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Hironori Maeda[a]; Hiroaki Egawa[a]; Akinori Jyo[b]
[a] DEPARTMENT OF INDUSTRIAL CHEMISTRY, KUMAMOTO INSTITUTE OF TECHNOLOGY, KUMAMOTO, JAPAN [b] DEPARTMENT OF APPLIED CHEMISTRY FACULTY OF ENGINEERING, KUMAMOTO UNIVERSITY, KUMAMOTO, JAPAN

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Preparation of Chelating Resins Selective to Boric Acid by Functionalization of Macroporous Poly(Glycidyl Methacrylate) with 2-Amino-2-hydroxymethyl-1,3-propanediol

HIRONORI MAEDA and HIROAKI EGAWA
DEPARTMENT OF INDUSTRIAL CHEMISTRY
KUMAMOTO INSTITUTE OF TECHNOLOGY
IKEDA, KUMAMOTO 860, JAPAN

AKINORI JYO
DEPARTMENT OF APPLIED CHEMISTRY
FACULTY OF ENGINEERING
KUMAMOTO UNIVERSITY
KUROKAMI, KUMAMOTO 860, JAPAN

ABSTRACT

Macroporous chelating resins containing polyol groups (RGB) were prepared by the reaction of poly(glycidyl methacrylate) beads with 2-amino-2-hydroxymethyl-1,3-propanediol, and the behavior of the resulting RGB in the uptake of boric acid was studied. The RGB exhibited high affinity for boric acid in the pH range of 5 to 9 and took up boric acid selectively from geothermal power waste solutions in which various minerals were contained. The boric acid adsorbed on the RGB was easily eluted with 1 mol/dm^3 hydrochloric acid.

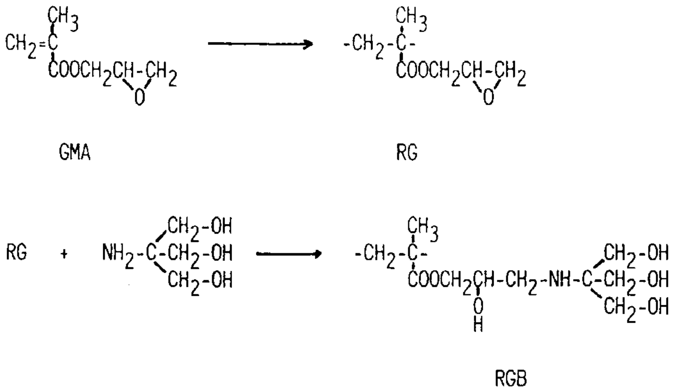
INTRODUCTION

It is well known that resins having functional groups, in which hydroxyl groups are in the cis position, are able to adsorb boric acid through the formation of borate–diol complexes (1–5). However, these kinds of resins as reported to date are based on styrene–divinylbenzene copolymer matrices. We have reported various kinds of chelating resins from macroporous beads (RGs) obtained by suspension polymerization of glycidyl methacrylate in the presence of pertinent crosslinkers as well as porogens (6–8). Epoxy groups in RGs are useful for the introduction of various functional groups, such as polyamines (6), thiol (7), phosphoric acid (8), and so on. The introduction of polyol groups into RGs in order to develop resins selective for boric acid is thus of interest. In this work a new type of resin offering high selectivity toward boric acid is developed by the functionalization of RGs with 2-amino-2-hydroxymethyl-1,3-propanediol. Although this ligand does not have hydroxyl groups on its adjacent carbon atoms, the resulting resins (RGBs) are able to take up boric acid in the presence of various inorganic electrolytes contained in geothermal waters in large excess. This paper describes the preparation and properties of RGBs as well as our attempt to recover boric acid from geothermal waters.

EXPERIMENTAL

Preparation of Resins Containing Polyol Groups (Scheme 1)

Precursory polymer beads (RGs) were prepared by suspension polymerization of glycidyl methacrylate (6). Here, divinyl-benzene and 2,2,4-trimethylpentane were used as crosslinker and porogen, respectively, and their amounts were systematically varied to find optimal polymers for the functionalization. Detailed compositions of the monomeric mixtures are described in later sections. The resulting RGs were meshed, and the beads from 35 to 60 mesh were used in the subsequent functionalization. The precursor RGs (1 g) were functionalized by treating them in refluxed 1,4-dioxane solution (20 cm^3) of 2-amino-2-hydroxymethyl-1,3-propanediol



(2.6 g) for 5 hours. The resulting resins (RGBs) were washed with deionized water until the washings were neutral pH. After air-drying the resins, they were dried in vacuo.

Anion-Exchange Capacities

A sample of a RGB in the free amine form (0.5 g) was taken into a 100-cm^3 Erlenmeyer flask with a ground joint stopper, and then 0.1 M hydrochloric acid was added to the flask. The flask was allowed to stand for 24 hours under occasional shaking. An aliquot of the supernatant was pipetted from the flask and titrated against a standardized sodium hydroxide solution. From the decrease in hydrochloric acid concentration in the aqueous phase, the anion-exchange capacity of the RGB was calculated.

Adsorption and Elution of Boric Acid

Uptake of boric acid by RGBs was examined by means of batchwise and columnar methods. In the batchwise method, 0.25 g of a RGB and 50 cm^3 of 0.01 M boric acid solution were taken into a 100-cm^3 Erlenmeyer flask, and the flask was allowed to stand for 48 hours under occasionally shaking. An aliquot of the supernatant was sampled and the amount of boric acid in the aqueous phase was determined according to a reported method (9). When necessary, the pHs of sample solutions were adjusted with sodium hydroxide to a suitable pH for the determination of boric acid. In batchwise elution of the adsorbed acid, 0.25 g of a boric acid-loaded RGB and 50 cm^3 of a given eluent were shaken for 1 hour at 30°C. Hydrochloric and sulfuric acids were used as eluting reagents. The boric acid eluted into the aqueous phase was determined as described (9).

In the columnar method, a glass column (inner diameter 6 mm, length 20 cm) packed with 2 cm^3 of RGB in the swollen state was used. The length of the resin bed was ca. 70 mm. Boric acid solution (5 mmol/dm^3) was supplied to the column at a space velocity of 15 h^{-1}. Here, the space velocity represents the ratio of the flow rate (cm^3/h) of the feed to the resin bed volume (cm^3). The boric acid adsorbed on the column was eluted by supplying 0.5 M sulfuric acid to the column at a space velocity of 7.5 h^{-1}. All column effluents were fractionated, and the boric acid concentration in each fraction was determined (9). After elution of the boric acid, deionized water was supplied to the column until the column effluent became neutral pH for regeneration of the resin. The regenerated column was used for subsequent adsorption and elution operations. The adsorption and elution of boric acid from geothermal waters (Otake Geothermal Power Station, Oita Prefecture, Japan) were also conducted in the columnar mode to evaluate the practical usefulness of the resin.

RESULTS AND DISCUSSION

Preparation of RGBs and Their Properties

In order to determine the pertinent time for the functionalization, the RG, which was prepared by suspension polymerization of glycidyl methacrylate without divinylbenzene in the presence of the porogen (volume ratio of the porogen to the monomer: 50 vol%), was functionalized by changing the reaction time. Since the anion-exchange capacities of the resulting RGBs correspond to the amounts of functional groups introduced, their anion-exchange capacities were determined. The results are summarized in Table 1 together with their boric acid uptake. Since the precursory polymer RG itself is inert to the adsorption of boric acid, as is also shown in Table 1, it can be concluded that the adsorption of boric acid by the RGBs can be ascribed to complexation of boric acid with the functional groups introduced, although the present functional groups do not have hydroxyl groups on adjacent positions, contrary to the case of Wofatit MK 51. The anion-exchange capacities as well as the uptake of boric acid markedly increase with the reaction time up to 3 hours. Further increases after 3 hours are minor. Thus, a functionalization time of 5 hours was used in further studies.

In order to examine the effect of the porosity of precursors on the functionalization as well as on the uptake of boric acid, a series of RGBs was derived from homopolymer beads of glycidyl methacrylate (RGs) which were prepared by changing the amount of the porogen (volume ratio of the porogen to the monomer: 10–90 vol%). Anion-exchange capacities of the resulting RGBs are summarized in Table 2 along with their boric acid uptakes. They become maximum at 50 vol% porogen per monomer. This means that the functionalization is affected by the porosity of

TABLE 1
Effect of Reaction Time on the Introduction of Functional Groups

Reaction time (h)	Anion exchange capacity (meq/g)	Uptake of boric acid (mmol/g)
0	—	0.02
1	1.54	0.47
2	2.71	0.85
3	3.20	1.25
5	3.34	1.29
7	3.41	1.30

TABLE 2
Properties of RG and RGB

Porogen[a] (vol%)	DVB[b] (mol%)	RG specific surface area (m^2/g)	RGB	
			C_A[c] (meq/g)	Uptake of boric acid (mmol/g)
10	0	—	0.12	0.06
30	0	0.57	3.00	1.15
50	0	0.95	3.38	1.29
70	0	1.67	3.21	1.25
90	0	1.66	2.31	1.06
50	1	1.21	3.22	1.06
50	3	1.40	1.53	0.39
50	5	2.33	1.25	0.26
50	7	3.30	0.94	0.20

[a] (Volume of 2,2,4-trimethylpentane/volume of monomeric mixture) × 10^2.
[b] Nominal mol% of divinylbenzene (DVB) in monomeric mixture.
[c] Anion-exchange capacity.

the precursors. In addition to the results mentioned above, the effect of the degree of crosslinking on the functionalization was examined. A series of RGBs was derived from the corresponding precursors RGs which were prepared by changing the composition of the monomers (divinylbenzene: 0–7 mol%, volume ratio of the porogen to the monomeric mixture: 50 vol%). Anion exchange capacities and boric acid uptakes of the resulting RGBs are also given in Table 2. The anion-exchange capacities decrease markedly with an increasing amount of divinylbenzene (degree of crosslinking). The uptake of boric acid is closely correlated to the amount of functional groups introduced (anion-exchange capacities). These results suggest that the functionalization of RG is sensitive to steric hindrance caused by the crosslinked networks formed by divinylbenzene. Thus, the RGB derived from the porous RG (pore volume 0.70 cm^3/g, specific surface area 0.95 m^2/g, average pore radius 1070 nm), which was prepared by suspension polymerization of glycidyl methacrylate in the presence of 50 vol% porogen per monomer, was used in a detailed study on the adsorption or desorption of boric acid.

Effects of pH and Foreign Ions on Uptake of Boric Acid

In order to avoid an ambiguous effect from pH buffers, the effect of pH was examined by adjusting the pH of the aqueous phases with hydrochloric acid and/or sodium hydroxide. The results are shown in Fig. 1, in which the uptake of boric acid is shown as a function of the equilibrium pH. Between pH 6 and 7, the uptake of boric acid is almost quantitative. Below pH 6, the uptake decreases markedly with decreasing pH, since complexation of boric acid with hydroxyl groups generates protons. Above pH 7, the boric acid uptake also decreases with increasing pH because of the acid-dissociation of boric acid itself ($pK_{a_1} = 9.2$).

Table 3 lists mineral compositions of geothermal water of the Otake Power Station. The main ionic components are sodium, potassium, calcium, chloride, bicarbonate, sulfate, and borate. In particular, large amounts of sodium and chloride ions are contained. Referring to these data, uptake of the boric acid was examined in the presence of sodium chloride and calcium chloride. The results are given in Table 4. Sodium chloride and calcium chloride do not interfere with the uptake of the acid up to 46,000 and 300 mg/dm^3, respectively. However, large amounts of calcium chloride slightly interfere with the acid uptake, although the interference is not serious.

Elution of Boric Acid Adsorbed on RGB

Table 5 summarizes the results of batchwise elution. The boric acid adsorbed on the RGB can be semiquantitatively eluted with 0.1–1.0 M

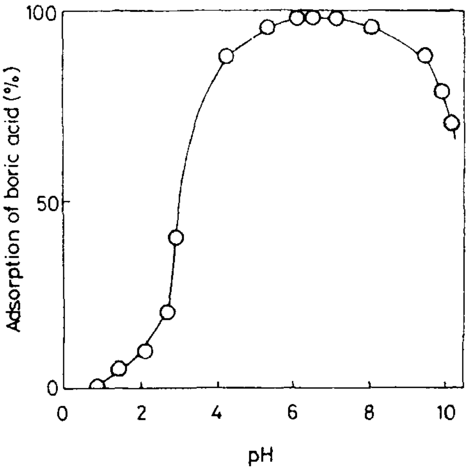


FIG. 1 Effect of pH on the adsorption of boric acid. 25 cm^3 of 0.01 mol/dm^3 boric acid solution and 0.5 g of resin, room temperature, 48 hours.

TABLE 3
Compositions (mg/dm^3) and pH of Geothermal Water (10)

Constituents	Concentration	Constituents	Concentration
Na^+	1030–1050	Cl^-	1738–1774
K^+	124–132	F^-	2.35–2.95
Li^+	4.73–4.79	HCO_3^-	57–77
Ca^{2+}	28.4–29.7	SO_4^{2-}	145–193
Mg^{2+}	0.01–0.21	SiO_2	433–531
As	2.0–2.1	HBO_2	78–84
pH	8.44–8.57		

TABLE 4
Effect of Foreign Ions on the Uptake of Boric Acid

Salts added	Concentration of coexisting ions (mg/dm^3)		Uptake of boric acid[a] (mmol/g)
	Na^+ or Ca^{2+}	Cl^-	
None	0	0	1.32
0.5 M NaCl	11,500	17,750	1.30
1 M NaCl	23,000	35,500	1.31
2 M NaCl	46,000	71,000	1.32
0.00125 M $CaCl_2$	50	89	1.34
0.0025 M $CaCl_2$	100	178	1.32
0.00375 M $CaCl_2$	150	266	1.33
0.0075 M $CaCl_2$	300	533	1.33
0.5 M $CaCl_2$	20,000	35,500	1.15
1 M $CaCl_2$	40,000	71,000	0.94

[a] Batchwise method.

TABLE 5
Batchwise Elution of Boric Acid Adsorbed on RGB

Eluent	Elution (%)[a]
0.1 mol/dm^3 HCl	89.4
0.5 mol/dm^3 HCl	90.8
1.0 mol/dm^3 HCl	92.7
0.05 mol/dm^3 H_2SO_4	90.1
0.25 mol/dm^3 H_2SO_4	91.4
0.5 mol/dm^3 H_2SO_4	93.1

[a] 0.25 g resin on which 0.31 mmol boric acid was adsorbed, 50 cm^3 eluent, shaking at 30°C for 1 hour.

hydrochloric acid and with 0.05–0.5 M sulfuric acid. In the column-mode elution, on the other hand, elution is quantitative; i.e., the recovery of boric acid is 100%. Figure 2 shows the column-mode elution of boric acid. The boric acid is smoothly eluted within 6 bed volumes of 0.5 M sulfuric acid without tailing of the solute. Since the present resins have ester bonds between the polymer backbones and the functional groups, stability of the RG to acids was examined by immersing the resins in 1 M hydrochloric acid for 7 days under ambient conditions. No change in the capacity for boric acid was observed. The results described in this section exhibit the possibility that the RGB will be useful for recycle use in the adsorption and elution of boric acid.

Recycle Test of the RGB Column and Recovery of Boric Acid from Geothermal Water

A recycle test of the RGB column in the adsorption and elution of boric acid was made. The adsorption from 0.005 M boric acid solution and the elution of the adsorbed acid with 0.5 M sulfuric acid were repeated 4 times. As judged from the results shown in Fig. 3, no deterioration of the resin was observed during the recycle test.

Finally, the recovery of boric acid from geothermal water was tested. The concentration of boric acid in the geothermal water was adjusted to

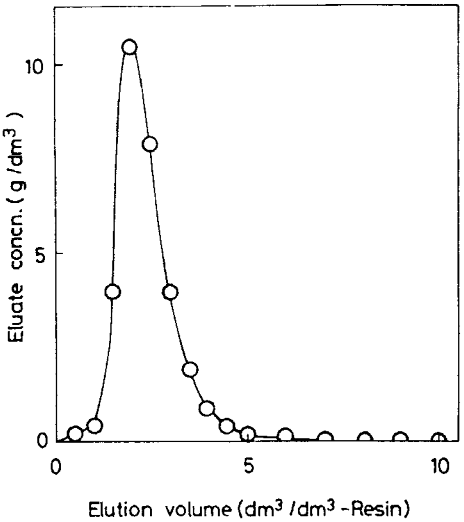


FIG. 2 Elution curve of boric acid. Eluent: 0.5 mol/dm³ H_2SO_4. Flow rate: SV 7.5 h^{-1}.

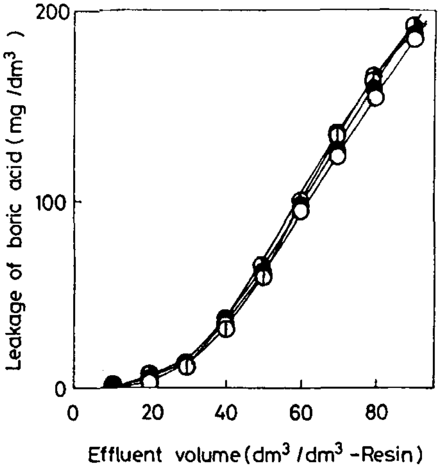


FIG. 3 Recycle test. Cycle number: (○) 1, (●) 2, (◑) 3, (◐) 4. Resin bed: RGB 2 cm³ (6 mmϕ × 70 mm). Loading solution: H_3BO_3, 5 mmol/dm³. Flow rate: SV 15 h^{-1}. Elution: 0.5 mol/dm³ H_2SO_4, 10 dm³/dm³ resin, SV 7.5 h^{-1}.

0.005 M. The geothermal water, to which boric acid was spiked, was supplied to the column. Figure 4 shows a breakthrough curve for boric acid. It can be seen that the resin can selectively adsorb boric acid even though the geothermal water contains many electrolytes as well as non-

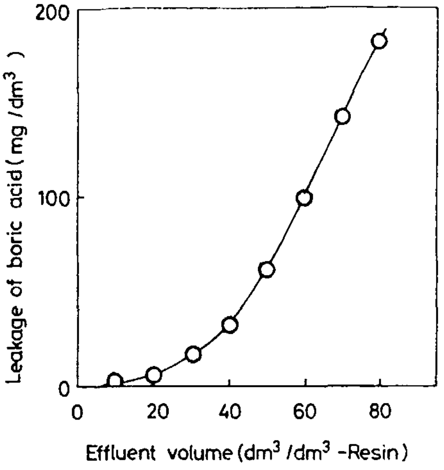


FIG. 4 Breakthrough curve of boric acid. Resin bed: RGB 2 cm³ (6 mmϕ × 70 mm). Loading solution: geothermal water (the concentration of boric acid was adjusted to 0.005 mol/dm³). Flow rate: SV 15 h^{-1}.

electrolytes. However, the shape of the breakthrough curve means that the adsorption rate of boric acid should be improved. Work on improving the adsorption rate is now in progress.

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