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The Sorption Capacity of Boron on Anionic-Exchange Resin

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ABSTRACT

Boron sorption capacities on anionic-exchange resins vary with temperature, concentration, and resin crosslinkage. A semiempirical correlation, developed from boron solution chemistry, is presented to account for these variations. The relationship, based on boron chemistry and changes in Gibb's energy, can be stated approximately as $Q = a_1 C_B^{a_2} z^{a_3} \exp[-(a_4 T + a_5 T^2 + a_6 z^{0.5})]$. Correlation parameters, which vary with resin type, are evaluated experimentally. Parameter values for macroporous resin Diaion PA 300 and for gel-type resins Diaion SA10 and Amberlite IRN 78LC are presented. The resulting expression is used to determine boron sorption and desorption limitations on ion exchangers at various temperatures and concentrations, and to determine the interfacial boron concentration in equilibrium and rate models.

INTRODUCTION

The sorption capacities of strong-base anion-exchange resins for boron vary with temperature, concentration, and resin crosslinkage (1–5). The temperature effect has been exploited in the boron thermal regeneration system

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(BTRS) for nuclear power plants to improve chemical shim control in pressurized water reactors (PWR). The exchange mechanism, however, is not well known due to complicated polyborate formation—both in solution and within the resin—over ranges of temperature, concentration, and pH. A detailed interpretation of boron sorption would allow predictions of boron behavior on ion-exchange resins.

The selection of BTRS anion-exchange resins was evaluated by Peterka (1), who found that capacity depends strongly on the degree of resin crosslinking. His experiments showed maximum boron-sorption capacity near 7% crosslinkage. Tomizawa (2, 3) studied concentration and temperature dependencies of boron capacity using OH^- form Diaion SAN-1 resin. Results were:

- At 25°C, as solution concentration increases from 0.00925 to 0.647 mol/L, the average moles of boric acid sorption on resin increases from 1.46 to 4.22 mol/L-resin.
- For 5 and 70°C, capacity drops from 3.78 to 2.94 mol/L-resin and from 1.58 to 1.15 mol/L-resin at constant solution concentrations of 0.278 and 0.00925 mol/L, respectively.
- The pH within borate-form resin increases with rising temperature at constant concentration (the range of pH inside the resins is from 9 to 14).

Tomizawa assumed that from 5 to 70°C, orthoborate, $B(OH)_4^-$, tetraborate (monovalent and divalent, B_4^- and B_4^{2-}), and pentaborate (monovalent and divalent, B_5^- and B_5^{2-}) were present within the resin. He suggested that nominal equilibrium constants could be estimated for these five borate species. His trends agree with Peterka's work, but his postulation seems questionable since the formation of the divalent species requires an excess of OH^- ions, especially at high boron concentration.

Na (5) studied boron-sorption equilibrium on strong-base anion resin using Amberlite IRN 78LC. He observed results similar to Tomizawa. With boron concentration near 0.0925 mol/L, the average number of boron atom per site increases from about 1.6 to 2.1 from 60 to 10°C, an increase of 31% capacity.

All these researchers showed similar boron sorption tendencies on strong-base anionic resins. Lower temperature and higher concentration favor boron sorption, while desorption occurs easily at higher temperature and lower concentration. With application of the BTRS cycle, the need for a concise relationship for boron sorption on ion-exchange resins becomes important in predicting system performance.

In this paper an equilibrium isotherm for boron sorption on anionic resins is developed by examining boron solution chemistry, changes in Gibbs energy, and diffusion characteristics. Equation parameters are obtained from data by multiple nonlinear regression methods. The values for seven commercial resins are given. Results are within 5% of experimental data.

DISTRIBUTION OF BORON IN SOLUTION AND RESIN

There is no general agreement of all the boron forms in aqueous solution. For nuclear power applications (boron concentration below 0.185 mol/L), there is no need to account for every boron species, since boric acid and orthoborate predominant. Other polyborates, such as $B_3(OH)_{10}^-$, are significant boron carriers, and are included in the model to improve accuracy.

Boron in Aqueous Solution

In general, two boric acid types exist in the free state, metaboric (HBO_2) and orthoboric ($B(OH)_3$). Each type may be converted to the other by either hydration or dehydration at certain conditions. In solution, metaboric acid converts rapidly to orthoboric acid due to hydration.

Boric acid in solution dissociates weakly to form monoborate and some polyborates, depending on temperature, concentration, and pH. The primary species at the acidic and basic extremes are $B(OH)_3$ and $B(OH)_4^-$, respectively. At low concentration ($<$0.025 M as boron), $B(OH)_4^-$ is the only significant species in solution, while at higher concentration polyborates—triborates, tetraborates, and pentaborates—along with $B(OH)_4^-$, may exist. The polyborate with three boron atoms and one negative charge is most important (6–9).

There are two major postulations about the trimer borate. Due to the ring-type structure of trimeric hydroxyborate ($B_3O_3(OH)_4^-$) and its high solution stability, Edwards (6) suggested the following reaction to form $B_3O_3(OH)_4^-$,

$$2B(OH)_3 + B(OH)_4^- \Leftrightarrow B_3O_3(OH)_4^- + 3H_2O \tag{1}$$

while Mesmer et al. (9, 10) assumed the reaction

$$2B(OH)_3 + B(OH)_4^- \Leftrightarrow B_3(OH)_{10}^- \tag{2}$$

leads to the formation of $B_3(OH)_{10}^-$. The equilibrium constant, K, according to these authors, agrees within about two orders of magnitude.

Polyborates also appear in solution. Cotton and Wilkinson (10) postulated Eq. (3) for traces of tetraborate that can be found at high boron concentration:

$$2B(OH)_3 + 2B(OH)_4^- \leftrightarrow B_4O_5(OH)_4^{2-} + 5H_2O \tag{3}$$

The formation of pentaborate

$$4B(OH)_3 + B(OH)_4^- \leftrightarrow B_5O_6(OH)_4^- + 6H_2O \tag{4}$$

was reported by Ross and Edwards (8).

Mesmer et al. (9) postulated that the distribution of boron forms can be determined quantitatively under various conditions as illustrated in Figs. 1 and 2. Polyborates are most likely to be formed within the pH range of 7 to 9, especially at high concentration. The report of the pH effects on adsorption or desorption of boric acid on ion-exchange resin by Maeda and his coworkers (11) implied this tendency.

Boron within the Resin

Polyborate reactions within the resin may obey similar restrictions to those in solution [Barbier et al. (12), Kakihana et al. (13), Tomizawa (2, 3, 14); and

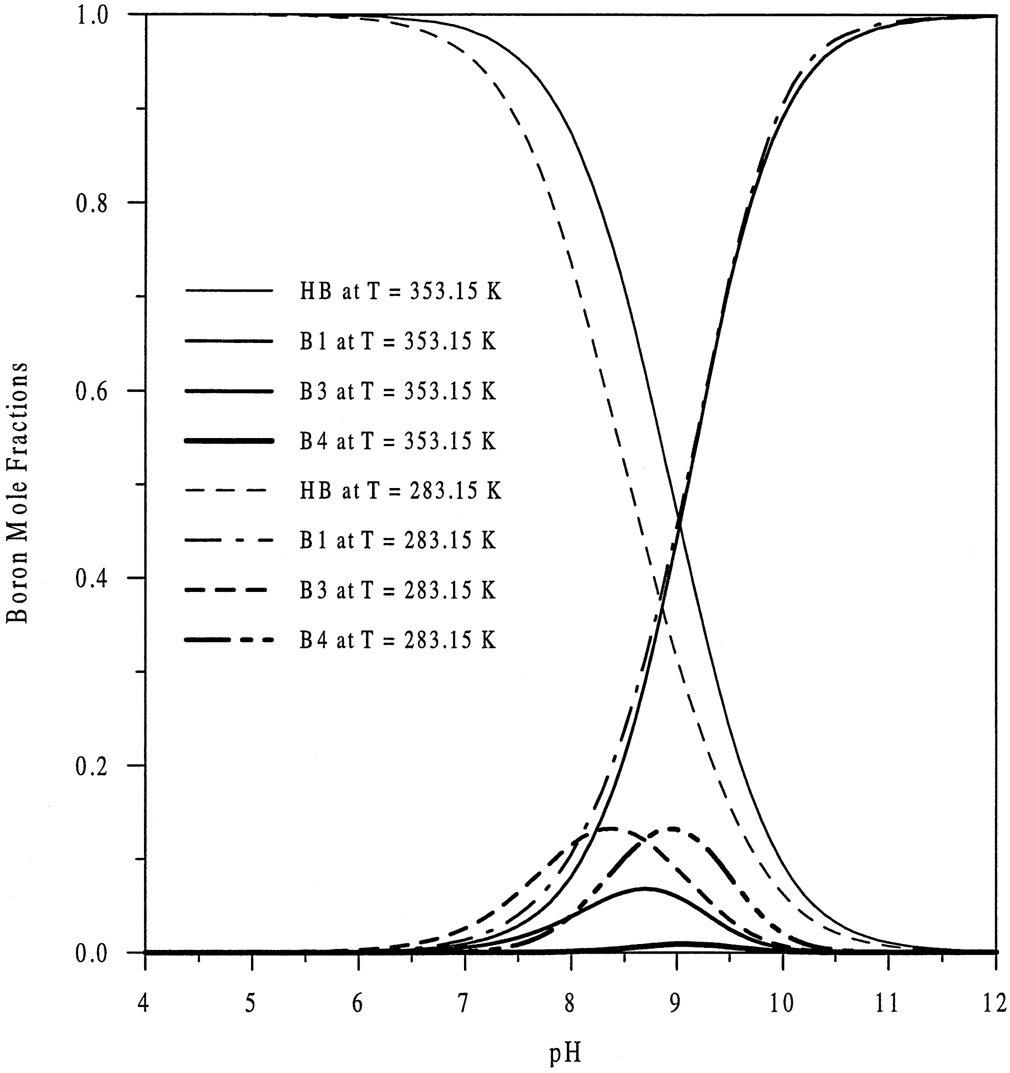

FIG. 1 Distribution of boron forms in solution as a function of boron concentration, temperature, and pH. [HB = H_3BO_3, B1 = $B(OH)_4^-$, B2 = $B_2(OH)_7^-$, B3 = $B_3(OH)_{10}^-$, B4 = $B_4(OH)_{14}^{2-}$], Boron concentration is 0.0925 M.

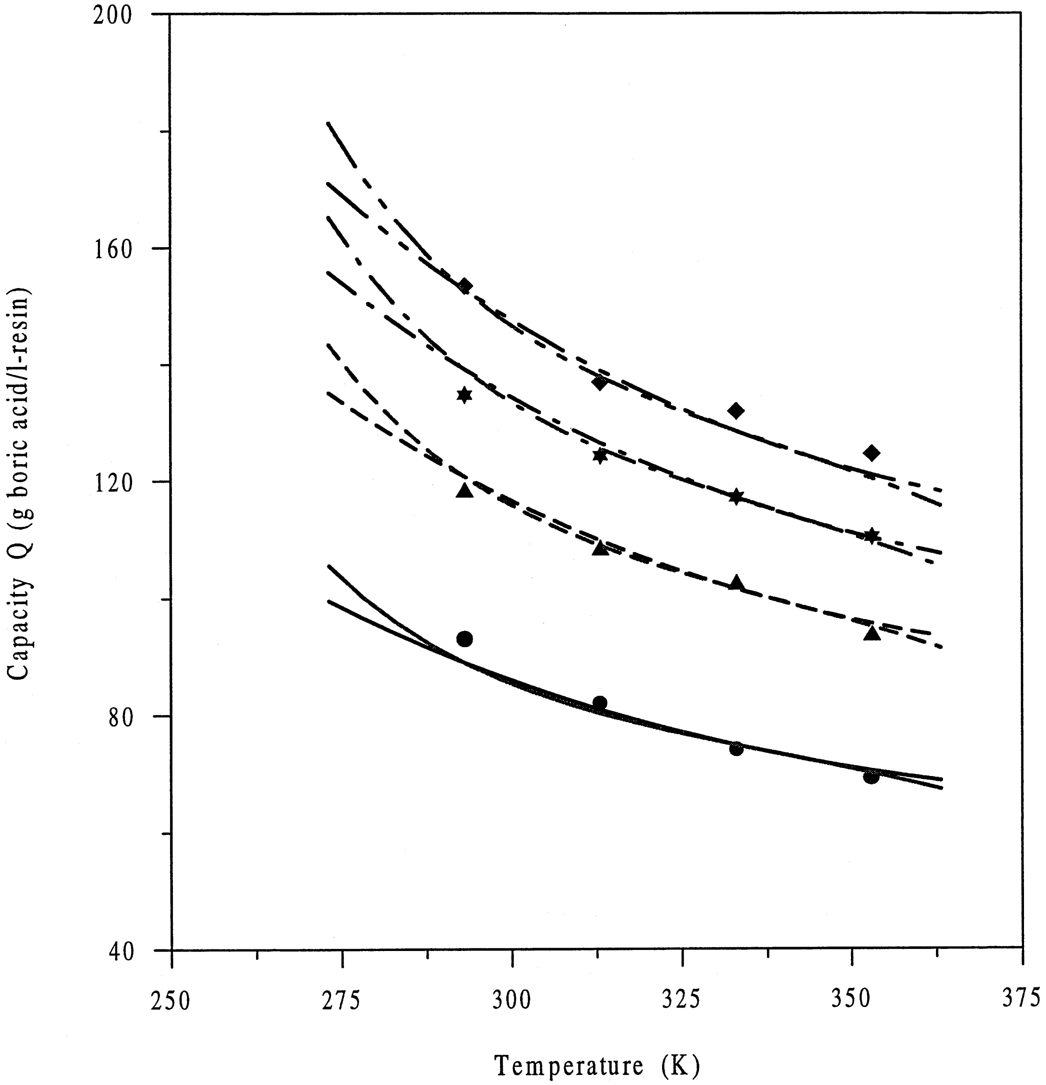

FIG. 2 Comparison of regression results for Diaion SA10A from Eqs. (27) and (28). Solution concentrations of 1.0, 3.0, 5.0, and 7.0 g/L are represented by line groups from bottom to top, respectively. Experimental data are presented by discrete, solid symbols.

Miera et al. (15)]. Within the resin, pH and the electrical field strength are relatively high, which favors boric acid ionization. As boron concentration increases within the resin, pH decreases and conditions are more favorable for the formation of hydroxy polyborates. Results by Dobrevsky and Konova (4), Perie et al. (16), and Na (5) verified the presence of hydroxy polyborates.

Miera and his coworkers (14) suggested the following reaction steps to indicate the possible polyborate species inside the resin, and they account for boron atom fixation on an active site. Dissociation of boric acid inside the resin, and exchange on the active site:

$$B(OH)_3 + OH^- \rightarrow B(OH)_4^- \quad (5)$$

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at the same site, reactions indicated by Eqs. (1) and (6):

$$2B(OH)_3 + B_3O_3(OH)_4^- \Leftrightarrow B_5O_6(OH)_4^- + 3H_2O \tag{6}$$

may take place as concentration increases. They did not considered divalent polyborate formation [as $B_3O_3(OH)_5^{2-}$ and $B_3O_5(OH)_4^{2-}$] inside the resin due to the requirement for an excess of OH^- in these reactions.

The studies of boric acid solution equilibrium indicate that as temperature decreases the polyborate concentrations with more boron atoms increase, and that their peak concentrations appear at higher pH. The distribution—varying with temperature and concentration—of boron inside the resin is postulated as follows:

- At a given temperature, orthoborate $B(OH)_4^-$ is the major boron species inside the resin at the beginning of sorption. As total boron concentration increases, orthoborate decreases.
- Multivalent polyborates are less likely inside the resin, but may appear at the early stage of sorption due to high hydroxide concentration.
- Of polyborates, ring-type polyborates [primarily $B_3O_3(OH)_4^-$] are more likely inside the resin as concentration inside the resin increases due to their stable structure.
- As temperature increases, polyborates convert rapidly to $B(OH)_4^-$ depending on solution concentration and pH within the resin.

DERIVATION OF CORRELATION

Assuming that the possible reactions within the resin are represented by

$$\gamma B(OH)_3 + \xi OH^- \xleftrightarrow{K_\mathrm{i}} B_\gamma(OH)^{\xi-}_{\xi+3\gamma} \tag{7}$$

The total resin capacity is

$$Q = \sum \bar{C}_{B_n} = \bar{C}_{\mathrm{Br},\gamma} \tag{8}$$

where n is the number of boron atoms for the ith polyborate; B indicates borate with a single boron atom; B_n is the borate with n boron atoms; and $B_{r,\gamma}$ is a pseudospecies as the representative polyborate with average boron atoms γ. According to Eq. (7), the concentration of the pseudospecies can be expressed as

$$\bar{C}_{\mathrm{r},\gamma} \propto K_\mathrm{r} \bar{C}^{\gamma}_{B(OH)_3} \tag{9}$$

and

$$Q = \beta K_\mathrm{r} \bar{C}^{\gamma}_{B(OH)_3} \tag{10}$$

where K_r is the overall reaction equilibrium constant and β is a proportionality coefficient. The relationships between K_r and temperature, and between boron concentration within the resin $\overline{C}^{\gamma}_{B(OH)_3}$ and the liquid $\overline{C}_{B(OH)_3}$, must be determined.

Temperature Effects

The effects of temperature on the reaction equilibrium constant can be described by the change of Gibbs' energy:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) \tag{11}$$

Suppose there are m reactions occurring inside the resin to form polyborates. Applying Eq. (11) to each reaction:

$$K_i = \exp\left(-\frac{\Delta G^\circ_i}{RT}\right) \tag{12}$$

and summing gives

$$K_r = \prod_{i=1}^{m} K_i = \exp\left(-\frac{\sum_{i=1}^{m} \Delta G^\circ_i}{RT}\right) = \exp\left(-\frac{\Delta G^\circ_r}{RT}\right) \tag{13}$$

The dependence of ΔG° on temperature T may be expressed as

$$\frac{d(\Delta G^\circ/RT)}{dT} = \frac{-\Delta H^\circ}{RT^2} \tag{14}$$

Therefore, the effect of temperature on the equilibrium constant can be given by

$$\frac{d \ln K_r}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{15}$$

If the temperature dependence of ΔH°, the standard enthalpy change of reaction, is approximately given by

$$\Delta H^\circ = \int \Delta C^\circ_p dT + I_1 = \int (a_0 + b_0 T + c_0 T^2) dT + I_1 \tag{16}$$

in which I_1 is the integration constant. Substitute Eq. (16) into Eq. (15), integrate, and rearrange to give

$$K_r = a^0_1 T^{a_2} \exp[a_3 T^{-1} + a_4 T + a_5 T^2] \tag{17}$$

Therefore, the capacity will be

$$Q = \alpha_1^* \overline{C}_{\mathrm{B}}^{\gamma} \cdot T^{a_2} \exp[a_3 T^{-1} + a_4 T + a_5 T^2] \tag{18}$$

For constant temperature, if the standard entropy change of reaction is negligible, we may use the standard enthalpy change of reaction approximately to replace the change in standard Gibbs energy. The temperature dependence of the representative equilibrium constant of reaction K_{r} reduces to

$$K_{\mathrm{r}} = b_1^0 \cdot \exp[-(b_2^0 T + b_3^0 T^2)] \tag{19}$$

where b_i^0 is a proportional constant at a given concentration, and reflects the reaction characteristics and the effects of adsorption on a given resin. Therefore, the resin capacity may be approximately expressed as

$$Q = b_1' \overline{C}_{\mathrm{B}}^{\gamma} \cdot \exp[-(b_2^0 T + b_3^0 T^2)] \tag{20}$$

Concentration Effects

Because the reactions in both the solution and resin phases occur rapidly, diffusion is the controlling step for the rate of boron sorption or desorption. At constant temperature the increase of boron concentration inside the resin can be described by the particle rate:

$$\frac{d\overline{C}_{\mathrm{Br},\gamma}}{dt} = -a_{\mathrm{s}} \sum D_i \frac{dC_{\mathrm{B}i}}{dr} \tag{21}$$

From related reactions in solution, based on the stoichiometry:

$$C_{\mathrm{B}m} = f(C_{\mathrm{B(OH)_3}}^{m}) \tag{22}$$

A similar way to handle boron concentration inside the resin is to define a pseudospecies in solution with concentration $C_{\mathrm{Br},m}$, equivalent, in terms of boron, to that of all these species containing boron in Eq. (21). By referencing Eq. (22),

$$\frac{d\overline{C}_{\mathrm{Br},\gamma}}{dt} = -\lambda_0 a_{\mathrm{s}} D_{\mathrm{er}} \frac{dC_{\mathrm{Br},m}}{dr} = -\lambda_1 D_{\mathrm{er}} \frac{dC_{\mathrm{B(OH)_3}}^{m}}{dr} \tag{23}$$

where D_{er} is the effective diffusivity of the pseudospecies and λ_i is the proportionality constant at a certain temperature. With the assumptions of a linear driving force and negligible interfacial concentration, Eq. (23) can be expressed approximately as

$$\frac{d\overline{C}_{\mathrm{Br},\gamma}}{dt} = \lambda_2 k_{\mathrm{er}} C_{\mathrm{B(OH)_3}}^{m} \tag{24}$$

where k_{er} is the mass-transfer coefficient of the representative species with m boron atoms. Integrating Eq. (24), ignoring the equilibrium concentration at the end of sorption, and replacing concentration by the initial concentration at zero time gives

$$\overline{C}_{\mathrm{Br},n} = \lambda_3 C^{\eta}_{\mathrm{B(OH)}_3,f} \tag{25}$$

or

$$\overline{C}^{\gamma}_{\mathrm{B(OH)}_3} = \lambda^* C^{\eta}_{\mathrm{B(OH)}_3,f} \tag{26}$$

where $C_{\mathrm{B(OH)3,f}}$ is the boric acid feed concentration, λ_i and λ^* are proportional constants at a given temperature, and η is the exponent of the boric acid feed concentration accounting for interactions among these species in the solution.

For a given resin the dependence of the equilibrium capacity on boron concentration and temperature can be obtained by substituting Eq. (26) into Eq. (18) or (20) and rearranging:

$$Q = a_1 \cdot C^{\eta}_{\mathrm{B(OH)}_3,f} \cdot T^{a_2} \exp[a_3 T^{-1} + a_4 T + a_5 T^2] \tag{27}$$

or

$$Q = b_1 \cdot C^{\eta}_{\mathrm{B(OH)}_3,f} \cdot \exp[-(b_2 T + b_3 T^2)] \tag{28}$$

where the parameters a_i, b_i, and η are determined experimentally.

Determination of Parameters

Either Eq. (27) or Eq. (28) is a nonlinear algebraic equation whose parameters may be determined by the method of nonlinear least squares. This method requires an initial guess of each parameter. Fortunately, to improve initial guesses, the nonlinear equation can be linearized with respect to the parameters by taking the logarithm of both sides in the equation. For example, the linearization of Eq. (28) may be proceeded as

$$\ln Q = \ln b_1 + \eta \ln C_{\mathrm{B(OH)}_3,f} - (b_2 T + b_3 T^2) \tag{29}$$

or

$$y = A_1 + A_2 \ln C_{(\mathrm{OH})_3,f} - (A_3 T + A_4 T^2) \tag{30}$$

in which

$$y = \ln Q; \qquad A_1 = \ln b_1; \qquad A_2 = \eta;$$
$$A_3 = b_2; \qquad A_4 = b_3$$

Equation (30) shows that the dependence of y on parameters A_i is linear. In a similar way the linearized version of Equation (27) may be expressed as

TABLE 1
Parameter Values in Eq. (30)

Resin types	A_1	A_2	A_3	A_4
Amberlite IRN78LC	5.06	0.286	-3.04×10^{-3}	1.45×10^{-5}
Diaion PA306	4.28	0.316	-1.79×10^{-4}	5.28×10^{-6}
Diaion PA308	7.85	0.308	0.0202	-2.59×10^{-5}
Diaion PA312	5.02	0.264	-4.15×10^{-4}	6.60×10^{-6}
Diaion PA316	8.33	0.263	0.0203	-2.56×10^{-5}
Diaion PA318	5.72	0.246	0.0481	-1.51×10^{-6}
Diaion SA10A	7.88	0.278	0.0180	-2.18×10^{-5}

$$y = A_1^* + A_2^* \ln C_{\mathrm{B(OH)_3},f} + A_3^* + A_4^* T^{-1} + A_5^* T + A_6^* T^2 \qquad (31)$$

Results from both the linearized version (Eq. 30) and the original nonlinear form (Eq. 28) are given in Tables 1 and 2 for comparison.

In addition, this model is two-dimensional since y or Q depends on two independent variables—the feed concentration $C_{\mathrm{B(OH)_3,f}}$ and temperature T. Each data point corresponds to a value of y, T, and $C_{\mathrm{B(OH)_3,f}}$. In order to minimize error in the unknown parameters in Eqs. (27), (28), (30), and (31), a method of multiple regression is applied.

RESULTS

A comparison of Eqs. (27) and (28) for Diaion SA10A resin is given in Fig. 2. Results indicate that both forms work well, though Eq. (27) is more sound theoretically while Eq. (28) is more easily manipulated. We thus limit the presentation and interpretation of results to discussion with Eq. (28).

Tables 1 and 2 list some commercial anion resins and the corresponding values of the parameters in Eqs. (30) and (28), respectively. The data used to obtain these parameters were reported by Peterka (1) and Na (5). The boric

TABLE 2
Parameter Values in Eq. (28)

Resin types	η	b_1 (1/L-resin)	b_2 $(1/K)$	b_3 (K^{-2})
Amberlite IRN78LC	0.291	6.30×10^{2}	5.99×10^{-3}	-4.55×10^{-8}
Diaion PA306	0.321	4.34×10	-3.16×10^{-3}	9.68×10^{-6}
Diaion PA308	0.302	1.08×10^{3}	0.0149	-1.78×10^{-5}
Diaion PA312	0.262	9.10×10	-3.39×10^{-3}	1.09×10^{-5}
Diaion PA316	0.259	2.27×10^{3}	0.0167	-2.03×10^{-5}
Diaion PA318	0.249	3.31×10^{2}	0.0545	-2.65×10^{-6}
Diaion SA10A	0.282	4.80×10^{3}	0.0219	-2.80×10^{-5}

acid concentration range was about 1 to 10 g/L (0.0162 to 0.162 mol/L as boron) and the experimental temperature range was 10–80°C.

Errors in Q predicted by the multiple nonlinear regression method are acceptable. The minimized errors by the sum of squared residuals for Eq. (30), defined in Eq. (32), are order of magnitude 10^{-4}.

$$\text{Error} = \frac{\sum_{i=1}^{N}[y_i - (A_1 + A_2 \ln C_i - A_3 T_i - A_4 T_i^2)]^2}{N - P} \tag{32}$$

The standard deviation for Eq. (28), is defined as

$$\text{SD} = \left\{ \frac{\sum_{i=1}^{N}[Q_{\exp} - Q_{\text{pred}}]^2}{N - P} \right\}^{\frac{1}{2}} \tag{33}$$

with about 10^0 order of magnitude. The average and maximum relative errors, defined in Eqs. (34) and (35), are

$$\text{Average error of } Q = \frac{1}{N} \cdot \left| \sum_{i=1}^{N} \frac{Q_{i,\exp} - Q_{i,\text{pred}}}{Q_{i,\exp}} \right| \times 100\% \tag{34}$$

$$\text{Maximum error of } Q = \max \left| \frac{Q_{i,\exp} - Q_{i,\text{pred}}}{Q_{i,\exp}} \right| \times 100\% \tag{35}$$

about 1.0×10^{-2} and 5.0×10^{-2}%, respectively. The error values for different resins are given in Tables 3 and 4.

TABLE 3
Minimized Errors and Maximum Errors by Eq. (30)

Resin types	Number of date points N	Minimized errors of y	Maximum errors of y	Maximum errors % of Q
Amberlite IRN78LC	20	3.65×10^{-4}	4.74×10^{-2}	4.63
Diaion PA306	20	5.20×10^{-4}	3.91×10^{-2}	3.84
Diaion PA308	20	5.31×10^{-4}	5.11×10^{-2}	4.98
Diaion PA312	20	5.10×10^{-4}	4.16×10^{-2}	4.07
Diaion PA316	20	4.96×10^{-4}	4.64×10^{-2}	4.53
Diaion PA318	20	5.09×10^{-4}	3.42×10^{-2}	3.36
Diaion SA10A	20	4.18×10^{-4}	4.34×10^{-2}	4.25

TABLE 4
Standard Deviation and Relative Errors by Eq. (28)

Resin types	Number of date points *N*	Standard deviation	Average errors %	Maximum errors %
Amberlite IRN78LC	20	9.08	1.29	5.38
Diaion PA306	20	2.42	1.78	4.11
Diaion PA308	20	3.20	1.70	4.83
Diaion PA312	20	5.97	1.59	4.51
Diaion PA316	20	5.31	1.46	5.91
Diaion PA318	20	5.83	1.74	3.91
Diaion SA10A	20	7.20	1.74	5.29

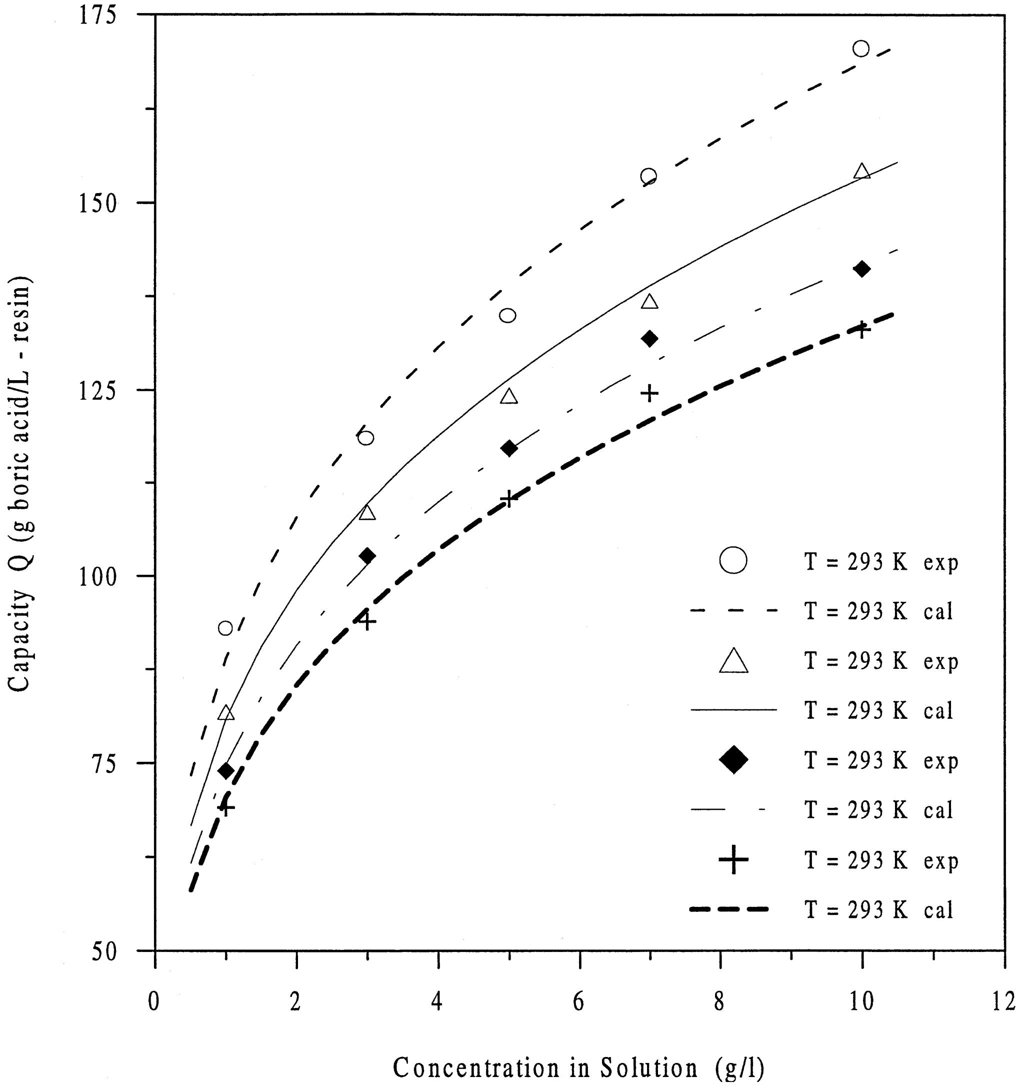

FIG. 3 Data correlation of boron solution concentration and sorption capacity of Diaion SA10A resin.

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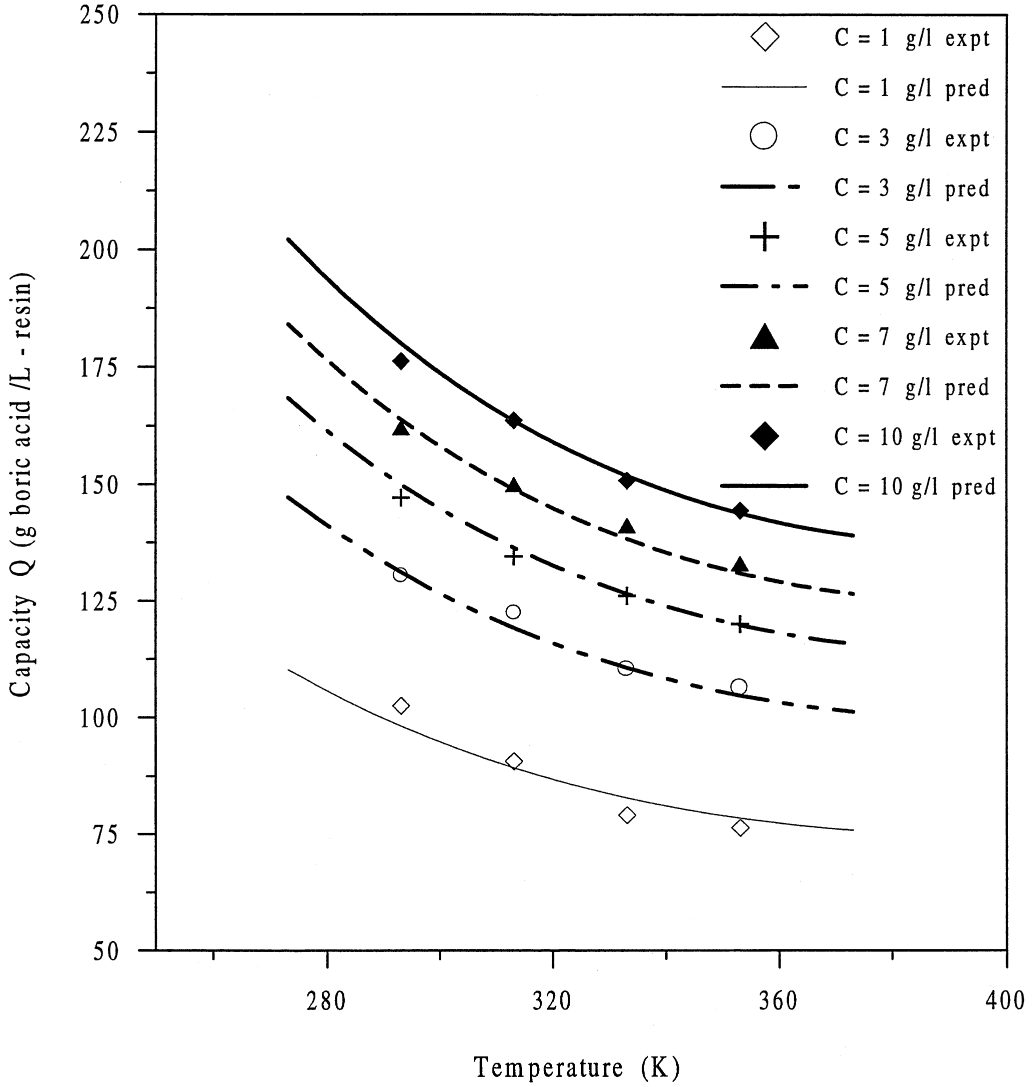

FIG. 4 Data correlation for temperature on boron sorption capacity of Diaion PA316 resin.

Results calculated from Eq. (28) are plotted in Figs. 3 and 4 for the following anionic resins: Diaion SA10A and Diaion PA316. Data are given in these figures for comparison. We also used this equation to predict resin capacity with comparison to the data from Na (5) for Amberlite IRN78LC, which is presented in Fig. 5. The curves reflect the temperature and concentration effects on boron equilibrium capacity. As expected, resin equilibrium capacity increases with increasing boron solution concentration and decreasing temperature.

DISCUSSIONS

The correlation, derived from the change of Gibbs' energy, gives the familiar exponential (Arrhenius) dependence (Eq. 28) of equilibrium capacity

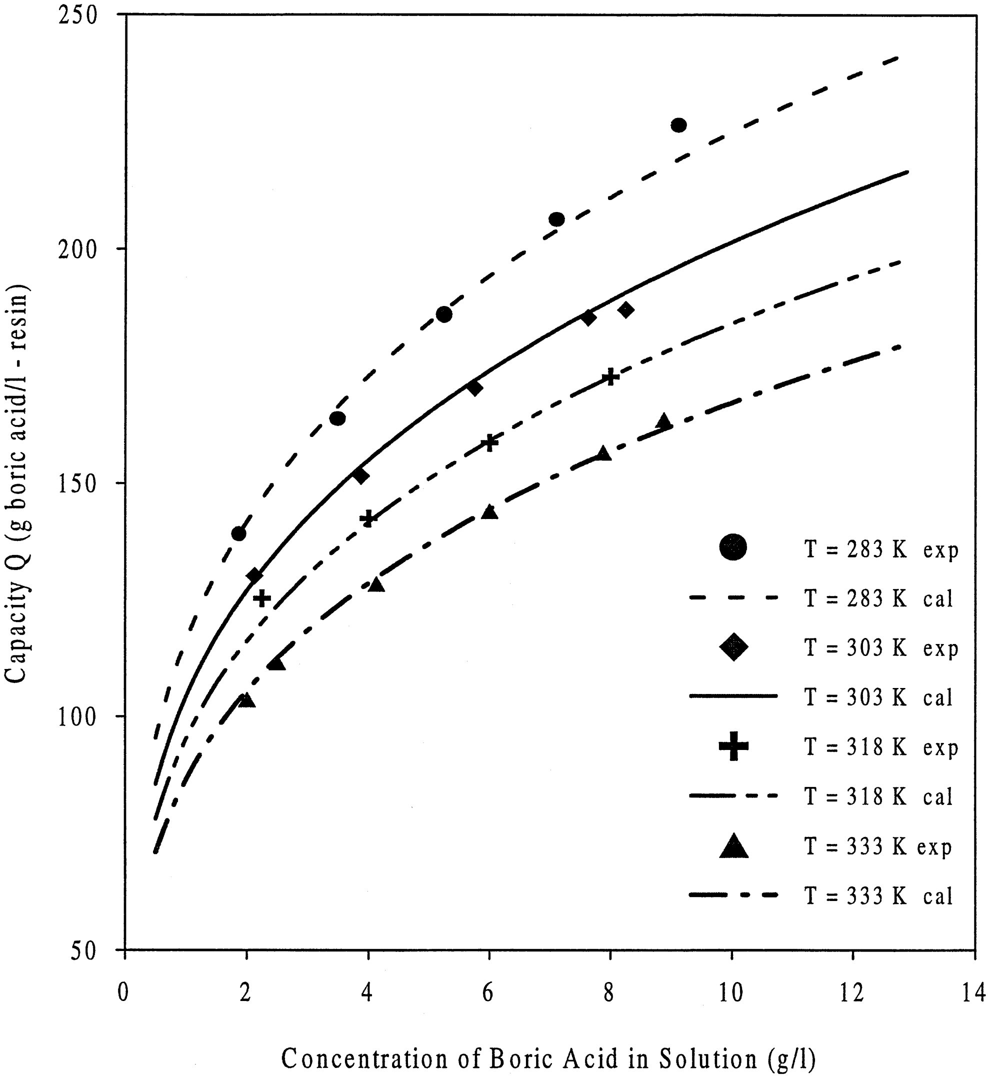

FIG. 5 Data correlation for temperature on boron sorption capacity of Amberlite IRN78 LC resin.

on absolute temperature at constant concentration. The exponential term indicates that only a part of the reaction leads to an increase in equilibrium capacity. In other words, there must be some reversible reactions reflecting local unfavorable conditions for polyborate formation. At constant temperature the relationship between equilibrium capacity and boric acid concentration shows Freundlich-type adsorption. In this isotherm the exponential η is less than 1, which indicates favorable equilibrium toward boron sorption on the ion-exchange resin. The proportionality constant b_1 accounts for resin characteristic effects—such as the minimum capacity and selectivity, the intraparticle resistance to mass transfer, and the relation between crosslinking and resin swelling—on equilibrium capacity. In addition, this parameter reflects the effects of the liquid side conditions, such as the boron concentration gradient and diffusion resistance on equilibrium capacity.

Results presented in Table 2 and Figs. 2–6 show that the proposed equations match experimental data quite well. The parameter values vary among resin because of differences in

- Their minimum total capacities and selectivity.
- Functional groups, which result in various bond forces with borates so that there are different effects on possible reactions and the replacement of borates.
- The degrees of swelling and structures which result in the overall resistance to boric acid and borates transfer, etc.

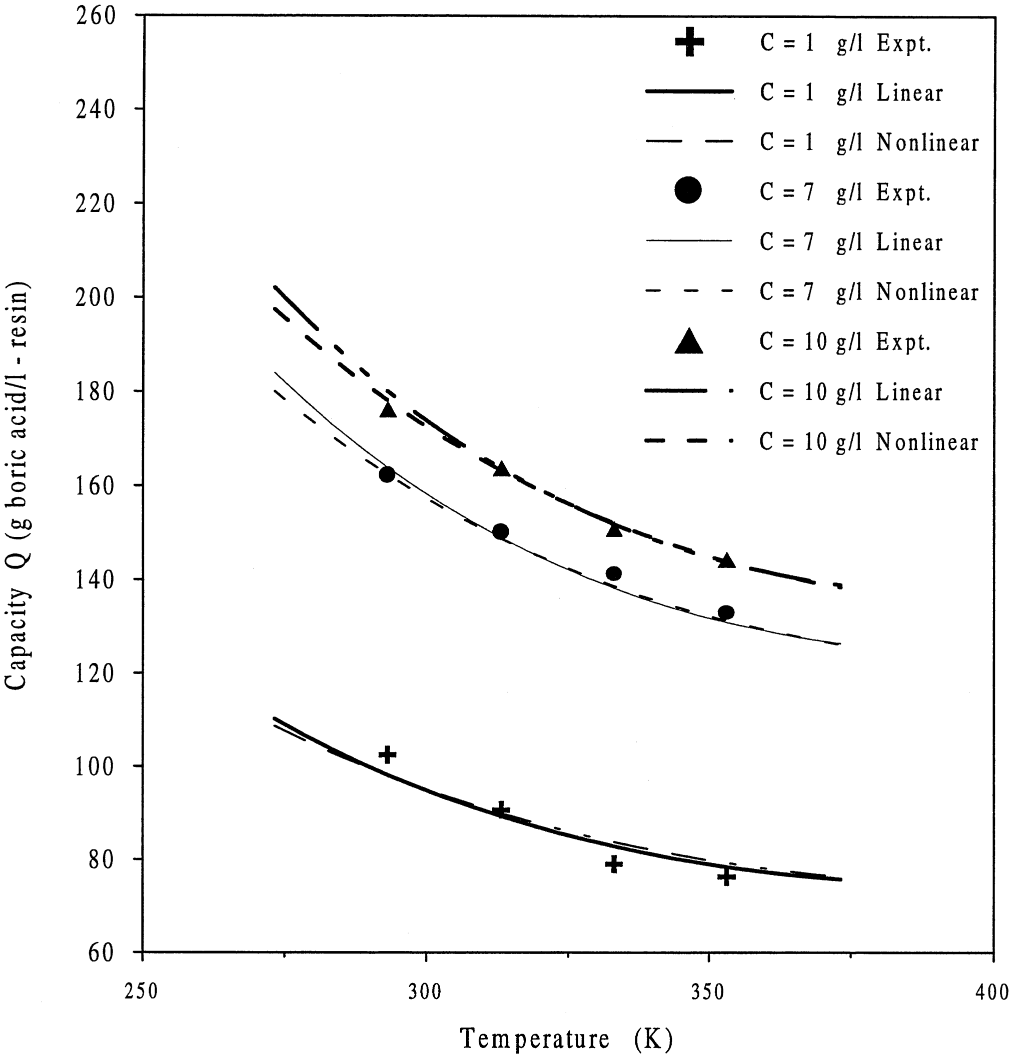

FIG. 6 Linear and nonlinear regression of Diaion PA316 resin data under boric acid solution concentrations of 1.0, 7.0, and 10.0 g/L.

Tables 3 and 4 give error ranges for resins correlated using Eqs. (30) and (28), respectively. Both linear and nonlinear regression forms work well. The original nonlinear form (Eq. 28), however, gives better match at higher concentration and lower temperature (top curves), which is a more accurate reflection of the conditions used to derive the model. Comparison of these two forms with experimental data is given in Fig. 6. The use of either linear or nonlinear form is chosen by convenience.

The increase in resin capacity for boron sorption is due to the formation of polyborates in the bulk liquid and inside the resin. According to Eq. (8), the degree of polyborate formation inside the resin is limited, under a constant temperature, by the supply of boric acid or monoborate, which is related directly to the mass transfer process and rate. In addition, the transport of polyborates from the bulk liquid is restricted by intraparticle diffusion resistance. In this way the resin crosslinkage influences the boron sorption equilibrium capacity, which is accounted for in the parameter b_1 in Eq. (28).

The relation between the parameter b_1 and crosslinkage may be written as

$$\ln b_1 = b' + b'' \ln z - b''' z^{0.5} \tag{36}$$

where z indicates the crosslinkage, and b', b'', and b''' are constants, reflecting the effect of crosslinkage on swelling, selectivity, and intraparticle diffusion resistant. These constants are determined by experimental data for a given resin type. The second and third terms on the right side of Eq. (36) account for the effects of crosslinkage on resin selectivity and swelling, respectively. Combining Eqs. (36) and (28) gives the relationship between equilibrium capacity Q and initial boric acid concentration C_B, temperature T, and resin crosslinkage z, that is:

$$Q = b_1^* C_\mathrm{B}^{b_2^*} z^{b_3^*} \exp[-(b_4^* T + b_5^* T^2 + b_6^* z^{0.5})] \tag{37}$$

the linearized expression of Eq. (37) is

$$y^* = c_1 + c_2 \ln C_\mathrm{B} + c_3 \ln z - c_4 T - c_5 T^2 - c_6 z^{0.5} \tag{38}$$

where

$$y^* = \ln Q; \qquad c_1 = \ln b_1^*; \qquad c_2 = b_2^*;$$
$$c_3 = b_3^*; \qquad c_4 = b_4^*; \qquad c_5 = b_5^*;$$
$$c_6 = b_6^*$$

The form of Eq. (38) is easily regressed to obtain these parameters. The results for Diaion PA300 series porous-type resins are given in Table 5.

The maximum relative error for Q in Eq. (38) is about 16%. Comparison of experimental data and the Eq. (38) prediction is given in Fig. 7. Equation (38) does not work as well as Eqs. (28) and (30), but does reveal the equilibrium capacity tendency with crosslinkage and shows the maximum equilibrium capacity at a resin crosslinkage of 7%, consistent with experimental observation of Peterka (1).

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TABLE 5
Regression Results of Parameters in Eq. (38)

Resin type	c_1	c_2	c_3	c_4	c_5	c_6
Diaion PA300	26.5	4.27	0.279	8.94×10^{-2}	28.22×10^{-5}	32.8

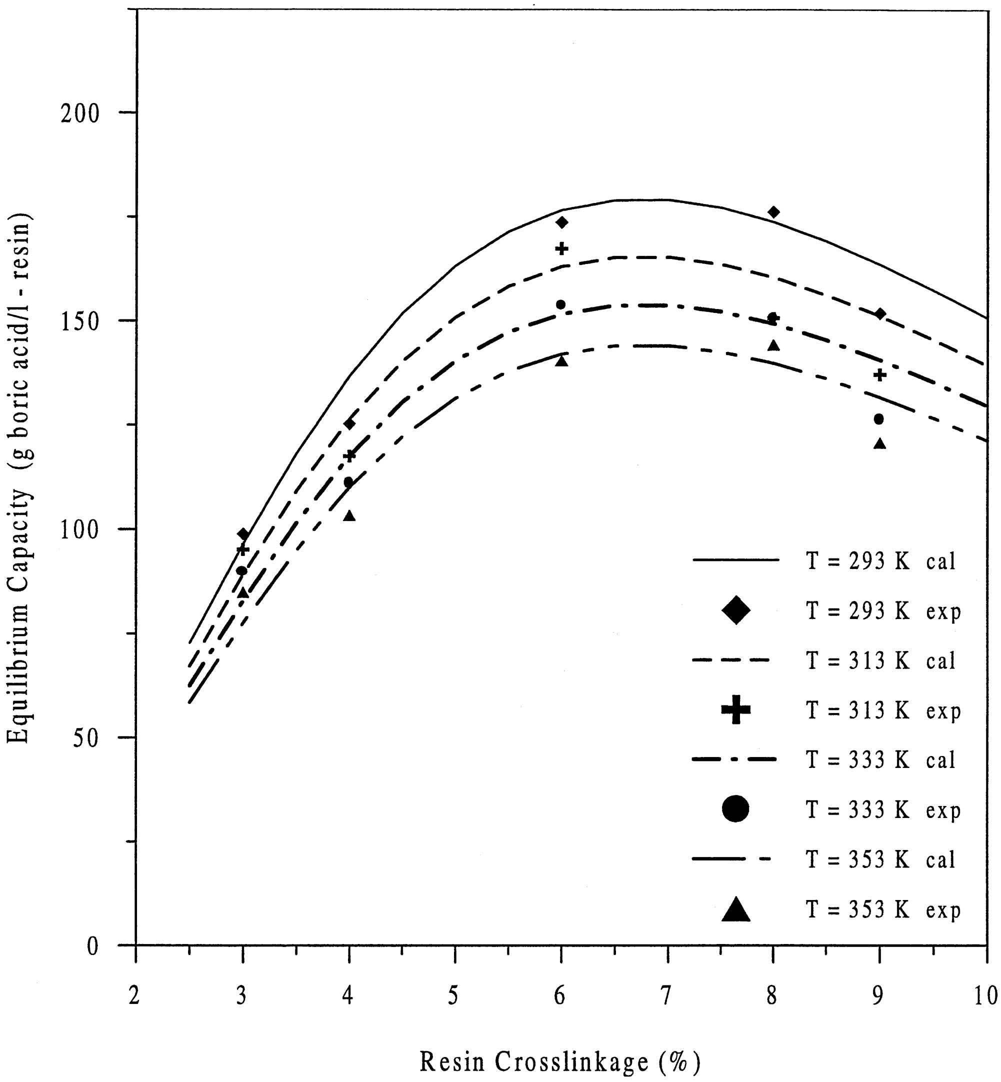

FIG. 7 Comparison of data with Eq. (35) for capacity of Diaion PA300 resin with a boric acid concentration of 10 g/L.

CONCLUSIONS

A satisfactory relationship among sorption capacities of strong-base anion resins with temperature, concentration, and resin crosslinkage is presented. Parameter values have been determined for five porous-type Diaion PA300 series resins, gel-type Diaion SA10A, and Amberlite IRN78LC. Model predictions compared with experimental data from different sources are quite good.

Equations (28), (30), and (38) can be applied conveniently, based on influent concentration, to estimate the ion-exchange limitation of column or batch operations under various operation conditions. This correlation can be used to obtain the interfacial boron concentration for rate models using bulk liquid concentrations. This approach can also be used for equilibrium models; however, we recommend using Eq. (27) for this purpose.

These correlating forms are particularly applicable in the nuclear power industry, where boron sorption and desorption are important in the boron thermal regeneration system and coolant demineralization processes. For these applications the recommended operating conditions are 10–80°C with boron concentrations from 0.00925 to 0.185 mol/L.

NOTATION

a_i	parameters in correlation
a_s	specific area of resin ($\mathrm{cm^2/cm^3}$)
b_i	parameters in correlation
A_i	parameters in correlation
C_i	concentration of *i*th species in solution (g/L)
C_i	concentration of *i*th species in resin (g/L dry resin)
D_er	effective diffusivity of pseudospecies ($\mathrm{cm^2/s}$)
D_i	self-diffusivity of *i*th species ($\mathrm{cm^2/s}$)
G	Gibbs' energy (J)
H	heat (J)
k_er	mass transfer coefficient of pseudoborate (cm/s)
K_i	equilibrium constant of reaction
N	total number of data points
P	total number of parameters
Q	resin equilibrium capacity (g/L dry resin)
$Q_{i,\mathrm{exp}}$	resin capacity measured from experiment (g/L dry resin)
$Q_{i,\mathrm{pred}}$	resin capacity calculated from correlation (g/L dry resin)
R	gas constant (J/mol/K)
T	temperature (K)
z	resin crosslinkage

Greek Symbols

α	intermediate parameter in derivation
β	intermediate parameter in derivation
η	exponential of boron solution concentration
λ	intermediate parameter in derivation

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