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SELECTION OF ANION-EXCHANGE RESINS FOR BORON THERMAL-REGENERATION SYSTEMS

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SUMMARY

Changes in the concentration of boron in the reactor coolant are effected by using a development called a boron thermal-regeneration system (BTRS). Thermal regeneration refers to the use of ion-exchange resins either to retain or to release borate ions as a function of temperature. For the BTRS, the equilibrium capacities of commercial and special anion-exchange resins have been investigated as a function of the degree of cross-linking of the resins. The equilibrium capacity increases as the temperature decreases and depends strongly on the degree of cross-linking, reaching a maximum at *ca.* 7% of divinylbenzene (DVB). The temperature coefficient of equilibrium capacity of boric acid is also a function of the concentration of the external solution and of the cross-linking, also reaching a maximum at *ca.* 7% of DVB. Other basic characteristics of anion-exchange resins have been also investigated.

INTRODUCTION

The boron thermal-regeneration system (BTRS) was designed to adjust the concentration of boric acid in the coolant of a pressurised-water reactor (PWR) by means of ion-exchange resins¹. In this system, boric acid was used to compensate for xenon transient and other reactivity changes resulting from daily operation in the PWR. Anion-exchange resins can be used reversibly to change the boric acid concentration because the amount of boric acid adsorbed by the resin varies with temperature. A key problem in BTRS technology is the selection of suitable resins.

The research described in this paper was prompted by the lack of detailed information of the kind necessary for selection of the most suitable resins for BTRS applications. In addition, this research aimed to elucidate the effects of anion-exchange resin structure on the adsorption capacity and on the mechanism of adsorption and desorption. Experiments were carried out in laboratory ion-exchange columns in order to obtain the necessary data. The design and operation of these experiments were based on the known basic principles of ion exchange, on literature data, on plant operating experience and on previous laboratory work¹⁻⁵.

TABLE I
ION-EXCHANGE RESINS USED

<i>Resin type</i>	<i>Effective size (mm)</i>	<i>Maximum operating temperature (°C)</i>	<i>Brand name</i>	<i>Minimum total capacity (mequiv./ml)</i>
Strongly basic anion-exchange Porous type I Cross-linked polystyrene matrix	0.35-0.55	60 (OH ⁻ form) 80 (Cl ⁻ form)	Diaion PA306 Diaion PA308 Diaion PA312 Diaion PA316 Diaion PA318	0.8 1.0 1.2 1.3 1.3
Strongly basic anion-exchange Gel type I Cross-linked polystyrene matrix	0.35-0.55	60 (OH ⁻ form) 80 (Cl ⁻ form)	Diaion SA10A	1.3
Weakly basic anion-exchange Highly porous type	0.35-0.55	100 (OH ⁻ form)	Diaion WA30	1.5
Strongly basic anion-exchange Nuclear type	0.40-0.50	60 (OH ⁻ form)	Amberlite IRN78 (high-purity, chloride-free Amberlite IRA-400)	1.2 (IRA-400)
Strongly basic anion-exchange Nuclear type	0.35-0.55	60 (OH ⁻ form) 80 (Cl ⁻ form)	Diaion SAN-1 (high-purity, chloride- free Diaion SA Type I)	3.7 (OH ⁻ form)
Chelating resin	0.25-0.55	150 (Cl ⁻ form)	Diaion CR40 Sirotherm TR20	0.7 (Cu ²⁺ form)

APPARATUS

Ion-exchange resins

The anion-exchange resins most widely used in large-scale cooling-water-treatment operations are strongly basic resins having *ca.* 8–12% of divinylbenzene (DVB) cross-linking⁵. Nevertheless, it is useful also to study the performance of several other types of resin under conditions such as are encountered in BTRS equipment. In this work, the properties of several Type-I (porous-type) polystyrene nuclear-type strongly basic anion-exchange resins were compared in order to examine the effect of cross-linking. Those properties were also compared with the performance of the corresponding series of gel-type resins, and with weakly basic resins of analogous structure; some special types of resin were also tested. Basic data on these resins are presented in Table I.

Experimental conditions

The initial volume of the resin bed in each of the experimental columns was *ca.* 20 ml. The feed-solution flow-rate was 20 ml/h per 1 ml of bed-volume (400 ml/h for a 20-ml resin bed). Feed-solution concentrations were 1.0, 3.0, 5.0, 7.0 and 10.0 g/l of boric acid. Measurements were made at temperatures of 20.0, 40.0, 60.0 and 80.0°C.

Experimental equipment

The columns used were of I.D. 2 cm and were *ca.* 20 cm long; they were enclosed in jackets through which water from a thermostat circulated. In order to maintain uniform solution temperature in high-temperature experiments, the feed solution was passed through a heat exchanger mounted at the top of each ion-exchange column. The flow-rate was maintained at a constant value by peristaltic pumps. This apparatus is illustrated in Fig. 1.

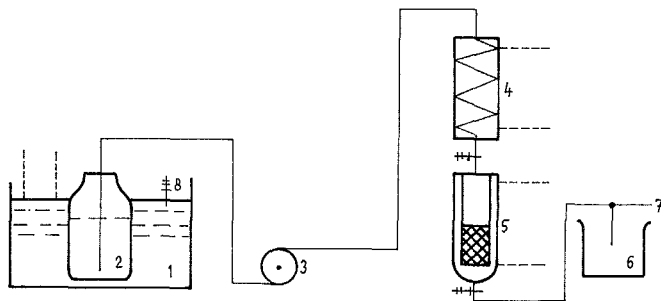


Fig. 1. Apparatus. 1, Thermostat; 2, H_3BO_3 feed solution; 3, peristaltic pump; 4, heat exchanger; 5, column packed with ion-exchange resin; 6, effluent collector; 7, effluent-sampling port; 8, thermometers.

PROCEDURES

Preparation of ion-exchange resins

Commercial ion-exchange resins were used in all experiments. Since these resins include beads of various mesh sizes and usually contain some water-soluble

organic substances, it was necessary to screen the resins to select beads of 30–50 mesh and to remove all impurities before use. This so-called conditioning was carried out in the usual way, treating the resin alternately with 1 *M* HCl and 1 *M* NaOH.

Equilibrium adsorption measurement

Ion-exchange resins in OH⁻ form, prepared as described above, were packed into the columns and treated with boric acid solution, which was supplied from a reservoir. In order to establish equilibrium between the resin in the column and the feed solution, an amount greater than the theoretical total exchange capacity of the resin bed was fed into each column. The establishment of equilibrium between the resin and feed solution was confirmed by titration of the effluent from the column; when feed and effluent concentrations were equal, dynamic equilibrium had been established.

After equilibrium had been established, some of the resin (*ca.* 3 ml) was picked up from the column, centrifuged to remove adhering solution and weighed. The adsorbed boric acid was eluted with 1 *M* HCl and measured by titration. The resin was converted into OH⁻ form and weighed after being dried in an air bath at 50°C for *ca.* 15 h.

Measurement of resin swelling and pH

In order to compare resin-capacity measurements with existing data, it was necessary to measure the volume of the resin bed. This was done by the tapping method⁶. The relationship between the weight of dry resin and the volume of wet resin is shown in Table II; Fig. 2 indicates the effect of cross-linking on resin swelling.

The pH of the external boric acid solution and that of the resin in equilibrium with the same solution were measured. Small amounts of pH indicators were added to testtubes containing resin and solution, and the resin-phase pH was estimated from the colour of the indicator. The purpose of these measurements was to clarify the mechanism of boric acid adsorption; this will be discussed elsewhere.

Experimental uncertainty of measurement

The accuracy of these measurements depends on many factors, including errors

TABLE II
SWELLING CHARACTERISTICS OF RESINS

<i>Resin</i>	<i>Degree of swelling (ml/g dry resin)</i>
Diaion PA306	5.71
Diaion PA308	4.92
Diaion PA312	3.48
Diaion PA316	2.97
Diaion PA318	2.72
Diaion SA10A	3.08
Diaion WA30	2.80
Diaion SAN-1	3.45
Diaion CR40	5.13
Amberlite IRN78	2.80
Sirotherm	4.21

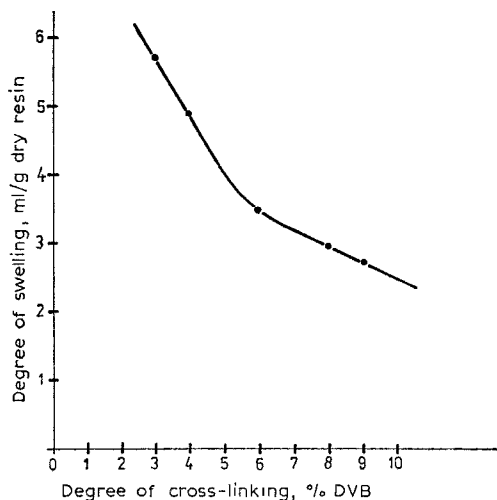


Fig. 2. Effect of cross-linking on resin for Diaion PA300 series resins (OH^- form).

arising in the operations of centrifuging and drying the resin beads, and titrating the boric acid solutions with mannitol. The uncertainty due to errors in these operations was roughly calculated and experimentally checked; it ranged from ± 1.5 to 2.0 g of boric acid per l of resin phase.

RESULTS AND DISCUSSION

Experiments were performed to determine the effects of solution concentration and temperature on the boric acid adsorption capacity of anion-exchange resins of differing structures. The results are shown in Figs. 3–15 and in Tables III–V.

The equilibrium resin capacity at temperature T_j and solution concentration C_i is $Q_r(C_i, T_j)$. The amount of boric acid desorbed when the temperature is raised is

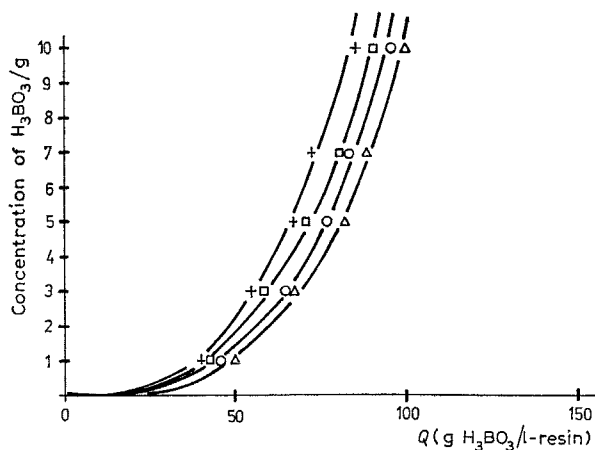


Fig. 3. Equilibrium relation for Diaion PA306. Δ , At 20°C; \circ , at 40°C; \square , at 60°C; $+$, at 80°C.

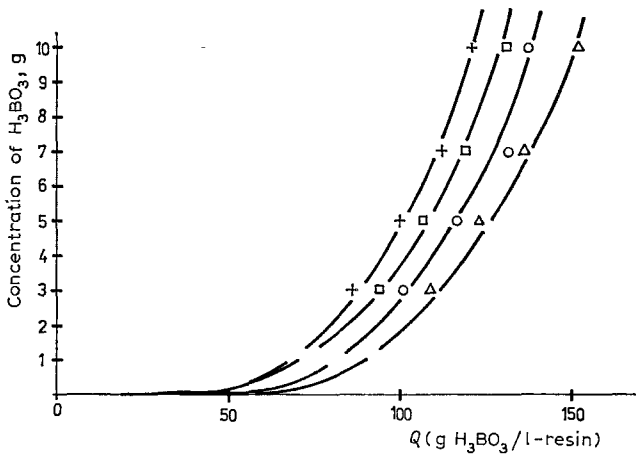


Fig. 4. Equilibrium relation for Diaion PA308. Symbols as in Fig. 3.

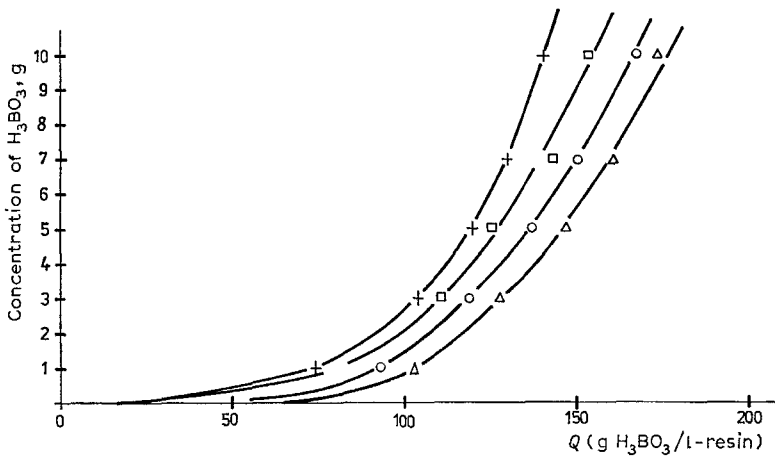


Fig. 5. Equilibrium relation for Diaion PA312. Symbols as in Fig. 3.

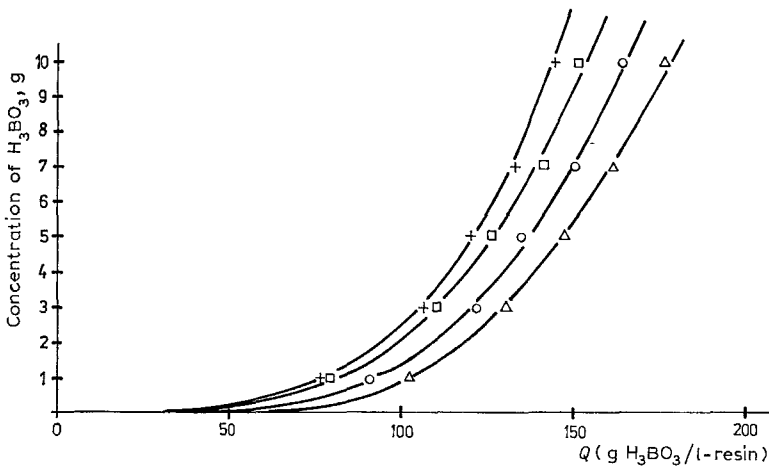


Fig. 6. Equilibrium relation for Diaion PA316. Symbols as in Fig. 3.

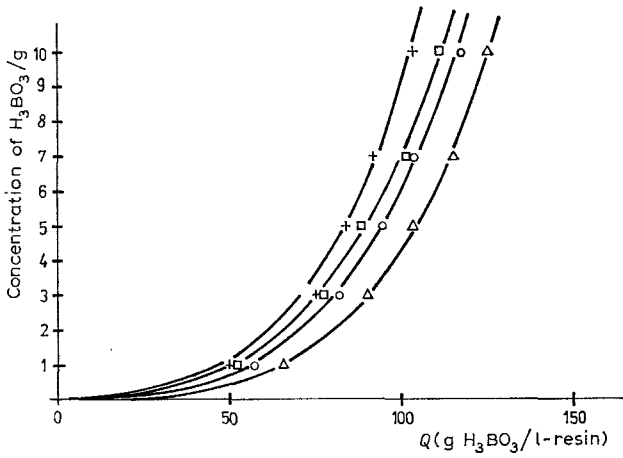


Fig. 7. Equilibrium relation for Diaion PA318. Symbols as in Fig. 3.

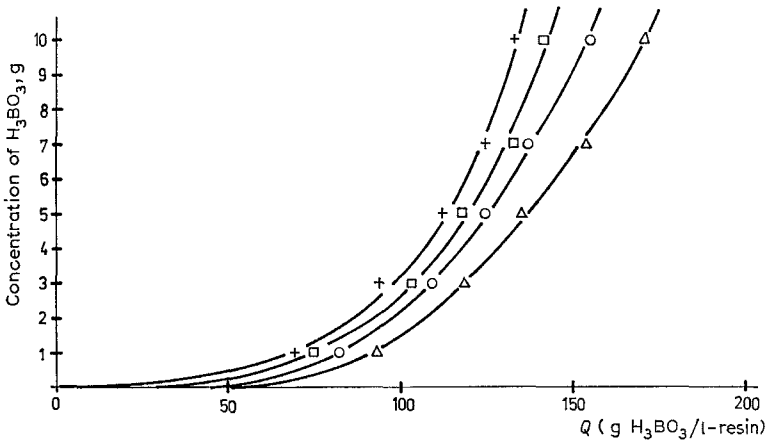


Fig. 8. Equilibrium relation for Diaion SA10A. Symbols as in Fig. 3.

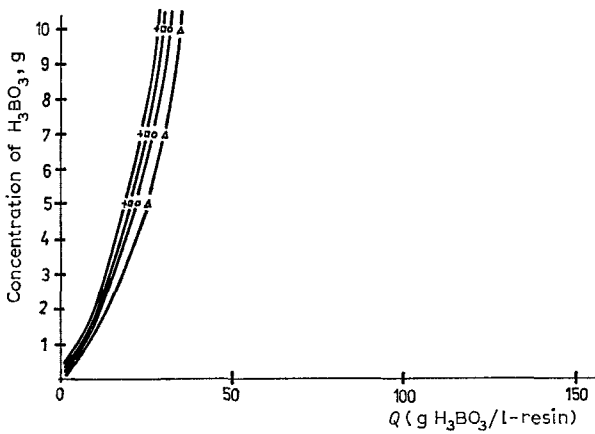


Fig. 9. Equilibrium relation for Diaion WA30. Symbols as in Fig. 3.

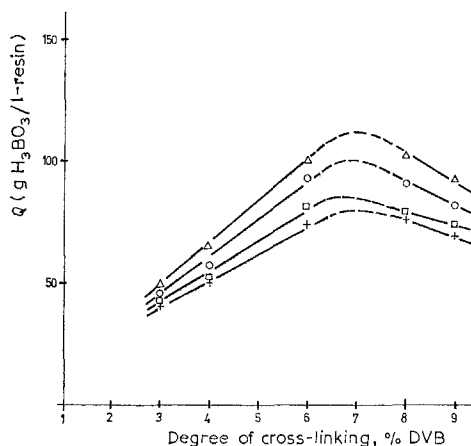


Fig. 10. Equilibrium capacity of Diaion PA300 series resins. Symbols as in Fig. 3. Concentration of H₃BO₃ solution, 1.0 g/l.

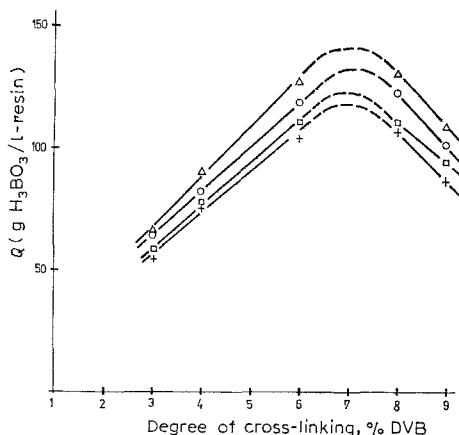


Fig. 11. Equilibrium capacity of Diaion PA300 series resins. Symbols as in Fig. 3. Concentration of H₃BO₃ solution, 3.0 g/l.

denoted by m , defined as $m = Q_r(C_i, T_1) - Q_r(C_i, T_2)$. The average values of m for a temperature change of 1°C are presented in Table IV.

The capacities measured at $T = 80^\circ\text{C}$ were not used in these calculations because of the possibility of loss of capacity due to a Hofmann degradation reaction in the Type I strongly basic resins. For the same reason, it was most satisfactory to

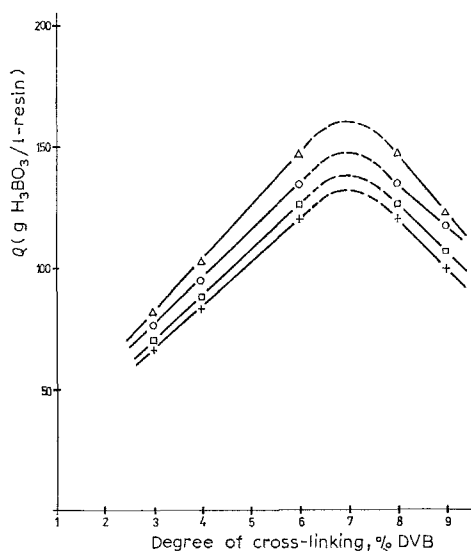


Fig. 12. Equilibrium capacity of Diaion PA300 series resins. Symbols as in Fig. 3. Concentration of H₃BO₃ solution, 5.0 g/l.

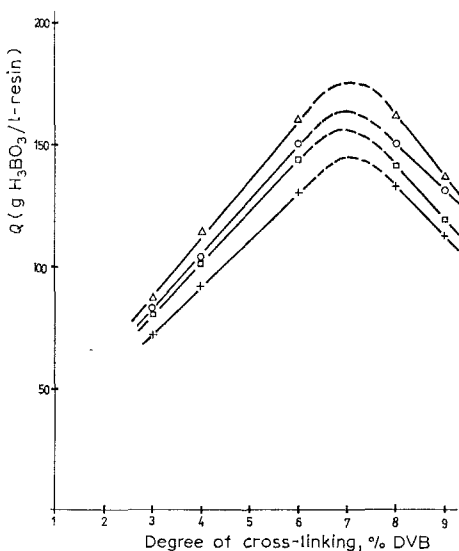


Fig. 13. Equilibrium capacity of Diaion PA300 series resins. Symbols as in Fig. 3. Concentration of H₃BO₃ solution, 7.0 g/l.

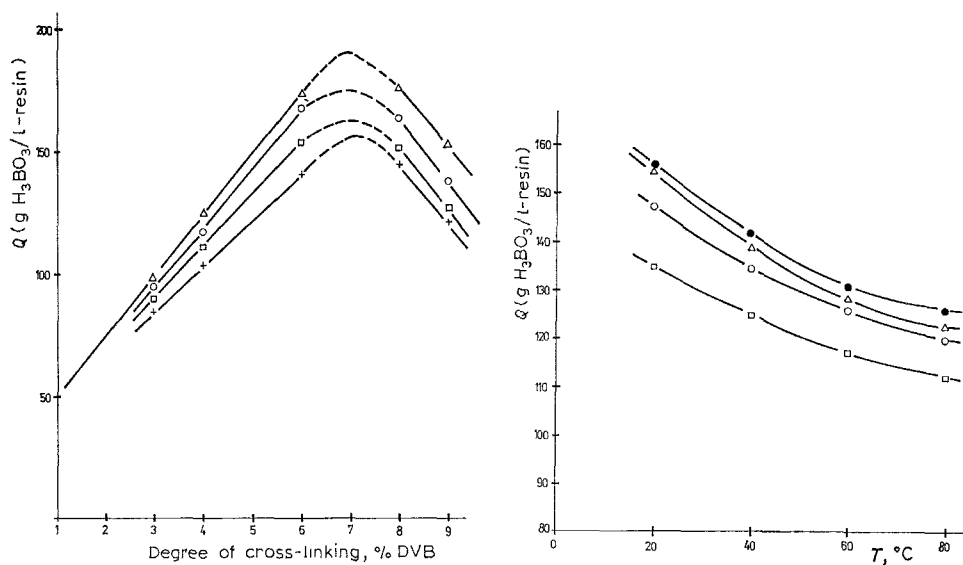


Fig. 14. Equilibrium capacity of Diaion PA300 series resins. Symbols as in Fig. 3. Concentration of H_3BO_3 solution, 10.0 g/l.

Fig. 15. Comparison of equilibrium capacities of three resin types. \circ , Diaion PA316; \square , Diaion SA10A; \bullet , Amberlite IRN78; \triangle , Diaion SAN-1. Concentration of H_3BO_3 solution, 5 g/l.

measure the desorption process (varying T from 20 to 80°C), rather than adsorption. (Previous research¹ has shown that the adsorption and desorption processes proceed quantitatively and reversibly.)

The pH of boric acid solutions varied, but this did not affect the results because the resin capacities were found to be independent of pH for pH < 6 in the solution concentration range from 1 to 10 g/l of boric acid.

The following conclusions can be drawn from the results presented in Tables III-V and Figs. 3-15:

(a) The adsorption capacity of resins increased as the feed concentration of boric acid increased, and decreased as the temperature increased. This change of capacity with temperature is most pronounced at high concentrations.

(b) Diaion WA30 resin is useful because of its good temperature resistance, but the equilibrium capacity of this resin is very low.

(c) Sirotherm (ref. 7) is a thermally regenerable amphoteric resin for use in desalination. Like Diaion WA30, its adsorption capacity is very low, and, further, it is highly susceptible to radiation damage. Hence it must be regarded as unsuitable for BTRS applications.

(d) The equilibrium resin capacity is strongly dependent on the degree of cross-linking at all solution concentrations used. Resins with 6-8% of cross-linking have the highest equilibrium adsorption capacities.

(e) The porous-type Diaion 312 and 316 resins have the highest equilibrium capacities; the capacity of the gel-type Diaion SA10A is in the same range.

(f) Diaion SAN-1 and Amberlite IRN78 resins appear satisfactory for BTRS applications in view of the temperature dependence of their equilibrium capacities.

TABLE III
EQUILIBRIUM CAPACITY MEASUREMENTS

Concentration of H_3BO_3 (g/l)	Q_r (g H_3BO_3 /l resin)					Q_r (mequiv. H_3BO_3 /g dry resin)							
	PA306	PA308	PA312	PA316	PA318	SA10A	WA30	PA316	SA10A	WA30	PA316	SA10A	WA30
<i>At T = 20°C</i>													
1.0	49.7	65.0	100.9	102.5	87.3	92.9	—	5.20	4.63	—	5.20	4.63	—
3.0	66.3	90.3	127.6	130.3	108.7	118.5	—	6.26	5.90	—	6.26	5.90	—
5.0	82.1	103.2	147.1	147.2	122.8	134.8	25.2	7.07	6.71	1.14	7.07	6.71	1.14
7.0	87.9	114.8	160.6	162.2	135.8	153.4	29.8	7.79	7.64	1.35	7.79	7.64	1.35
10.0	98.9	125.3	173.7	176.2	151.9	170.4	34.8	8.46	8.49	1.58	8.46	8.49	1.58
<i>At T = 40°C</i>													
1.0	45.3	57.2	93.1	90.6	81.2	81.8	—	4.35	4.07	—	4.35	4.07	—
3.0	64.5	81.8	118.7	122.4	100.9	108.6	—	5.88	5.41	—	5.88	5.41	—
5.0	76.9	94.5	137.2	134.5	116.6	124.3	22.4	6.46	6.19	1.01	6.46	6.19	1.01
7.0	82.5	103.5	150.0	150.0	131.1	136.9	27.1	7.21	6.82	1.23	7.21	6.82	1.23
10.0	95.2	117.5	167.5	163.7	137.2	154.4	32.0	7.86	7.69	1.45	7.86	7.69	1.45
<i>At T = 60°C</i>													
1.0	42.8	52.2	81.1	79.0	71.9	74.0	—	3.79	3.69	—	3.79	3.69	—
3.0	58.0	77.2	110.4	110.2	93.7	102.7	—	5.29	5.12	—	5.29	5.12	—
5.0	70.2	87.9	125.1	126.1	106.4	117.2	20.9	6.06	5.83	0.95	6.06	5.83	0.95
7.0	80.2	101.2	143.6	141.1	119.2	131.9	25.0	6.78	6.57	1.13	6.78	6.57	1.13
10.0	89.8	110.9	153.8	150.8	126.4	141.2	29.9	7.24	7.03	1.35	7.24	7.03	1.35
<i>At T = 80°C</i>													
1.0	40.4	50.1	74.2	76.3	67.1	69.1	—	3.67	3.44	—	3.67	3.44	—
3.0	54.6	75.8	103.8	106.4	86.1	93.9	—	5.11	4.68	—	5.11	4.68	—
5.0	66.8	83.7	120.0	120.0	99.7	89.4	18.8	5.76	5.57	0.85	5.76	5.57	0.85
7.0	72.1	91.9	130.3	132.9	112.4	124.6	23.3	6.38	6.21	1.06	6.38	6.21	1.06
10.0	85.0	103.3	140.5	144.3	120.7	133.1	28.8	6.93	6.63	1.30	6.93	6.63	1.30

TABLE IV

TEMPERATURE COEFFICIENT OF RESIN CAPACITY

Values expressed as g H₃BO₃/l resin/°C. Average values between 20 and 60°C.

Resin	Solution concentration (g/l)				
	1.0	3.0	5.0	7.0	10.0
Diaion PA306	0.17	0.21	0.30	0.19	0.23
Diaion PA308	0.32	0.33	0.38	0.34	0.36
Diaion PA312	0.49	0.43	0.55	0.42	0.50
Diaion PA316	0.58	0.50	0.53	0.53	0.63
Diaion PA318	0.38	0.38	0.41	0.34	0.63
Diaion SA10A	0.47	0.40	0.44	0.54	0.73
Diaion WA30	—	—	0.11	0.12	0.12

TABLE V

COMPARISON OF RESIN TYPES

Concentration of H₃BO₃ solution 5 g/l.

Resin	Equilibrium capacity (g H ₃ BO ₃ /l resin)				Average temperature coeff. of capacity (g H ₃ BO ₃ /l resin/°C)
	20°C	40°C	60°C	80°C	
Diaion SA10A	134.8	124.3	117.2	111.9	0.44
Diaion PA316	147.2	134.5	126.1	120.0	0.53
Diaion SAN-1	155.0	138.4	128.5	122.4	0.66
Amberlite IRN78	156.2	142.1	131.1	125.9	0.63
Diaion WA30	25.2	22.4	20.9	18.8	0.11
Sirotherm TR20	14.1	9.8	8.1	7.8	0.15
Diaion CR40	64.2	48.6	39.2	35.1	0.62

(g) The amount of desorption was greater than expected in the experiment using feed concentration of 1.0 g/l of boric acid, even in the temperature range 20–60°C. It is possible that the strongly basic functional groups underwent some thermal degradation at 60°C. Because the solution flow-rate was the same in all experiments, longer periods were required to charge a stoichiometric excess of boric acid in the form of dilute solutions than in the form of more concentrated solutions. Hence the resin in the bed remained in the OH⁻ form for a relatively longer period at 60°C.

CONCLUSION

A satisfactory relationship between equilibrium capacity and degree of cross-linking was found for porous-type Diaion anion-exchange resins; the capacity of the gel-type Diaion SA10A resin is in the same range. The study of Amberlite IRN78 (a nuclear-type resin, but not developed especially for BTRS) shows that this type of resin may be economical in commercial use. Other types of anion-exchange resin, however, are not suitable for BTRS applications.

In view of these results, it seems necessary to develop some special strongly basic anion-exchange resins for BTRS applications. Experiments should also be conducted to compare the kinetic properties of porous- and gel-type resins. It was verified that only strongly basic anion-exchange resins are suitable for BTRS.

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