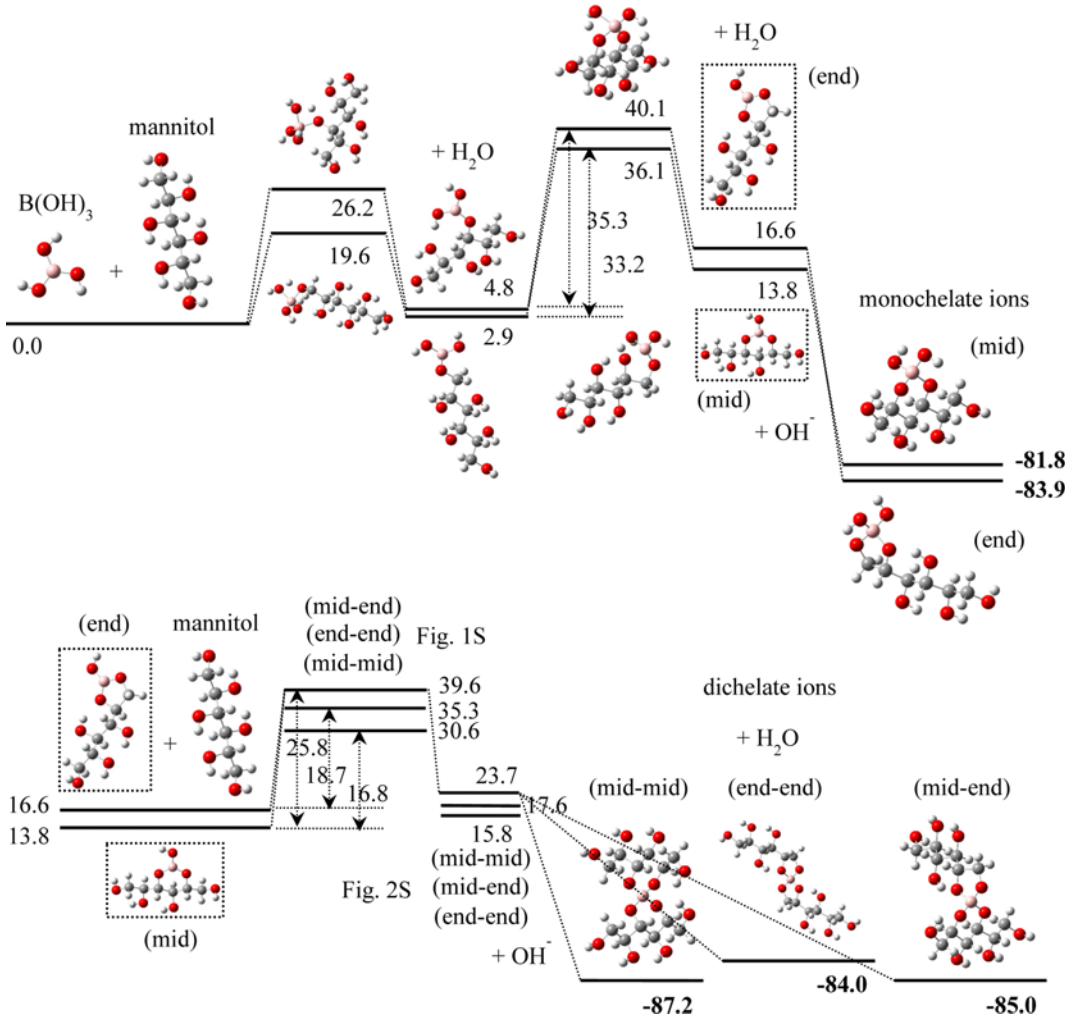

Fig. 2. Calculated energetics for the complexation of $B(OH)_3$ with mannitol. Red, white, gray, and incarnadine balls indicate oxygen, hydrogen, carbon, and boron, respectively. All the energy values are in kcal/mol.

with mannitol and xylitol, respectively. Because $B(OH)_3$ is attached either to the end and middle of a monochelate complex ion, three combinations (end-end, mid-mid, and end-mid) are possible for a dichelate complex ion. According to the energetics, the monochelate complex ion with $B(OH)_3$ attached to the end (end) is more stable than its counterpart (mid); however, two monochelate complexes with $B(OH)_3$ attached to the middle of them render the dichelate complex ion (mid-mid) the most stable, for both mannitol and xylitol. The calculated reaction energies for the formation of dichelate complex ions (mid-mid) were −87.2 and −98.1 kcal/mol for mannitol and xylitol, respectively, indicating highly exothermic characteristics of the reactions, and the thermodynamic favorableness of the 1 : 2 molar ratio of $B(OH)_3$ to polyol was also valid for both polyols. Meanwhile, the highest activation barrier only slightly increased up to 35 kcal/mol for mannitol (compared to 30 kcal/mol for glycerol), and thus the kinetic readiness of the whole reaction would be equivalent. In the calculations for the energetics in Figs. 2 and 3, several steps after the release of three moles of water were replaced by the simple insertion of hydroxyl ion (OH^-) because of our limited computational capacity. However, the omitted reaction pathways are expected to be similar to the pathway for glycerol shown in Fig. 1. Regarding the size of dichelate complex ions, the distance between the boron and the most remote element was calculated roughly as 3.76, 8.00, and 7.33 Å for glycerol, mannitol, and xylitol, respectively, indicating that the dichelate complex ions of $B(OH)_3$ with mannitol and xylitol become almost as large as ~1.5 nm. Considering that the nominal pore size of RO membranes is ~1.0 nm [9], the complexation by using polyols will be an excellent approach to improve the efficiency of the removal of boron by size in the RO processes.

3. Thermodynamic Favorableness for the Complexation of $B(OH)_3$ with Polyols

As mentioned, the complexation of $B(OH)_3$ with polyols is very viable from the kinetic viewpoint, and the complexation reactions have highly exothermic characteristics. The calculated reaction energies for the formation of monochelate and dichelate complex ions when using three polyols (glycerol, mannitol, and xylitol) as the complexing agents are shown in Fig. 4. By the comparison with the calculated reaction energy (−75.7 kcal/mol) for the standard boron chemistry in an aqueous solution, $B(OH)_3+OH^- \rightarrow B(OH)_4^-$,

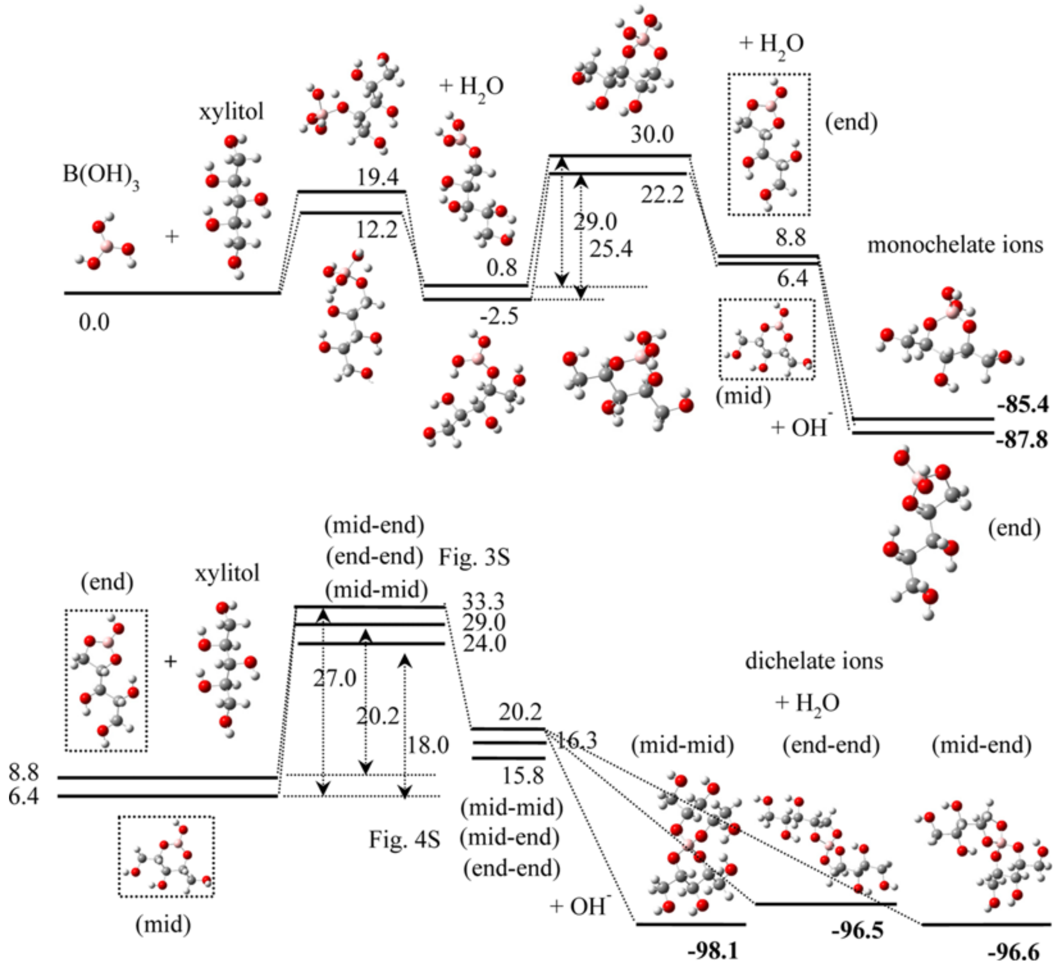

Fig. 3. Calculated energetics for the complexation of $B(OH)_3$ with xylitol. Red, white, gray, and incarnadine balls indicate oxygen, hydrogen, carbon, and boron, respectively. All the energy values are in kcal/mol.

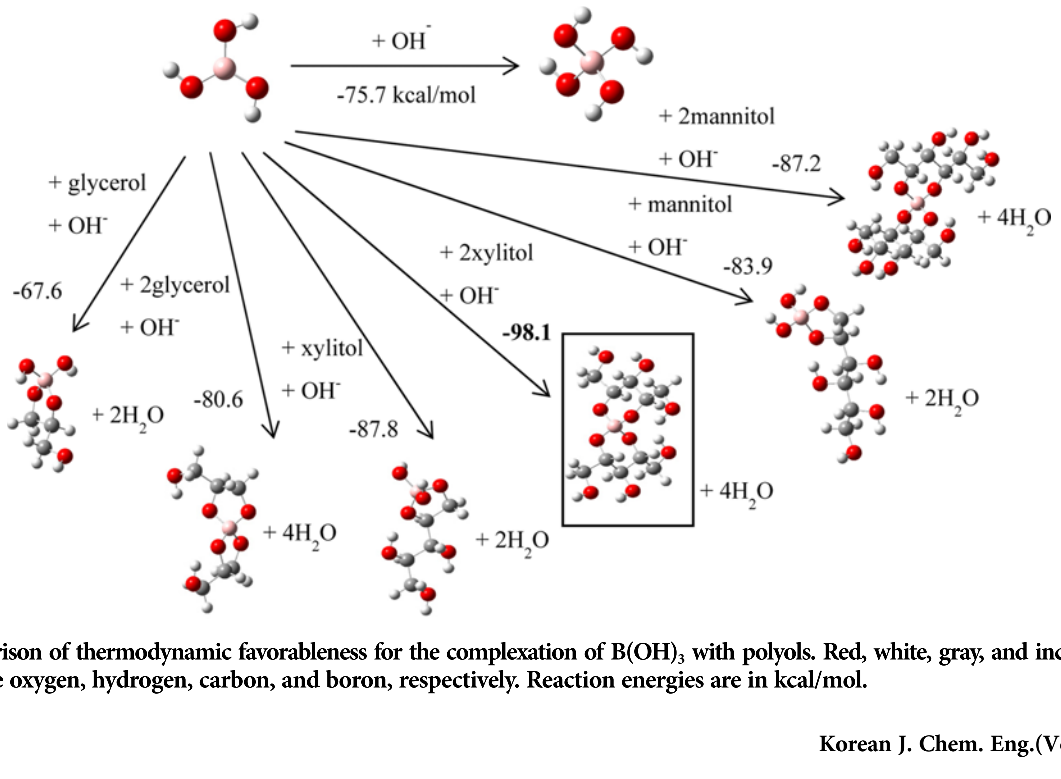

Fig. 4. Comparison of thermodynamic favorableness for the complexation of $B(OH)_3$ with polyols. Red, white, gray, and incarnadine balls indicate oxygen, hydrogen, carbon, and boron, respectively. Reaction energies are in kcal/mol.

the complexation of $B(OH)_3$ with polyols is much more favorable from the thermodynamic viewpoint, except for the case (–67.6 kcal/mol) of 1 : 1 molar ratio of $B(OH)_3$ to glycerol. Fig. 4 also shows that a 1 : 2 molar ratio of $B(OH)_3$ to polyol is more favorable than a 1 : 1 molar ratio by about 4-12 kcal/mol. Moreover, xylitol with one less hydroxyl group (−98.1 kcal/mol) is more favorable for the complexation than mannitol with one more hydroxyl group (–87.2 kcal/mol). Interestingly, the latest lab-scale RO experiments [26] showed that the results support our computational prediction, as shown in Figs. 5S and 6S (the Supplementary Information (SI)). At pH 7, the application of xylitol as the complexing agent with a 1 : 2 molar ratio of $B(OH)_3$ to xylitol had ~80% efficiency for boron removal compared to ~50% with no complexing agent (Fig. 5S in the SI). Mannitol and glycerol followed xylitol in that order. Moreover, although a 1 : 2 molar ratio of $B(OH)_3$ to xylitol was the most effective, a 2 : 1 molar ratio still had more than 10% higher efficiency of boron removal than the case with no complexing agent applied (Fig. 6S in the SI).

CONCLUSION

Computational chemistry was used to discover the reaction pathways and their energetics for the complexation of $B(OH)_3$ and polyols in an aqueous solution for the first time. The calculated activation barriers for the complexation reactions were in the range of 20-35 kcal/mol, sufficiently low enough to lift off the kinetic constraint for the reactions, while the complexation reactions had highly exothermic characteristics, in other words, thermodynamically favorable. Among the considered polyols (glycerol, mannitol, and xylitol), xylitol has the lowest reaction energy (–98.13 kcal/mol) for the formation of dichelate complex ion with a 1 : 2 molar ratio of $B(OH)_3$ to xylitol, indicating that xylitol with one less hydroxyl group is more effective as the complexing agent than mannitol with one more hydroxyl group. The latest lab-scale RO experiments supported our computational prediction to verify the complexation of $B(OH)_3$ with polyols as an excellent pathway to improve the efficiency of boron removal in the RO processes.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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