

## INFLUENCE OF SOIL SOLUTION SALINITY ON BORON ADSORPTION BY SOILS

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**Boron (B) adsorption on two arid-zone soils from the San Joaquin Valley of California was investigated as a function of equilibrium solution B concentration (0–250 mg L<sup>-1</sup>), solution pH (3–12), and electrical conductivity (EC, 0.3 or 7.8 dS m<sup>-1</sup>). Boron adsorption on both soils increased with increasing pH, reached a maximum near pH 9, and decreased with further increases in pH. Boron adsorption as a function of solution pH was independent of solution salinity from pH 3 to 9. Above pH 9, B adsorption was increased from the solution of higher EC. Boron adsorption for both soils as a function of solution B concentration conformed to the Langmuir adsorption isotherm equation. The B adsorption maxima obtained with the Langmuir equation for both EC were not statistically significantly different at the 95% level of confidence. The constant capacitance model, a surface complexation model, was able to describe B adsorption as a function of solution B concentration and solution pH. Boron adsorption was predicted using the soil chemical properties surface area, organic carbon content, inorganic carbon content, and aluminum oxide content. The predictions are suitable for transport modeling and will be used to describe B movement in large soil columns. Our results are advantageous because they indicate that under agricultural conditions (pH 3–9), B adsorption can be described without consideration of changes in soil solution salinity. (Soil Science 2008;173:368–374)**

**Key words:** Constant capacitance model, electrical conductivity, surface complexation model.

**B**ORON (B) is an important micronutrient element in crop production. The soil solution B concentration range between plant deficiency and toxicity symptoms is narrow (Reisenauer et al., 1973). Boron deficiency symptoms are observed in areas of plentiful rainfall because of low soil solution B concentrations and high amounts of leaching water. Boron deficiency is also more common in sandy soils (Keren and Bingham, 1985), where there is less adsorption of B as compared with high clay content soils. Plant B toxicity is observed in arid areas because of both high levels of B in the soil solution and application of high amounts of B via the irrigation water (Nable et al., 1997).

Both B deficiency and toxicity conditions decrease plant growth leading to marked yield reductions of crop plants and economic losses. Therefore, detailed knowledge of the fate and transport of B in soil and groundwater is required to understand and address a range of agricultural problems.

Adsorption sites on organic matter, oxide minerals, clay minerals, and carbonates act as sources and sinks for B in soils; B adsorbed on these solids equilibrates with solution B concentrations (Goldberg, 1993). Boron adsorbed on soil surfaces is neither directly available to nor perceived as toxic by plants (Keren et al., 1985). Plant availability of B is affected by a variety of factors including soil texture, soil moisture, soil temperature, soil salinity, and competing anion concentration (Goldberg, 1993).

Boron adsorption reactions by soil minerals and soils have generally been studied in single anion solutions or at most in the presence of

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Received Jan. 28, 2008; accepted Mar. 5, 2008.

DOI: 10.1097/SS.0b013e3181773a0e

one competing anion species. Some previous studies have evaluated the effect of competing chloride, nitrate, sulfate, phosphate, or silicate concentrations on B adsorption by clay minerals (Jasmund and Lindner, 1973; Goldberg and Glaubig, 1986; Goldberg et al., 1996) and soils (Bingham and Page, 1971; Schalscha et al., 1973; Goldberg et al., 1996). Chloride, nitrate, sulfate, or silicate concentrations equimolar to B concentrations had little effect on B adsorption by clays (Jasmund and Lindner, 1973; Goldberg and Glaubig, 1986; Goldberg et al., 1996), whereas equimolar phosphate concentrations considerably reduced B adsorption on kaolinite (Goldberg et al., 1996) and illite (Jasmund and Lindner, 1973). The effect of equimolar phosphate on B adsorption by montmorillonite was contradictory: adsorption was halved on Santa Rita montmorillonite (Jasmund and Lindner, 1973) and unaffected on Wyoming bentonite (Goldberg et al., 1996). Little competitive effect on B adsorption by soils was observed in the presence of sulfate, phosphate, silicate, and molybdate ions (Bingham and Page, 1971; Schalscha et al., 1973; Goldberg et al., 1996).

In natural systems, adsorption takes place from solutions of mixed electrolyte composition. The effect of salinity on B adsorption has been investigated for aluminum (Al) oxide (Choi and Chen, 1979) and clay minerals (Fleet, 1965; Couch and Grim, 1968; Keren and O'Connor, 1982). Boron adsorption by Al oxide as a function of solution pH was appreciably reduced when measured in one-third strength geothermal water (12% salinity) and one-third strength seawater (11% salinity) as compared with deionized distilled water (Choi and Chen, 1979). The effect of salinity on B adsorption was evident in the pH range 3 to 10. In contrast, B adsorption on the clay minerals illite (Couch and Grim, 1968), montmorillonite, and kaolinite increased with increasing salinity (Fleet, 1965) and increasing ionic strength (Keren and O'Connor, 1982). The effect of salinity on B adsorption by soils has not yet been evaluated.

Chemical models of B adsorption have more general predictive capability than empirical adsorption isotherm equations. This has been demonstrated in prior studies of B adsorption using the constant capacitance model (Goldberg et al., 2000, 2004, 2005). Prediction equations were developed that relate three surface complexation constants to the easily measured soil chemical parameters, surface area (SA), organic

carbon (OC) content, inorganic carbon (IOC) content, and free Al oxide content. The equations reliably predicted B adsorption as a function of solution pH with reasonable accuracy on 15 soils primarily from California (Goldberg et al., 2000) and B adsorption as a function of equilibrium solution B concentration on 22 Midwestern soils (Goldberg et al., 2004). These applications provided a completely independent evaluation of the predictive capability of the model to describe B adsorption by soils.

The purpose of this study is to evaluate the effect of mixed electrolyte solutions on B adsorption by soil samples that are being used in large soil columns to investigate B transport. The results will be described using the constant capacitance model. The ability of the model to predict B adsorption by these soil samples using the prediction equations of Goldberg et al. (2000) will be evaluated.

## MATERIALS AND METHODS

Boron adsorption was investigated using two surface soil samples (0–45 cm) obtained from section 4-2 of the Broadview Water District in the San Joaquin Valley of California. The soils were both classified as Lillis silty clay loam (very fine, smectitic, chromic, Halic Haploxerert) but differed in their clay content. These soils are being used in large soil columns to investigate B transport (Shouse et al., personal communication). Soil physical and chemical characteristics are listed in Table 1. Surface areas were measured using the ethylene glycol monoethyl ether adsorption method of Cihacek and Bremner (1979). Free Fe and Al oxides were extracted using the method of Coffin (1963). Iron and Al concentrations in the extracts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Organic carbon and IOC contents were quantified using a UIC Full Carbon System 150 with a carbon coulometer.<sup>1</sup>

Inorganic carbon was quantified using an acidification module and heating, total C was determined by combustion at 950 °C, and OC was determined by difference. A complete particle size distribution for the soil was obtained using the basic hydrometer method (Gee and Bauder, 1986) to determine the clay fraction.

<sup>1</sup>Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the product listed by the U.S. Department of Agriculture.

TABLE 1  
Characteristics of the soils

Soil	pH, 1:5 DDIW	Clay, %	SA, m <sup>2</sup> g <sup>-1</sup>	IOC, %	OC, %	Fe, %	Al, %
5/2002	8.15	48.9	168	0.245	0.76	1.13	0.0837
8/2002	8.12	35.4	173	0.245	0.72	1.16	0.0877

Boron adsorption experiments were carried out in batch systems to determine adsorption envelopes (amount of B adsorbed as a function of solution pH per fixed total B concentration) and adsorption isotherms (amount of B adsorbed as a function of equilibrium solution B concentration). For the B adsorption envelopes, 5 g of air-dried soil were added to 50-mL polypropylene centrifuge tubes and equilibrated with 25 mL of a mixed electrolyte solution on a reciprocating shaker for 20 h. The mixed electrolyte solutions had been prepared for the study of B movement in large soil column lysimeters (Shouse et al., personal communication), varied in B content and electrical conductivity (EC), and contained bromide as a conservative tracer. The chemical compositions of these solutions (also called tank waters) are presented in Table 2. The solutions had been adjusted to the desired pH range using 0.5 mL of a solution containing varying proportions of 1 M HCl, 1 M NaCl, and 1 M NaOH. The reaction temperature was 22.9 °C ± 0.1 °C. After the reaction, the samples were centrifuged, and the decantates were analyzed for pH, filtered, and analyzed for B, Na, Ca, K, Mg, and S concentrations using ICP-OES. Chloride was determined using the coulometric-ampereometric titration described by Cotlove et al. (1958). Bromide was analyzed using a Technicon Auto Analyzer II and the fluorescein method of Marti and Arozarena (1981). Boron release from the soils into 0.1 M NaCl electro-

lyte solutions was studied under identical experimental conditions as for the B adsorption envelope study. Boron adsorption values were corrected for B release at each solution pH. The total B present was corrected to account for the initial B content of the soil.

For the B adsorption isotherms, 200 g of soil were equilibrated with 110 mL of mixed electrolyte solution in 420 mL plastic containers. The containers were covered with snap-tight lids and equilibrated at 23.4 °C ± 0.1 °C for 18 h. The mixed electrolyte solutions consisted of 0.3, 1, 2, 5, 10, 15, 25, 50, 100, 150, 200, or 250 mg B L<sup>-1</sup> and were prepared using Tank 1 water: EC = 0.32 dS m<sup>-1</sup>, B = 0.309 mg L<sup>-1</sup> or Tank 4 water: EC = 7.9 dS m<sup>-1</sup>, B = 0.277 mg L<sup>-1</sup>. After equilibration, the soil pastes were transferred to funnels fitted with no. 50 Whatman<sup>1</sup> filter paper. The filtrate solutions were collected under vacuum and analyzed for B using ICP-OES. The amount of B adsorption was determined as the difference between the initial mixed electrolyte solution B concentration and the equilibrium B concentration. The Langmuir adsorption isotherm equation:

$$B_{ads} = \frac{KB_{eq}M}{1 + KB_{eq}} \quad (1)$$

where  $B_{ads}$  is the B adsorption (μmol g<sup>-1</sup>),  $B_{eq}$  is the equilibrium B concentration (mmol L<sup>-1</sup>),  $M$  is the maximum B adsorption (μmol g<sup>-1</sup>), and  $K$  is a parameter (L mmol<sup>-1</sup>), was fit to the B adsorption data.

TABLE 2  
Chemical constituents of the mixed electrolyte solutions

	pH	Cl <sup>-</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	B	Br <sup>-</sup>	EC
Tank 1	7.87	1.62	1.75	0.745	0.0415	0.729	0.078	1.41	0.309	17.9	0.32
Tank 2	7.85	1.59	1.71	0.757	0.0430	0.724	0.165	1.41	4.59	17.0	0.32
Tank 3	7.89	1.55	1.67	0.753	0.0395	0.706	0.0976	1.40	19.0	18.9	0.31
Tank 4	8.35	30.4	72.3	2.51	0.983	11.8	49.3	6.40	0.277	20.9	7.9
Tank 5	8.18	30.0	71.5	2.33	0.950	11.6	48.8	6.35	4.47	20.9	7.8
Tank 6	8.13	29.5	71.5	1.96	0.965	11.7	48.8	6.00	17.3	19.6	7.8

A detailed explanation of the theory and assumptions of the constant capacitance model of adsorption was provided by Goldberg (1992). In the present model application to B adsorption, three surface complexation reactions are considered:



where SOH, the surface functional group, represents both reactive surface hydroxyl groups on oxide minerals and aluminol groups on clay mineral edges in soils. Equilibrium constants for the surface complexation reactions are:

$$K_+(int) = \frac{[SOH_2^+]}{[SOH][H^+]} \exp(F\psi/RT) \quad (5)$$

$$K_-(int) = \frac{[SO^-][H^+]}{[SOH]} \exp(-F\psi/RT) \quad (6)$$

$$K_{B-}(int) = \frac{[SH_3BO_4^-][H^+]}{[SOH][H_3BO_3]} \exp(-F\psi/RT) \quad (7)$$

where square brackets indicate concentrations (mol L<sup>-1</sup>), *F* is the Faraday constant (C mol<sup>-1</sup>),  $\psi$  is the surface potential (V), *R* is the molar gas constant (J mol<sup>-1</sup> K<sup>-1</sup>), *T* is the absolute temperature (K), and the exponential terms represent solid-phase activity coefficients that correct for charges on the surface complexes. These reactions and equilibrium constants were previously considered in modeling and prediction of B adsorption envelopes (Goldberg et al., 2000) and isotherms (Goldberg et al., 2004) by diverse soils.

The computer code FITEQL 3.2 (Herbelin and Westall, 1996) uses a nonlinear least squares optimization routine to fit equilibrium constants to experimental data and contains the constant capacitance model of adsorption. As in prior studies (Goldberg et al., 2000, 2004), the FITEQL program was used to fit surface complexation constants to the experimental B adsorption data and to test the ability of the surface complexation constants calculated with the general regression model to predict B adsorption. The initial input parameter values were surface site density: *N* = 2.31 sites nm<sup>-2</sup> and capacitance: *C* = 1.06 F m<sup>-2</sup>. The general

regression model prediction equations for the surface complexation constants are (Goldberg et al., 2000):

$$\begin{aligned} \text{Log}K_{B-} = & -9.14 - 0.375 \ln(SA) \\ & + 0.167 \ln(OC) + 0.111 \ln(IOC) \\ & + 0.466 \ln(Al) \end{aligned} \quad (8)$$

$$\begin{aligned} \text{Log}K_+ = & 7.85 - 0.102 \ln(OC) \\ & - 0.198 \ln(IOC) - 0.622 \ln(Al) \end{aligned} \quad (9)$$

$$\begin{aligned} \text{Log}K_- = & -11.97 + 0.302 \ln(OC) \\ & + 0.0584 \ln(IOC) + 0.302 \ln(Al) \end{aligned} \quad (10)$$

where the units of surface area are km<sup>2</sup> kg<sup>-1</sup>, and units of OC, IOC, and Al are g kg<sup>-1</sup>. Surface complexation constants Log*K*<sub>B-</sub>, Log*K*<sub>+</sub>, and Log*K*<sub>-</sub> were calculated for each soil from the chemical properties SA, OC, IOC, and Al, and these equations. Using these predicted constants, B adsorption envelopes and isotherms were predicted for each soil and compared with

**Boron adsorption on BWTM 8/2002**

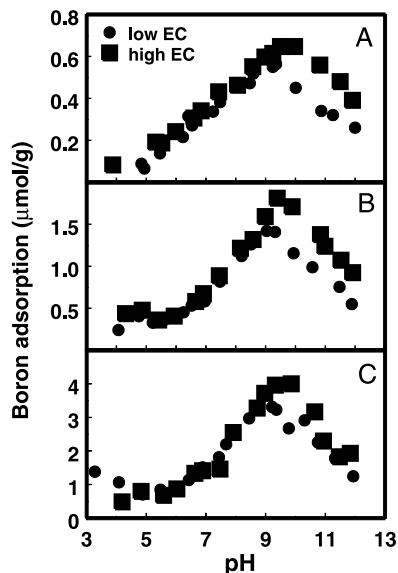


Fig. 1. Boron adsorption as a function of solution B concentration, pH, and EC. A, Low EC = 0.32 dS m<sup>-1</sup>, *B<sub>T</sub>* = 0.31 mg L<sup>-1</sup>; high EC = 7.9 dS m<sup>-1</sup>, *B<sub>T</sub>* = 0.28 mg L<sup>-1</sup>. B, Low EC = 0.32 dS m<sup>-1</sup>, *B<sub>T</sub>* = 4.6 mg L<sup>-1</sup>; high EC = 7.8 dS m<sup>-1</sup>, *B<sub>T</sub>* = 4.5 mg L<sup>-1</sup>. C, Low EC = 0.31 dS m<sup>-1</sup>, *B<sub>T</sub>* = 19.0 mg L<sup>-1</sup>, high EC = 7.8 dS m<sup>-1</sup>, *B<sub>T</sub>* = 17.3 mg L<sup>-1</sup>.

TABLE 3  
Surface complexation constants for the constant capacitance model

Soil	Optimized			From prediction equations		
	LogK <sub>B-</sub>	LogK <sub>+</sub>	LogK <sub>-</sub>	LogK <sub>B-</sub>	LogK <sub>+</sub>	LogK <sub>-</sub>
5/2002				-8.11	7.58	-11.36
Tank 1	-6.91	6.72	-10.09			
Tank 2	-7.30	6.84	-9.67			
Tank 3	-7.30	7.09	-9.27			
Tank 4	-6.59	6.90	-10.01			
Tank 5	-7.05	6.89	-9.87			
Tank 6	-7.74	6.69	-10.47			
8/2002	-7.25	6.87	-10.13	-8.11	7.56	-11.36
Mean	-7.16 ± 0.36	6.86 ± 0.13	-9.93 ± 0.38			

the experimentally determined B adsorption values.

## RESULTS AND DISCUSSION

Boron adsorption as a function of solution pH, solution B concentration, and salinity, EC, was determined for the two soil samples. Figure 1 presents the data for the 8/2002 soil. Boron adsorption envelopes on both soil samples

increased with increasing solution pH, reached an adsorption maximum near pH 9, and decreased with further increases in solution pH. This type of parabolic adsorption envelope is characteristic of B adsorption behavior on soils (Goldberg and Glaubig, 1986; Goldberg et al., 2000, 2005). Anion adsorption is maximal near the pK<sub>a</sub> of the acid (Hingston, 1981). Boron adsorption behavior by both soils was similar. The magnitude of B adsorption was independent of EC from pH 3 to 9. Above pH 9, B adsorption was greater for the high EC solution. These results would suggest that at agriculturally important soil solution pH, changes in salinity do not affect the extent of B adsorption.

The constant capacitance model was fit to the B adsorption envelopes of both soil samples

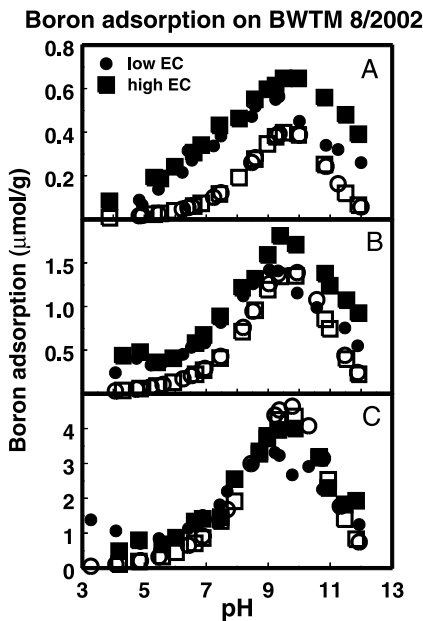


Fig. 2. Constant capacitance model prediction of B adsorption as a function of solution B concentration, pH, and EC. A, Low EC = 0.32 dS m<sup>-1</sup>, B<sub>T</sub> = 0.31 mg L<sup>-1</sup>; high EC = 7.9 dS m<sup>-1</sup>, B<sub>T</sub> = 0.28 mg L<sup>-1</sup>. B, Low EC = 0.32 dS m<sup>-1</sup>, B<sub>T</sub> = 4.6 mg L<sup>-1</sup>; high EC = 7.8 dS m<sup>-1</sup>, B<sub>T</sub> = 4.5 mg L<sup>-1</sup>. C, Low EC = 0.31 dS m<sup>-1</sup>, B<sub>T</sub> = 19.0 mg L<sup>-1</sup>; high EC = 7.8 dS m<sup>-1</sup>, B<sub>T</sub> = 17.3 mg L<sup>-1</sup>. Experimental data are represented by solid symbols. Model predictions are represented by open symbols.

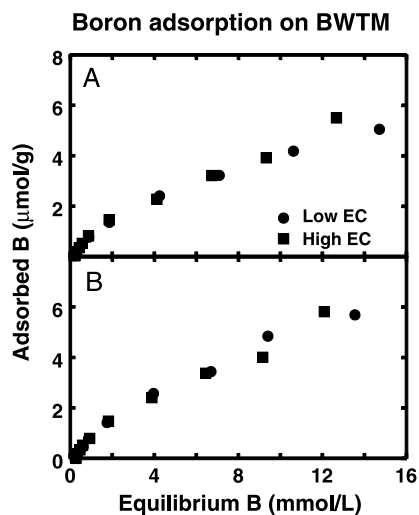


Fig. 3. Boron adsorption as a function of solution B concentration and EC. A, 5/2002 Soil, pH = 7.87 ± 0.08. B, 8/2002 Soil, pH = 7.55 ± 0.20; low EC = 0.32 dS m<sup>-1</sup> and high EC = 7.9 dS m<sup>-1</sup>.

TABLE 4  
Adsorption isotherm parameters

	5/2002			8/2002		
	<i>K</i>	<i>M</i>	<i>R</i> <sup>2</sup>	<i>K</i>	<i>M</i>	<i>R</i> <sup>2</sup>
Low EC	0.00496	265 ± 46	0.991**	0.00677	186 ± 17	0.995**
High EC	0.00270	409 ± 182	0.984**	0.00808	166 ± 29	0.989**

\*\* indicates statistical significance at the 95% level of confidence.

optimizing three surface complexation constants:  $\log K_{B-}(\text{int})$  for B adsorption,  $\log K_{+}(\text{int})$  for protonation, and  $\log K_{-}(\text{int})$  for dissociation. These three constants had been previously optimized to describe B adsorption envelopes on soils (Goldberg et al., 2000). Optimized values of the surface complexation constants are provided in Table 3. All three B concentrations and two salinity treatments were simultaneously optimized for the 8/2002 soil sample. Simultaneous optimization was not possible for the 5/2002 soil sample because the suspension density was not exactly constant between treatments. Therefore, each tank water treatment was individually optimized for the 5/2002 soil. The values of the surface complexation constants optimized in this study are not statistically significantly different at the 95% level of confidence from the average values of these constants determined for soils by Goldberg et al. (2000):  $\log K_{B-}(\text{int}) = -8.23 \pm 0.39$ ,  $\log K_{+}(\text{int}) = 8.18 \pm 0.65$ ,  $\log K_{-}(\text{int}) = -11.61 \pm 0.56$ .

The ability of the constant capacitance model to predict B adsorption as a function of solution pH and solution B concentration is indicated in Figure 2. To obtain the model results, surface complexation constants were calculated after entering the soil chemical properties SA, OC, IOC, and Al into the prediction equations Eq.(8) to Eq.(10). These surface complexation constants were subsequently used in the FITEQL 3.2 code to speciate the chemical system and to predict B adsorption. The open symbols represent the prediction of B adsorption behavior for the 8/2002 soil from its chemical properties (Goldberg et al., 2000). The model predictions are very close to the experimental data points for the high B treatments. For the intermediate B treatments, the model predictions are semi-quantitative in that the shapes of the adsorption curves are predicted very well as a function of solution pH. However, the model underpredicts B adsorption by an average of 50%. The

model predictions for the lowest B treatments are poor. This is likely because native B is desorbing and constitutes a significant portion of the total B in the system. The amounts of native B released into the 0.1 M NaCl solutions are not expected to be exactly identical to those released during the course of the B adsorption experiments.

The predictions are suitable for transport modeling applications and will be used to describe B movement in large soil columns packed with these soils. Because the model results were predictions, no model parameters were adjusted or optimized. The surface complexation constants obtained using this prediction approach are listed in Table 3.

Boron adsorption isotherms were determined on both soils under conditions of low (EC, 0.32 dS m<sup>-1</sup>) and high (EC, 7.9 dS m<sup>-1</sup>) electrolyte concentration (Fig. 3). The Langmuir adsorption isotherm equation was fit to the experimental data using the nonlinear least squares optimization program, ISOTHERM (Kinniburgh, 1985). The B adsorption maxima obtained in this manner for the two EC were not statistically significantly different at the 95% level of confidence (Table 4). This result indicates that in the range of EC 0.32 to 7.9 dS m<sup>-1</sup>, the magnitude of B adsorption is independent of soil solution salinity.

This investigation has shown that B adsorption as a function of solution B concentration and solution pH is independent of salinity in the pH range 4 to 9 up to EC 7.9 dS m<sup>-1</sup>. For the purposes of describing B transport in soils under agricultural conditions, these results are advantageous because they indicate that B adsorption can be described and predicted without consideration of changes in solution electrolyte concentration.

#### ACKNOWLEDGMENTS

The authors thank Mr H. S. Forster and Mr T. J. Foster for technical assistance.

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