Complexation and removal of trace boron from aqueous solution by an anion exchange resin loaded with chromotropic acid (disodium 2,7-dihydroxynaphthalene-4,5-disulfonate)

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An ion exchanger consisting of disodium 2,7-dihydroxynaphthalene-4,5-disulfonate (chromotropic acid) and strongly basic anion exchange resin has been prepared for the removal of trace boric acid/borate. The reaction of boric acid with chromotropic acid has been examined by ^{11}B, ^{1}H and ^{13}C NMR spectroscopy, and acid–base titration analysis. The NMR study suggests that chromotropic acid preferentially forms a stable bis-chelate type complex (L : B = 2 : 1) in an acidic pH range. The acid–base titration data are consistent with the NMR measurements. Adsorption of boric acid/borate on the resin has been examined with respect to the equilibrium adsorption, kinetics and % extraction of boric acid/borate as a function of pH. The adsorption characteristics have been compared with those of a disodium 4,5-dihydroxybenzene-1,3-disulfonate (Tiron) loaded resin and a commercially available chelating resin containing *N*-methylglucamine. Boric acid/borate is strongly retained on the chromotropic acid resin in the acidic region (pH 1.8–4.5), allowing quantitative removal of boron. The removal of trace amounts of boron from aqueous solution has been examined.

Complex formations of boric acid/borate with polyalcohols and polysaccharides having vicinally positioned hydroxyl groups have been most extensively studied and the equilibrium constants determined.[1] Chelating resins containing polyhydroxyl compounds have been developed and applied to the selective separation of boric acid/borate in water purification processes.[2–7] Based on the equilibrium constants reported, reagents having two sets of phenolic hydroxyl groups generally form much more stable borate complexes than those of alcohols.[8] Disodium 2,7-dihydroxynaphthalene-4,5-disulfonate (chromotropic acid) in which two phenolic hydroxyl groups are located in close position has been used for the spectroscopic determination of borate ion.[9,10] This reagent contains auxiliary sulfonate groups in addition to the metal binding site to attain a better solubility in water. Such type of reagents can be retained on common ion exchangers through ionic bonds, thus providing a simple method to prepare selective chelating resins.[11] In the present study we have examined borate complex formation with chromotropic acid by ^{11}B, ^{13}C and ^{1}H NMR spectroscopy and acid–base titration to elucidate the nature of complexation of this reagent. Furthermore we have immobilized chromotropic acid onto an anion exchanger in order to use the resin as a boron selective adsorbent. The adsorption characteristics of the present resin with respect to the capacity, % extraction and kinetics for boric acid/borate have been investigated along with those of disodium 4,5-dihydroxybenzene-1,3-disulfonate (Tiron) loaded on an anion exchanger and the chelating resin functionalized with *N*-methylglucamine (*N*-methyl-1-amino-1-deoxy-D-glucitol). The performance of the present resin for removal of trace boric acid/borate has been examined using a continuous column adsorption system.

Chromotropic acid

Tiron

N-Methylglucamine resin
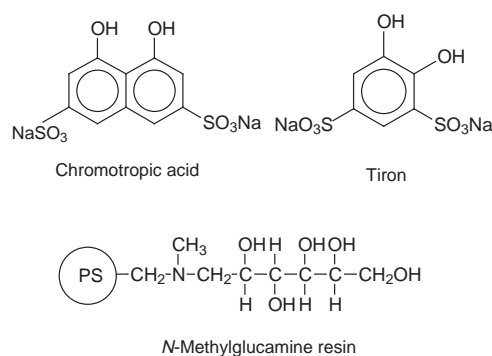
Experimental

Measurements

The metal ion concentration was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES), SEIKO Model SPS-1200A. Acid–base titration was carried out with a Metrohm 645-Multi-Dosimat auto titrator. A digital pH meter, TOA HM-265, was used for the pH measurements. The pH values of solutions were adjusted with acetate buffer in the pH range of 4–7 and with ammonia–ammonium chloride buffer in the pH 7–10 region. Hydrochloric acid and NaOH were used to adjust pH below 4 and above 10, respectively. The ^{1}H, ^{13}C and ^{11}B NMR spectra were measured at room temperature with a Varian INOVA-500 spectrometer. The ^{11}B NMR chemical shifts were expressed relative to the signal of boric acid. The UV-visible absorption spectra were recorded with a Hitachi U-3410 spectrophotometer.

Chemicals

Reagent grade chromotropic acid, Tiron and *N*-methylglucamine resin (Mitsubishi Chemical Co.) were used as received. Stock solutions of boric acid/borate were prepared by dissolution of reagent grade boric acid in deionized water. Strongly basic anion exchange resin (Lewattitt MP 500WS, Bayer AG) was used as the polymer support. The resin beads were treated with 20% sodium hydroxide and then washed thoroughly with water, ethanol and dried under reduced pressure.

Preparation of chromotropic acid loaded resin

In a three-necked flask, 72 g of anion exchange resin (OH⁻ form) were placed with 450 cm³ of water and the solution was adjusted to pH 8.1. Chromotropic acid (25 g) was dissolved in 180 cm³ of water. While stirring the resin, the solution of chromotropic acid was added dropwise for 3 h. Stirring was continued for 12 h and then the resin was filtered off, washed thoroughly with water, ethanol and dried at 50 °C under reduced pressure. The sulfur content of the resin was 5.78%, which corresponds to a ligand content of 0.9 mmol per gram resin. Loading of Tiron onto the anion exchanger was carried out in a similar manner to that of chromotropic acid. The sulfur content of the Tiron loaded resin was 8.1%, which corresponds to a ligand content of 1.25 mmol per gram resin. Leaking of chromotropic acid from the resin matrix was examined by treatment of the resin with various concentrations of HCl or NaOH solutions. The ligand leached out of the resin was analysed by spectrophotometry. Since the absorption spectrum changes with pH, the leached solution was neutralized and then buffered to constant pH prior to the measurement of absorption spectra.

Preparation of the borate complex of chromotropic acid

Chromotropic acid (4 g, 0.01 mol) in 20 cm³ of water and boric acid (0.3 g, 0.005 mol) in 20 cm³ of water were mixed and the pH of the solution was adjusted to 2.0 with sodium hydroxide solution. To this solution, 100 cm³ of ethanol were added and then allowed to stand at room temperature overnight. The needle-like crystals deposited were filtered off, washed with ethanol and then dried under reduced pressure. Yield 1.8 g (Found: C, 27.22; H, 2.57; B, 12.63; S, 14.88. Calc. for $C_{20}H_8$-$Na_4O_{16}S_4\cdot8H_2O$: C, 27.31; H, 2.73; B, 12.29; S, 14.57%).

Acid–base titration

Acid–base titration of chromotropic acid and its borate complex was carried out at 25.0 °C in aqueous solution.[12] A 100 cm³ of aqueous solution containing chromotropic acid (0.25 mmol), $NaClO_4$ (0.1 M, M = mol dm⁻³) and various amounts of borate was titrated with standardized NaOH solution (0.1004 M) at 25.0 °C. The temperature of the reaction solution was kept constant by circulation of thermostatted water through a jacket. Nitrogen gas was bubbled into the solution during the titration. The standard base solution was added through a capillary tip beneath the surface of the solution, and measured by a piston type burette. The pH was measured with a glass electrode after each addition. The pH meter was calibrated by use of buffer solutions at pH 4.01, 6.86 and 9.18.

Adsorption capacity and % extraction measurements

The equilibrium adsorption capacity and % extraction of boric acid/borate with the present resins were typically determined by the following procedure. Samples containing a 0.5 g portion of resin, 33 cm³ of water, 1 cm³ of buffer solution and 5 cm³ of borate solution of either 0.2 or 0.02 M were prepared for capacity and % extraction measurements respectively. The whole system was shaken for 6 d in a thermostatted room at 25 °C. In a similar manner, a Langmuir equilibrium study was carried out by shaking 0.5 g of the resin with various concen-

Table 1 Leakage of chromotropic acid from the resin matrix on treating with different concentrations of HCl and NaOH solutions[a]

Reagent	Concentration/M	% Leakage
HCl	0.05	0.4
	0.1	1.7
	0.4	12.7
	0.6	22.9
	0.8	28.8
NaOH	0.05	—
	0.1	—
	0.5	—
	1.0	0.14

[a] A 0.5 g portion of the resin was shaken for 3 d with 50 cm³ of acid or base solution at 25 °C.

trations of boric acid/borate solution at fixed pH. The equilibrium pH and the amount of borate in the solutions were determined. The capacity and % extraction were then calculated from the change of the boron concentration in the initial and the equilibrated solutions.

Kinetic study

A 4 g amount of resin was stirred with 250 cm³ of buffered solution containing 13.5 ppm (ppm = mg dm⁻³) of boron. The reaction temperature was kept at 25.0 °C by immersing the vessel in a thermostatted water-bath. While stirring at a speed of 65 rpm, a small portion of the solution was withdrawn at appropriate intervals and the concentration of boric acid/borate was determined by ICP-AES. The kinetic data were analysed by Vermeulen's approximation.[13,14]

Column adsorption experiments

Column tests were typically performed by using a 1.0 × 14 cm column packed with 4 g (22 cm³) of the chromotropic acid resin. A feed solution containing 9 ppm of boron at pH 1.7 was continuously supplied to the column. The flow rate was adjusted to 0.4 cm³ min⁻¹, which corresponds to a space velocity (SV) of 2.2 beds h⁻¹. The solution passed through the column was fractionated into 19 cm³ portions and the concentration of boron in each 10th fraction was determined by ICP-AES.

Results and discussion

Preparation of the resin

The anion exchange resin was functionalized with chromotropic acid simply by mixing the resin beads with an aqueous solution containing an excess amount of chromotropic acid. The strongly basic anion exchanger, Lewattitt MP 500WS, based on macroporous cross-linked polystyrene, was used as the support matrix. The ligand capacities in dry resin determined by microanalysis of sulfur were around 0.8–0.9 mmol g⁻¹ on average. The resin loaded with Tiron was prepared in a similar manner, and the ligand content determined to be 1.25 mmol g⁻¹. The ligand capacity is likely to depend on the molecular size of the ligand loaded.

Leaking of ligand from the resin matrix was examined in the presence of HCl or NaOH solution. A 1 g portion of the resin was shaken for 3 d in the acid or base solution of various concentrations. The amount of ligand leached was analysed by a spectrophotometric method and the results are listed in Table 1. In acidic solution the leakage of chromotropic acid increased with increasing acid concentration, whereas in basic media only a small amount of the ligand was found in solution.

Borate complex formation of chromotropic acid

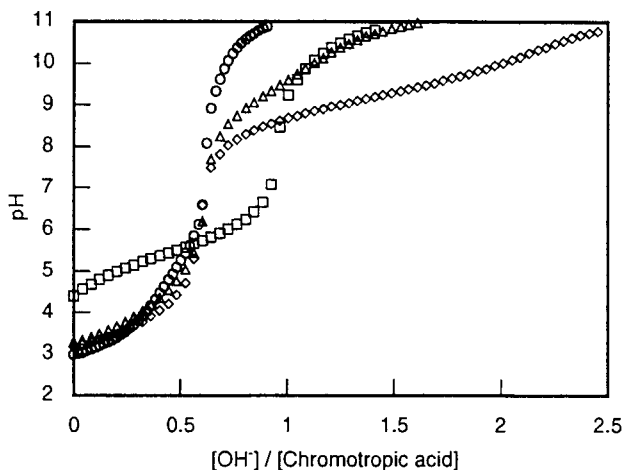Eqn. (1) shows the equilibrium of boric acid and borate ion in

Fig. 1 Acid base titration of chromotropic acid in the absence and presence of boric acid at 25 °C. □: Chromotropic acid 0.25 mmol. ◇: Chromotropic acid : boric acid = 2 : 1. ○: Chromotropic acid : boric acid = 1 : 1. △: Chromotropic acid : boric acid = 0.5 : 1. Initial volume 100 cm³, $I = 0.1$ M (NaClO₄), [NaOH] = 0.1004 M.
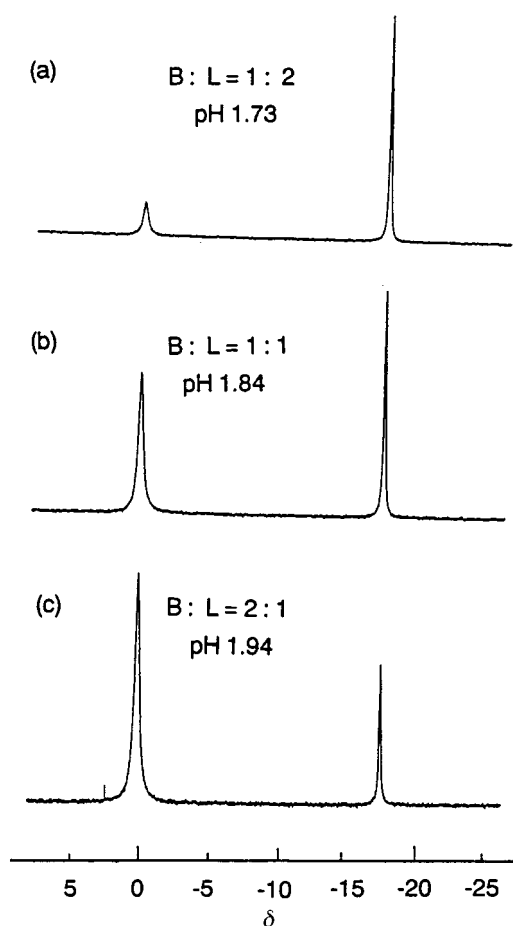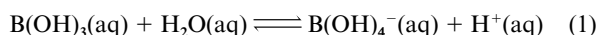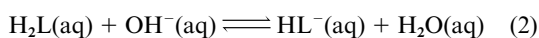

Fig. 2 The ¹¹B NMR spectra of boric acid in the presence of chromotropic acid at pH around 1.8 in D₂O. The ¹¹B chemical shift is relative to that of the boric acid peak. [boric acid] = 0.13 M.

$$B(OH)_3(aq) + H_2O(aq) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq) \quad (1)$$

aqueous solution. The acid dissociation constant (pK_a) of eqn. (1) is reported as 9.05 ($I = 0.1$ M with NaCl, 25 °C).[7] Proton dissociation of chromotropic acid (H₂L) can be expressed as in eqn. (2). The pK_a value of the first proton dissociation is 5.44

$$H_2L(aq) + OH^-(aq) \rightleftharpoons HL^-(aq) + H_2O(aq) \quad (2)$$

and the dissociation of the second proton takes place at pH higher than 12 (Fig. 1).[8] Lowering of pH was observed when
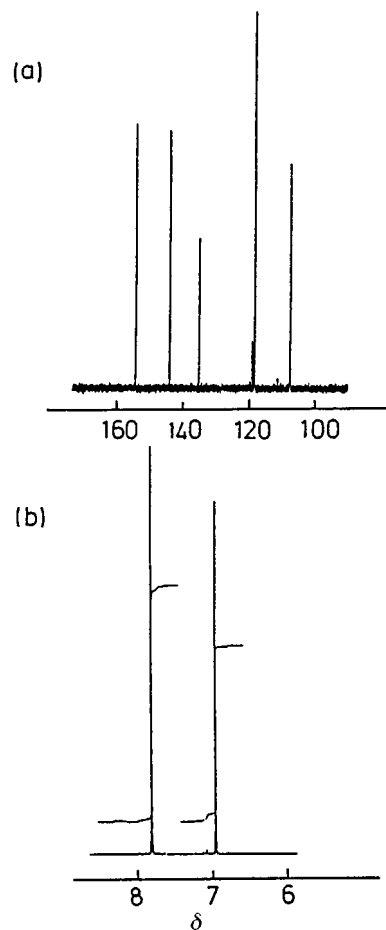

Fig. 3 (a) ¹³C NMR and (b) ¹H NMR spectra of chromotropic acid in the presence of an equimolar amount (0.13 M) of boric acid. pH 1.9, solvent D₂O, internal standard DSS (sodium 4,4-dimethyl-4-sila-pentane-1-sulfonate).

chromotropic acid was added to the boric acid/borate solution indicating the release of proton(s). Acid–base titration of chromotropic acid was carried out in the presence of boric acid of various L : B ratios. One proton is released from chromotropic acid in the absence of boric acid, which is in accordance with eqn. (2), whereas in the presence of boric acid inflection points are observed at around [OH⁻]/[L] = 0.5 irrespective of L : B ratio as shown in Fig. 1. This indicates the preferential formation of a 2 : 1 (L : B) complex, eqn. (3).

$$B(OH)_3(aq) + 2\,H_2L(aq) \rightleftharpoons$$
$$BL_2^-(aq) + 3H_2O(aq) + H^+(aq) \quad (3)$$
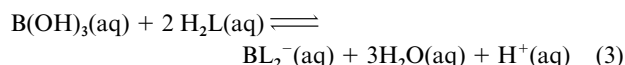
Boron-11 NMR spectroscopy has been used as a powerful tool to study the structure of borate complexes of sugars and alcohols.[6,7,15–17] We followed the complex formation of boric acid and chromotropic acid (H₂L) by the ¹¹B, ¹H and ¹³C NMR spectra in D₂O solution. Fig. 2 shows the ¹¹B NMR spectra for boric acid solution (pH 1.7–2.0) in the presence of different amounts of chromotropic acid. It has been pointed out that the ¹¹B signal appears at characteristic positions when borate forms complexes with polyols[15,16] and aminoalcohols.[17] A sharp peak which can be assigned to the chromotropic acid complex was observed in addition to the signal of free boric acid. Obviously the relative intensity of the peak due to boric acid decreased with the increase in chromotropic acid concentration. As in Fig. 2(b), an equimolar mixture of boric acid and chromotropic acid at around pH 2.0 gave two peaks of similar intensity. The same solution showed six ¹³C and two ¹H NMR peaks corresponding to the chromotropic acid complex (Fig. 3). When the amount of chromotropic acid was doubled (B : L = 1 : 2) the ¹¹B peak intensity of boric acid greatly decreased [Fig. 2(a)] and
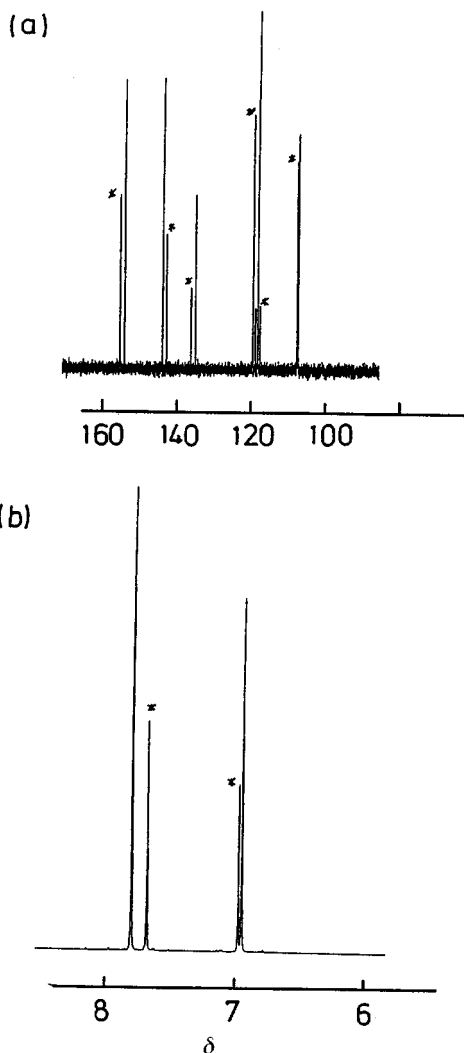
(a)

160 140 120 100

(b)

8 7 6

δ

Fig. 4 (a) ^{13}C NMR and (b) ^{1}H NMR spectra of boric acid solution in the presence of an excess of chromotropic acid (B:L = 1:3). The smaller peaks with asterisks correspond to those of free chromotropic acid. Chromotropic acid 0.39 M, boric acid 0.13 M. pH 2.0, solvent D_2O, internal standard DSS.

Fig. 5 Percentage extraction of boron by the chelating resins as a function of pH. ●: Chromotropic acid resin. ■: Tiron resin. ▲: N-Methylglucamine resin. Resin 0.5 g, [B] initial 28.2 ppm, shaking time 6 d at 25 °C.

Fig. 6 Absorption capacity of the boron selective resins as a function of pH. ●: Chromotropic acid resin. ■: Tiron resin. ▲: N-Methylglucamine resin. Resin 0.5 g, [B] initial 282 ppm, shaking time 6 d at 25 °C.

vice versa [Fig. 2(c)], whereas the number of ^{13}C and ^{1}H NMR peaks and chemical shifts remained unchanged. The simple features of the spectra indicate the formation of single species of high molecular symmetry in acidic solution. New peaks corresponding to "free" ligand appeared in both ^{13}C and ^{1}H NMR spectra when a 1 molar excess of chromotropic acid was added (B:L = 1:3) to this solution (Fig. 4). The formation of a symmetrical bis-chelate can explain the observed NMR spectra.

Crystals of the borate complex were successfully isolated from acidic solution (pH 2.0). On the basis of elemental analysis the complex isolated was assigned to the bis chromotropic type. Its ^{1}H and ^{13}C NMR spectra in D_2O coincide with those given in Fig. 3. This is a strong evidence of preferential formation of a bis complex in solution. At pH 8.4 the ^{13}C and ^{1}H peaks appeared almost at the same position as those observed at pH 1.9. Additional small peaks were observed in the ^{1}H NMR when the pH increased above 8, presumably because the formation of the 1:1 complex may take place at higher pH.

The present chromotropic acid complex may be stabilized due to the steric bulkiness of the aromatic moiety. In addition, π–π* interaction between phenolic groups and boron must be enhanced because the sulfonate group acts as a strong electron acceptor for the lone pairs on oxygen leading to an increase in the Lewis acidity as well as of the stability of the resulting complex. In consequence, the second ligand is bound much more easily producing a bis-chelated complex.
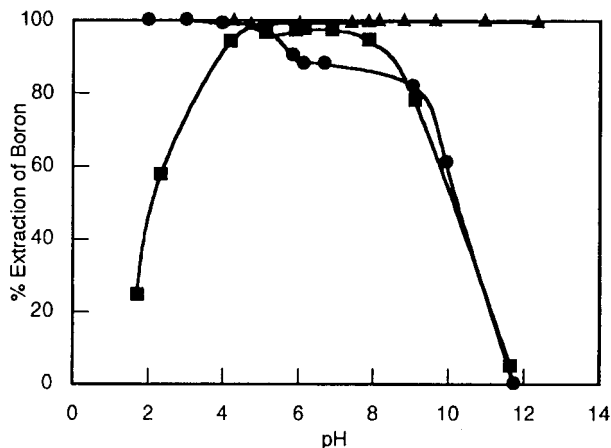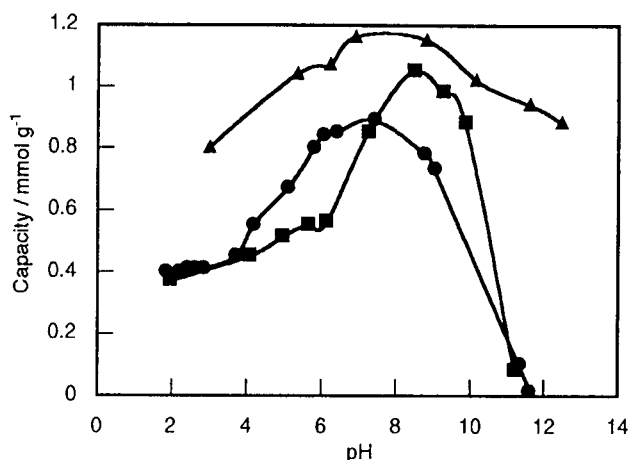
% Extraction of boric acid/borate

Fig. 5 shows the % extraction of boric acid/borate as a function of pH for chromotropic acid resin, Tiron resin and the chelating resin having N-methylglucamine groups. In the case of chromotropic acid resin almost complete extraction of boric acid/borate was attained at pH below 4.5, but the percentage decreases toward the higher pH region. Since the anion exchange resin did not retain boric acid in this pH region, firm retention of boric acid in an acidic region can be attributed to the stable complex formation with chromotropic acid as has been deduced from the titration and NMR data. For the Tiron resin the favorable pH region is limited to around the neutral region and a small amount of borate ion inevitably remains in solution. On the contrary, N-methylglucamine resin can retain borate ion effectively in a remarkably wide pH range. The high adsorption performance of this resin has been interpreted by the formation of a stable 1:1 tetradentate complex.[7]

Adsorption capacity for boric acid/borate

The adsorption capacities for boric acid/borate with the present resin, Tiron resin and N-methylglucamine resin were determined as a function of pH as shown in Fig. 6. The maximum capacity of the present resin for boric acid/borate is around 0.82 mmol g^{-1}. This value is close to the amount of chromotropic acid loaded on the resin. Thus 1:1 (L:B) complex formation is likely to occur in this pH region. The value at pH 2–4 is about a

Table 2 Langmuir constants for the adsorption of boric acid/borate at 25 °C

Resin	C_s/mmol g^{-1}	log K	Regression
Chromotropic acid	0.38	6.13	0.999
N-Methylglucamine	1.32	4.35	0.997

(a) Chromotropic acid resin
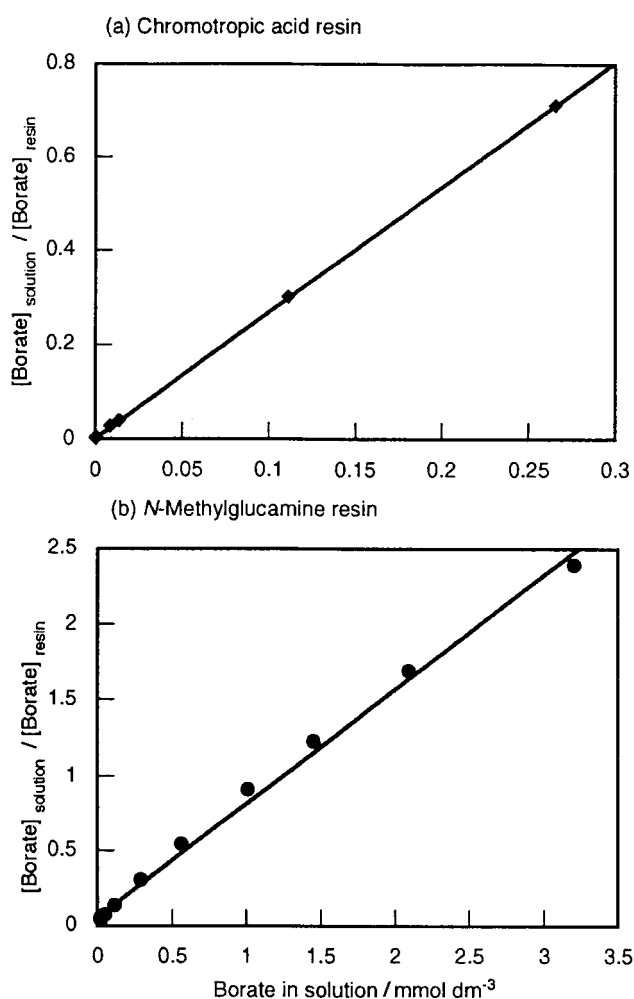

(b) N-Methylglucamine resin

Fig. 7 Langmuir plots for the adsorption of boric acid by (a) chromotropic acid resin at pH 1.8, and (b) N-methylglucamine resin at pH 8.5. Temperature 25 °C.

half of the ligand content, *i.e.* 0.4 mmol g^{-1}. This suggests the formation of a 2:1 complex in the acidic region where the strong affinity of chromotropic acid to boric acid has been realized in an aqueous solution. Migration of ligand may take place in the anion exchange resin in this pH region. The overall feature of the adsorption capacity of Tiron loaded resin is similar to that of chromotropic acid resin but shifted to a higher pH region. The apparent shift coincides with the difference of pK_a values between the two ligands, *i.e.* 5.4 for chromotropic acid and 7.3 for Tiron, whereas the difference in maximum capacity can be attributed to the amount of ligand loaded on the resin matrix.

The retainment of boric acid/borate has been analysed using the Langmuir model of adsorption. Eqn. (4) was used to

$$C/C_x = (1/KC_s) + (C/C_s) \qquad (4)$$

calculate the equilibrium constant (K) and the capacity of the resin C_s,[18] where C is the concentration of borate in solution and C_x is that in the resin at equilibrium. Fig. 7 shows plots of C/C_x against C for chromotropic acid resin and N-methylglucamine resin. A good straight line was obtained in each

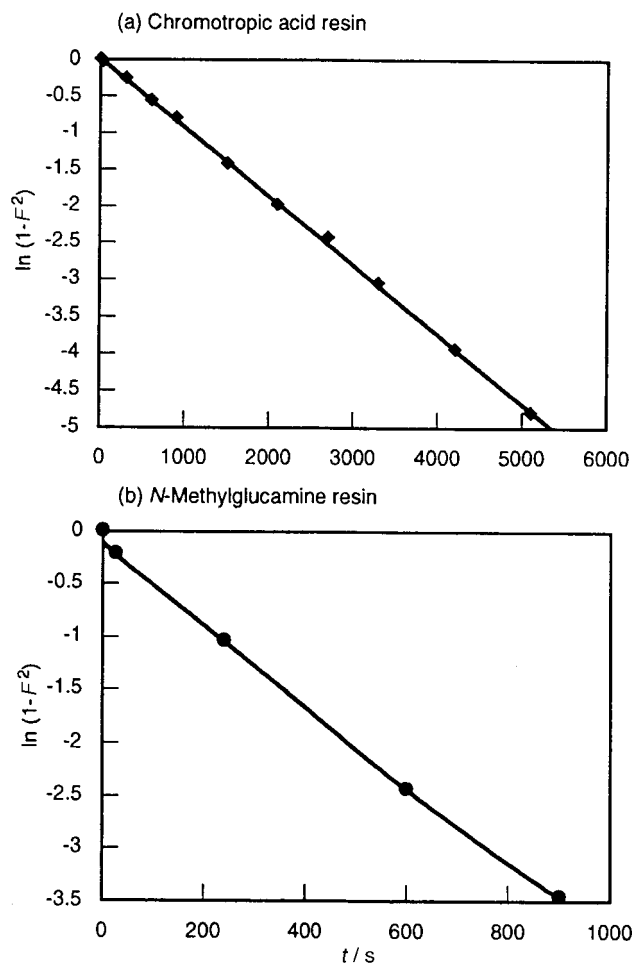(a) Chromotropic acid resin

(b) N-Methylglucamine resin

Fig. 8 Kinetic study of the adsorption of boric acid by (a) chromotropic acid resin and (b) N-methylglucamine resin at 25 °C. Resin 4 g, [boric acid] initial 13.6 ppm, pH 1.8, volume of solution 250 cm^3, stirring speed 65 rpm.

case ($R = 0.999, 0.997$). From the intercept and slope we derived log K and C_s for chromotropic acid and N-methylglucamine resins and those values are listed in Table 2. The binding constant K for chromotropic acid resin is two orders of magnitude larger than that of N-methylglucamine resin system. Therefore the former can retain boric acid/borate much more firmly than N-methylglucamine resin in their optimum pH region. Even though the capacity for boron adsorption is smaller, firm fixation is required to capture the trace amount of boron quantitatively.

Kinetic study

The kinetic study for the adsorption of boric acid/borate on chromotropic acid resin and commercially available N-methylglucamine resin was carried out at optimum pH conditions. To analyse the kinetic data we applied Vermeulen's approximation [13,14] expressed in eqn. (5) where $F = [M]_t/[M]_{eq}$ and k/s^{-1} is

$$\ln(1 - F^2) = -kt \qquad (5)$$

the experimentally observed overall rate constant; $[M]_t$ and $[M]_{eq}$ denote the borate concentrations (mmol g^{-1}) retained in the resin at time t and at equilibrium, respectively. Fig. 8 shows plots of ln $(1 - F^2)$ against time for the two resins. A good linear correlation was obtained in both cases indicating that the kinetic equation adopted is valid in these systems. The rate determining step appears to be the particle-diffusion process.[13,14] The kinetic data are listed in Table 3. The rate constant with the chromotropic resin at pH 1.8 was determined as 9.4×10^{-4} s^{-1} by a least-squares method. Therefore the half-life

Table 3 Kinetic data for the adsorption of boric acid/borate on chromotropic acid resin and N-methylglucamine resin at 25 °C

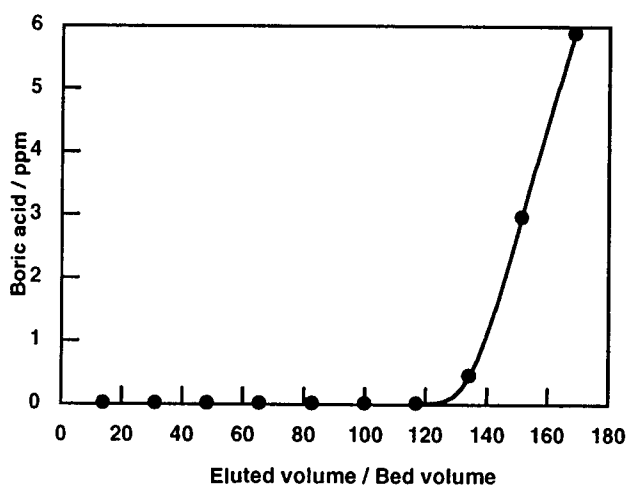| Resin	k/s^{-1}	Regression	$t_{1/2}$/min
Chromotropic acid	9.4×10^{-4}	0.9996	12.3
N-Methylglucamine	38.1×10^{-4}	0.9980	3.0

Fig. 9 Column breakthrough profile for the adsorption of boric acid by chromotropic acid resin. Resin 4 g, [boric acid] initial 8.95 ppm, pH 1.7, volume of column 11 cm³, flow rate 0.4 cm³ min⁻¹.

under the present conditions is approximately 12.3 min. The rate constant with N-methylglucamine resin was 38.1×10^{-4} s⁻¹ at pH 8.8 with a half-life of 3.03 min. The rate of boron uptake by the chromotropic acid resin is therefore 4 times slower than that by the N-methylglucamine resin.

Column experiments

We have made column adsorption tests by use of chromotropic acid resin. A solution containing 9 ppm of boric acid at pH 1.7 was continuously passed through a column packed with 4 g of the resin at a rate of 0.4 cm³ min⁻¹. The solution from the column was fractionated into small portions and the boron monitored by ICP-AES. Fig. 9 shows a typical column break-through curve. Nearly quantitative removal of boric acid was observed upon passaaage of a solution volume up to around 120 times that of the bed volume. About 11.9 mg of boron were retained on the resin phase, which corresponds to 68% of the total capacity of the resin at that pH. Almost all the boron was retained indicating the strong complexation as expected from equilibrium studies. Removal of a trace amount of boron was tested in order to apply this system to the production of ultra pure water. An aqueous solution containing boron (57.6 ppb) at pH 3.0 was passed through the column (50 cm³ resin bed) at flow rates ranging from 2.2 to 165 cm³ min⁻¹. The solution from the column was monitored by ICP-MS. The column perform-ance was found to be dependent on the flow rate. Thus the concentration of boron was close to the detection limit of ICP-MS (10 ppt) at a flow rate less than 5 cm³ min⁻¹ (SV = 4.16 beds h⁻¹). However, at a practical feed rate, i.e. 20 cm³ min⁻¹ (SV = 16.6 beds h⁻¹), approximately 1.2 ppb of boron leaked. Since the kinetic study showed that the adsorption rate is con-trolled by the particle diffusion step, reducing the particle size

and increasing the effective surface area in the matrix should improve the column performance.

Conclusion

Complexation of boric acid/borate with chromotropic acid was monitored by ¹H, ¹³C, ¹¹B NMR spectroscopy and acid–base titration. The major species in aqueous solution was suggested to be a 2:1 (L:B) complex in a wide pH range (1.8–10.5) irrespective of the ligand to boron ratio. Thus remarkably firm complexation is taking place in acidic aqueous solution. An adsorbent was prepared from chromotropic acid and strongly basic anion exchange resin. Its adsorption characteristics for boric acid/borate were examined with respect to adsorption capacity, % extraction, equilibrium and kinetic studies. The resin can retain boric acid very firmly at pH below 4.5. Langmuir isotherm analysis revealed that the chromotropic acid resin has a binding constant two orders of magnitude larger than that of a commercially available resin functional-ized with N-methylglucamine at their optimum pH condi-tions. The firm retention of boron was attributed to the formation of a stable bis-chelated complex in acidic media. The overall rate constant of the present resin system was 1/4 of that of N-methylglucamine resin. The rate determining step appeared to be the particle-diffusion process, and hence the adsorption rate could be improved by using a resin of much higher surface area and smaller particle size. The column experiments demonstrated that removal of boric acid was nearly quantitative. Thus the concentration of boron was close to the detection limit of ICP-MS (10 ppt) at a flow rate less than SV = 4.16 h⁻¹.

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