pH-Controlled Uphill Transport of Boric Acid through a Poly(vinyl alcohol) (PVA) Membrane

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ABSTRACT: The uphill transport of boric acid in aqueous solutions through a thermal-crosslinked poly(vinyl alcohol) (PVA) membrane was investigated. A normal permeation caused by the concentration difference of the boron along the PVA membrane was observed for equal pH conditions at both sides of the membrane, and higher flux was observed under an acidic condition at pH = 5.0 than under a basic condition at pH = 10.0. When the pH of one side is kept pH = 5.0 (acid side) and the other side was kept at pH = 10.0 (base side), uphill transport of boric acid from the acid side to the base side was observed under an equal initial concentration of both sides. Such an uphill transport was also observed against the concentration difference under the condition in which the initial concentration of the base side was higher than that of the acid side. The uphill transport could be explained by the difference in the permeation rates through the PVA membrane between $B(OH)_3$, the dominant form under lower pH, and $B(OH)_4^-$, the dominant form under higher pH, which makes a complex with diols in PVA. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1451–1455, 2007

Key words: boric acid; uphill transport; PVA membrane; pH-control

INTRODUCTION

Boron is widely distributed in nature, mainly in the forms of boric acid ($B(OH)_3$) or borax ($Na_2B_4O_7 \cdot 10H_2O$). Industrial applications of the boric compounds include glass manufacturing, soaps and detergents, flame retardants, doping in the semiconductor industries, and neutron absorption in nuclear power plants. However, due to acute and chronic health effects by the boric compounds, development of an efficient separation and recovery process of the boric compounds is required to reduce the emission to the environment.[1]

Several options have been proposed for separating boric acid from aqueous solutions such as solvent extraction,[2–4] coagulation sedimentation,[5] and membrane separation.[6–8]

It has been known that boric acid can form a complex with diols, and the selectivity of boric acid can be improved by using the complex formation of boric acid with diols.[8–11] Poly(vinyl alcohol) (PVA) is a poly 1,3-diol and forms a complex with boric acid with monoborate under basic conditions.[12] The complex formation mechanism is recognized as a ''di-diol'' complexation, where two diol units in PVA are combined with one monoborate ion.[12–15] Such a complex formation was applied to enhance the selectivity of boric acid to an ultrafiltration membrane separation process.[8] This study attempts to utilize the PVA membrane itself for the separation of boric acid dissolved in a water stream. The diol units in a PVA membrane can be considered as a fixed carrier for the boron permeation through the membrane. Since the complex formation is highly pH-dependent, the transport of boric acid through the PVA membrane could also be pH-dependent. In this study we investigated the effect of pH conditions on the permeation through a PVA membrane, and it was found that an uphill transport of boric acid through PVA membrane can occur under certain pH conditions.

EXPERIMENTAL

Membrane preparation

PVA membranes were prepared by casting an aqueous solution of a PVA of 6 wt%. The PVA was kindly supplied by Kuraray (Tokyo, Japan); the average mo-

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lecular weight was 100,000 and the degree of saponification was 88 mol %. After casting, the membrane was dried at 294 K for 2 days, then heat-treated at 383 K for 15 min. The membrane became insoluble in water through the formation of a crosslinking structure. The dry thickness of the membranes was adjusted to 100 μm.

Permeation and absorption experiments

Permeation experiments were carried out by using the permeation cell shown in Figure 1. The solution was vigorously agitated by a magnetic stirrer to avoid concentration polarization. The pH values in both sides of the cell were monitored by pH meters. The pH of both sides could be controlled manually by either dropping an aqueous solution of hydrochloric acid or aqueous solution of sodium hydroxide through glass burettes. A small portion of the solution in the permeation cell was intermittently sampled and the concentration of boric acid was determined as the concentration of boron atom in the aqueous phase by the ICP-AES technique. The solution of boric acid was prepared with a special grade reagent of boric acid and ultra-high-pure water.

Absorption equilibria of boric acid in the PVA membranes were measured by the following batch-type method. A known amount of PVA membrane was immersed in an aqueous solution of boric acid and the time variation of the boron concentration in the aqueous phase was measured by the ICP-AES technique. Attainment of the equilibrium absorption was confirmed by the unchanged concentration in the aqueous phase. The temperature was fixed at 298 K and the pH in the boric acid solution was controlled
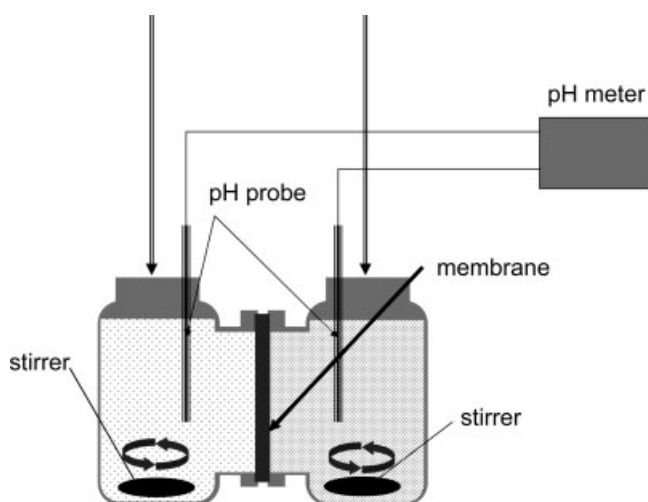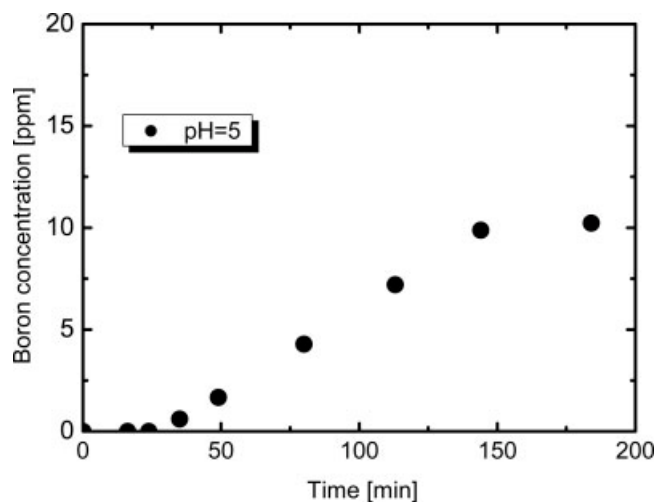

Figure 2 Time variation of the boron concentration in the permeate side of the PVA membrane under controlled pH = 5.0. Initial concentrations: feed = 100 ppm, permeate = 0 ppm.

by adding hydrochloric acid or sodium hydroxide aqueous solutions.

RESULTS AND DISCUSSION

Permeation of boric acid under equal pH conditions

Figures 2 and 3 show the time variation of the concentration of boron at the permeate side of the membrane under constant pH conditions (pH = 5.0 for Fig. 2 and pH = 10.0 for Fig. 3). The initial concentration of boron at the feed side of the membrane was set at 100 ppm, and that in the permeate side was set at 0 ppm
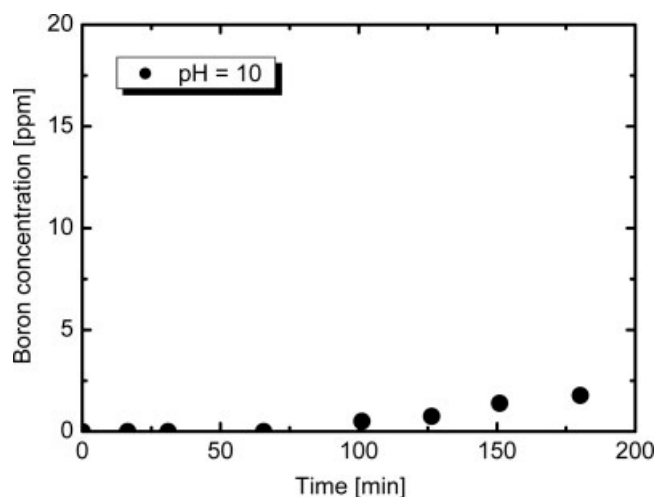

Figure 1 Schematic drawing for the membrane permeation cell.

Figure 3 Time variation of the boron concentration in the permeant side of the PVA membrane under controlled pH = 10.0. Initial concentrations: feed = 100 ppm, permeate = 0 ppm.
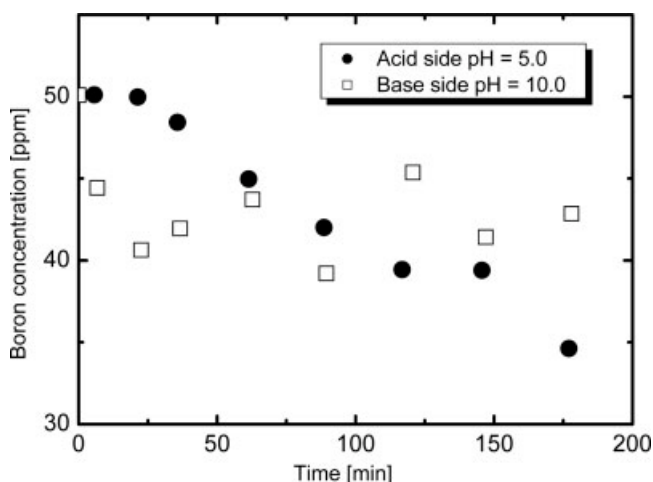
Figure 4 Time variation of the boron concentration in the acid side of the PVA membrane under controlled pH: acid side = 5.0, base side = 10.0. Initial concentrations: 50 ppm in both sides).

(pure water). The net transport of boron through the PVA membrane driven by the concentration difference along the membrane was observed. The apparent permeation flux of boron was $2.1 \times 10^{-5}\,\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$ at pH = 5.0, and $3.8 \times 10^{-6}\,\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$ at pH = 10.0, which is about 1/6 of that at pH = 5.0.

In an aqueous solution of boric acid, the following dissociation equilibrium is established:[16]

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ \qquad (1)$$

The dissociation constant, K_a, is given by:

$$K_a = \frac{[B(OH)_4^-][H^+]}{[B(OH)_3]} \qquad (2)$$

and $pK_a = -\log K_a = 9.25$ at 298.15 K. Under acidic conditions (lower pH), boric acid, $B(OH)_3$, is dominant, while monoborate ion, $B(OH)_4^-$, is dominant under basic conditions (higher pH). The experimental results showed that the permeation rate of boric acid is about 6 times higher than that of monoborate ion.

The sorption equilibria of boric acid into the PVA membrane were measured and it was found that the apparent sorption coefficients were 5.1 at pH = 5.0,

and 4.9 at pH = 10.0. The sorption coefficient, Q_a, was defined as:

$$C_m = Q_a C_f \qquad (3)$$

where C_m [mol $\cdot$ (kg-PVA)$^{-1}$] and C_f [mol $\cdot$ (L-water)$^{-1}$] are the boron concentrations in the membrane and in the aqueous solution, respectively. Based on the sorption-diffusion model,[17] the large difference in the apparent permeation flux between boric acid and monoborate would be mainly caused by the difference in the diffusivities in the PVA membrane. The apparent diffusivities were $4.1 \times 10^{-11}\,\mathrm{m^2 \cdot s^{-1}}$ at pH = 5.0 (boric acid) and $0.79 \times 10^{-11}\,\mathrm{m^2 \cdot s^{-1}}$ at pH = 10.0 (monoborate ion). The extremely smaller diffusivity of monoborate ion is due to the complex formation with diols in the PVA membrane: only monoborate can form complexes with diols.[12–15]

Uphill transport under controlled pH conditions

Figure 4 shows the time variation of the concentrations of boron under the condition where one side of the cell was kept at pH = 5.0 (acid side) and the other side at pH = 10.0 (base side). The initial concentration of boron (boric acid) at both sides of the membrane was set at 50 ppm. The boron concentration at the acid side decreased continuously, while that at the base side was almost unchanged after a slight decrease in the initial stage. The result demonstrated that an uphill transport of boron from the acid side to the base side occurs against the concentration gradient. The apparent flux of boron from the acid side to base side was $2.3 \times 10^{-5}\,\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$, which is on the same order of the observed flux under an acidic condition of pH = 5.0 at both sides (Fig. 2). The uphill transport was observed under other conditions and the results are summarized in Table I. When the initial concentrations of boron were set at 100 ppm under the same pH condition as in Figure 2, the observed flux was $2.9 \times 10^{-5}\,\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$, which is higher than the previous case. The apparent permeation flux was strongly dependent on the pH in the acid side. When the pH of the acid side was kept at 3.0, and that of the base side was kept at 10.0, the flux was $1.35 \times 10^{-4}\,\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$, which is four times larger than

TABLE I
Results of Uphill Transport of Boric Acid through the Crosslinked PVA Membrane

pH in acid side	Initial concentration acid side [ppm]	pH in base side	Initial concentration base side [ppm]	Apparent flux of boron [$\times 10^{-5}$ mol $\times$ m^{-2} $\times$ s^{-1}]
5.0	50	10.0	50	2.3
5.0	100	10.0	100	2.9
3.0	100	10.0	100	13.5
7.0	100	10.0	100	0

the case of Figure 2 (acid side pH = 5.0). On the other hand, when the acid side pH was 7.0, no uphill transport was observed. An uphill transport of boron from the acid side to the base side was also observed when the initial concentration at the base side was higher than that of the acid side (Fig. 5).

An uphill transport of boron can be explained by the large difference in the permeation rates between boric acid and monoborate ion. Since the permeation rate of boric acid through the PVA membrane is much higher than that of monoborate ion, the net transport of boric acid occurs from the acid side to the base side against the apparent concentration gradient of boron.

The effect of pH on the uphill transport could be explained based on the concentration profiles of boric acid and monoborate ion in the membrane. The concentrations of boric acid, $B(OH)_3$, and monoborate ion, $B(OH)_4^-$, could be determined from the proton concentration profile along with the dissociation equilibrium of boric acid (Eq. 2). It can be assumed that the proton concentration in the membrane decreases linearly from the acid side to the base side along the membrane due to its higher mobility. The concentrations of $B(OH)_3$ and $B(OH)_4^-$ at the membrane–aqueous solution boundary can be determined on the basis of the experimental results on the absorption of boric acid in the PVA membrane. Figure 6 shows the determined concentration profiles of $B(OH)_3$ and $B(OH)_4^-$ along the membrane in the vicinity of the base side of the membrane for the conditions with pH = 10 at the base side and various pH values at the acid side. The concentrations of both sides of the membrane were set at 100 ppm. Boric acid would exist in the form of $B(OH)_3$ in the part of the membrane with a constant concentration, which equals the equilibrium absorption amount at the acid side of the membrane. The net concentration gradient for the diffusion of $B(OH)_3$ would be concentrated in the vicinity of the base side
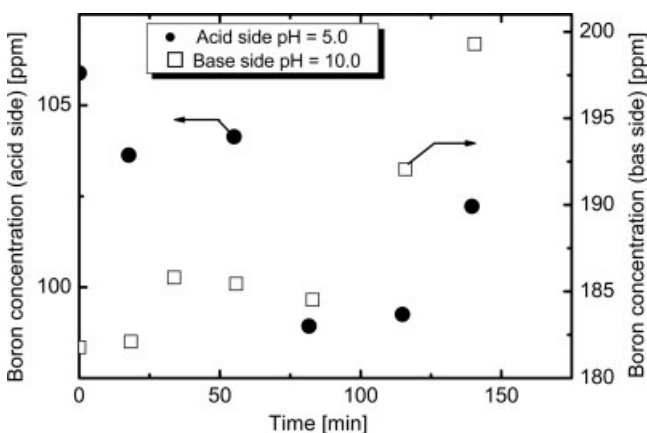

Figure 6   Schematic concentration profiles of $B(OH)_3$ and $B(OH)_4^-$ under equal concentration of boric acid (100 ppm) at both sides of the aqueous phase contacted with the membrane.

of the membrane. The apparent transport of boric acid, which can be attributed to that of $B(OH)_3$, would be mainly determined by the concentration gradient of $B(OH)_3$ in this region. When the pH in the acid side decreases (equivalently, an increase in the proton concentration), the concentration gradient of $B(OH)_3$ in the vicinity of the base side of the membrane would increase. As a result, the permeation of $B(OH)_3$ would increase with decreasing pH at the acid side of the membrane. This is consistent with the experimental result on the pH dependence of the permeation flux.

CONCLUSIONS

An uphill transport of boric acid was observed through a thermally crosslinked PVA membrane under the conditions where one side of the membrane was kept acidic and the other side was kept alkaline. The net transport of boric acid was observed from the acid side to the base side against the apparent concentration difference of boron. The result can be explained by the large difference of the permeation rates in the PVA membrane between two species, boric acid, $B(OH)_3$, which is dominant under acidic conditions, and monoborate ion, $B(OH)_4^-$, which is dominant under basic conditions. Due to the complex formation of $B(OH)_4^-$ with diols in the PVA membrane, the diffusivity of $B(OH)_4^-$ is much lower than that of $B(OH)_3$, with which no complex formation occurs with PVA. As a result, the net permeation of boric acid from the acid side to the basic side would occur against the concentration profile of boron.

Figure 5   Time variation of the boron concentrations under controlled pH: acid side = 5.0, base side = 10.0. Initial concentration: base side = 182 ppm, acid side = 106 ppm.
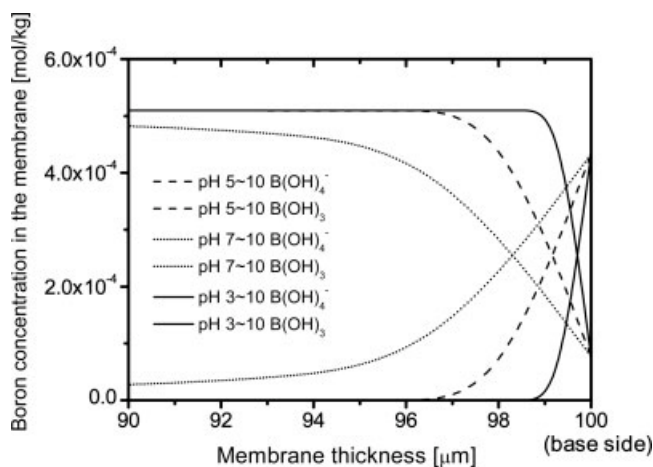
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