Modeling the cation-exchange properties of corn bran under simulated gastrointestinal ionic conditions

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Dietary fiber is known to exert many positive health benefits. However, evidence suggests that dietary fiber may decrease mineral bioavailability. In order to test the hypothesis that dietary fiber limits mineral availability through ion-exchange processes, an analytical model was developed which predicts the extent of binding of metal cations in the gastrointestinal tract. Corn bran, representing a typical insoluble dietary fiber, was tested in vitro against solutions of varying H^+, Na^+, K^+, Ca^{2+} and Mg^{2+} concentrations mimicking the range of gastrointestinal ionic conditions. The model relates solution composition to the extent of metal cation binding through a series of proton/metal exchanges with the dietary fiber carboxyl groups. In addition to equilibrium constants for each proton/metal exchange, solution and solid phase activity coefficients for all ions are required. It was found that an exponential function relating the activity coefficient of protonated exchange sites to their mole fraction was necessary and sufficient to make the model adequately sensitive to solution pH. Introduction of this expression produced a 6-fold improvement in the fit of the model to experimental observations of ion binding. The general nature of the model should permit its application to other dietary fibers, plant cell walls and synthetic ion-exchange resins.

Keywords: dietary fiber; mineral bioavailability; cell walls

Introduction

Proposed health benefits ascribed to dietary fiber are now legion.[1] Notwithstanding these admirable traits, concern has arisen over the potential for dietary fiber to limit or reduce mineral bioavailability.[2-12] It has been suggested that fibers may exert their influence on mineral absorption by either a physicochemical interaction with the intestinal mucosa,[13-16] or by reducing lumen mineral activity (concentration) through ion-exchange processes.[17-27] While the possibility is implied that ion-exchange capacity and ion affinity of dietary fiber are sufficiently high to impact mineral absorption, this hypothesis has yet to be tested rigorously. In this and subsequent papers, the interactions of minerals with a model dietary fiber source, corn bran, will be examined under both simulated (in vitro) and authentic (in vivo) gastrointestinal (GI) conditions.

Corn bran was selected for these studies for several reasons. It is a common component of human and animal diets. Dry-milled corn bran consists largely of insoluble fiber,[28,29] readily freed of non-fiber components such as starch and phytic acid. The absence of soluble components imparts corn bran with invariant exchange properties. Corn bran tissue remains intact and identifiable during passage through the GI tract, making retrieval and mineral content analysis feasible.[30] These characteristics make corn bran suitable for in vitro and in vivo testing.

The present work develops an ion-exchange model which permits accurate estimation of cation binding to corn bran under conditions approaching the ionic complexity of the mammalian, monogastric GI tract.

Materials and methods

Dry-milled corn bran (Lauhoff Grain Co., Danville, IL) was freed of adhering endosperm and adsorbed minerals by a series of extractions and washing steps. Corn bran (25 g), suspended in 50 mmol/L HCl (1 L),

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Received January 15, 1991; accepted May 7, 1991.

was stirred at room temperature for 2 hr. Bran particles were allowed to settle and the supernatant decanted. This procedure was repeated twice with distilled, demineralized water. Finally, the corn bran was rinsed briefly with ethanol to facilitate drying, collected by filtration, dried and stored under vacuum.

The mineral binding properties of corn bran were examined over a wide range of ionic conditions. Solution pH was controlled with 2.0 mmol/L concentrations of: acetate, pH 3.0, 4.0, or 5.0; 4-morpholineethanesulfonic acid, pH 6.0; or 4-morpholinepropanesulfonic acid, pH 7.0; adjusted with KOH. Details of the metal-cation composition of solutions are given in the Results section. Corn bran (0.1 g) was equilibrated for 2 hr at room temperature (25° C) with a stirred solution (0.1 L) and ambient atmospheric CO_2. Small aliquots of 1.0 mol/L KOH were added, as needed, after 1 hr to return solutions to their original pH. After equilibration, the corn bran was collected on nylon filters (5-μm pore size), transferred to tared vials, then dried under vacuum. The difference between sample wet and dry weight served as a measure of the solution content (hydration ratio) of the recovered bran. The mineral content of treated samples was determined by extraction of the bran with 50 mmol/L HCl (10 mL) and analysis of the extracts by ion chromatography.[31]

The total ion content of equilibrated tissue arises from two sources: cell-wall bound (adsorbed) and not bound (unadsorbed) ions. The unadsorbed ions are associated with free solution trapped in cell wall spaces. The unadsorbed ion concentration is assumed to be equal to the free solution ion concentration. For this study, only the bound-ion content was of interest. Therefore, the bound-ion content of samples was determined by subtracting the unadsorbed-ion amount from the total-ion content. The unadsorbed-ion amount was calculated from the hydration ratio and solution-phase ion concentrations at equilibrium. The difference between initial ion concentrations of solutions and ion concentrations at equilibrium was negligible. Mineral contents are expressed on the basis of the salt-free form of the dry tissue. The total cation-exchange capacity was determined by titrating corn bran to pH 7–8 with $Ca(OH)_2$ in the presence of 5.0 mmol/L $CaCl_2$.

Optimization of model parameters was achieved employing the program MINSQ (MicroMath Scientific Software, Salt Lake City, UT).

Theory

The binding of minerals to corn bran can be treated as a series of exchange reactions between the protonated form of carboxylic acid groups of the corn bran and solution phase cations. Because the model to be presented is applicable to insoluble dietary fibers, plant cell wall materials generally, and some synthetic ion-exchange resins, the terms resin, wall, and solid phase are used interchangeably herein to refer to the solid matrix of the corn bran tissue. Plant cell walls generally do not display binding preferences between monovalent cations, except H^+.[32] Therefore, the predominant monovalent cations found in mammalian GI fluids, Na^+, K^+ and NH_4^+, will be treated initially as a single species ($Mono^+$). Cell walls display selectivity among divalent cations.[33-37] Therefore, the major GI divalent cations, Ca^{2+} and Mg^{2+}, are treated individually. Other metals, such as zinc, copper, and iron, are likely in the form of chelates of varying or unknown charge. These species are not considered in the model. Corn bran ion-binding sites equilibrate with soluble ions within 30 min.[31] Therefore, it is assumed that equilibrium is achieved throughout GI transit. Thus, the exchange reactions of corn bran can be defined by a set of three equilibria.

$$Mono^+ + COOH \rightleftarrows COOMono + H^+$$

$$Ca^{2+} + 2\ COOH \rightleftarrows (COO)_2Ca + 2\ H^+$$

$$Mg^{2+} + 2\ COOH \rightleftarrows (COO)_2Mg + 2\ H^+$$

Although a number of models have been devised to describe ion interactions with resinous substrates, the formulation of Sposito[38-40] was selected as the basis for modeling cation binding to corn bran. The Sposito model was originally developed for the analysis of ion interactions with soils. However, it also has been applied to plant cell walls.[41] The Sposito model treats exchange reactions with strict thermodynamic formality. The equilibrium distribution of ion activities between aqueous solution and solid phases is driven by simple mass action.

In this model, the equations for the equilibrium constants for the three exchange reactions above are expressed as in Equations 1-3:

$$K_H^{Mono} = \frac{(H^+) \cdot (MonoX)}{(Mono^+) \cdot (HX)} \quad (1)$$

$$K_H^{Ca} = \frac{(H^+)^2 \cdot (CaX_2)}{(Ca^{2+}) \cdot (HX)^2} \quad (2)$$

$$K_H^{Mg} = \frac{(H^+)^2 \cdot (MgX_2)}{(Mg^{2+}) \cdot (HX)^2} \quad (3)$$

where X represents resin-phase exchange sites (i.e., COO^-) and parentheses indicate activities.

To transform Equations 1–3 into experimentally assessable quantities, solution- and resin-phase activities, except (H^+), are converted to activity coefficients and concentrations, C_i, for solution phase species, or mole fractions M_i, for resin phase species. Solution-phase proton activity is left unmodified since this is the most readily determined form (i.e., directly measured with a pH meter). The solution-phase, single-ion activity coefficient, γ^{zi}, for ion species i with charge z is calculated based on molar ionic strength (I).[42] See Equations 4 and 5.

$$\log \gamma^{zi} = -0.509\, z_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right] \quad (4)$$

Ionic strength is calculated by summing the prod-

ucts of (free) ion concentrations (including anions) and their charges.

$$I = \tfrac{1}{2} \sum_i C_i z_i^2 \quad (5)$$

Thus the three exchange equations become Equations 6-8:

$$K_H^{Mono} = \frac{(H^+) \cdot f_{Mono} \cdot M_{Mono}}{\gamma^+ \cdot [Mono^+] \cdot f_H \cdot M_H} \quad (6)$$

$$K_H^{Ca} = \frac{(H^+)^2 \cdot f_{Ca} \cdot M_{Ca}}{\gamma^{2+} \cdot [Ca^{2+}] \cdot \{f_H \cdot M_H\}^2} \quad (7)$$

$$K_H^{Mg} = \frac{(H^+)^2 \cdot f_{Mg} \cdot M_{Mg}}{\gamma^{2+} \cdot [Mg^{2+}] \cdot \{f_H \cdot M_H\}^2} \quad (8)$$

with brackets, [ ], signifying concentration, and f_i and M_i representing resin-phase activity coefficients and mole fractions, respectively.

In addition to Equations 6-8, a relationship expressing the electroneutrality of the resin phase is required to complete the system of equations defining the model. Equation 9 provides this, expressed in terms of mole fractions.

$$M_H + M_{Mono} + 2M_{Ca} + 2M_{Mg} = 1 \quad (9)$$

What remains to be determined are the resin-phase activity coefficients, f_i, and exchange constants, K_H^i. Unfortunately, no ready formulation exists for resin-phase activity coefficients (i.e., for species HX, MonoX, etc.). Previous workers have either arbitrarily assigned values of one to all f_i coefficients or employed graphical techniques for their estimation.[41] Sposito[38-40] has concluded that f_i values should be a function of M_i. It is shown herein that a simple expression relating f_H to M_H suffices. The remaining f_i terms may be assigned values of one. K_H^i values are determined by applying appropriate curve-fitting procedures to data sets consisting of solution phase ion concentrations and resin phase mole or equivalent fractions.

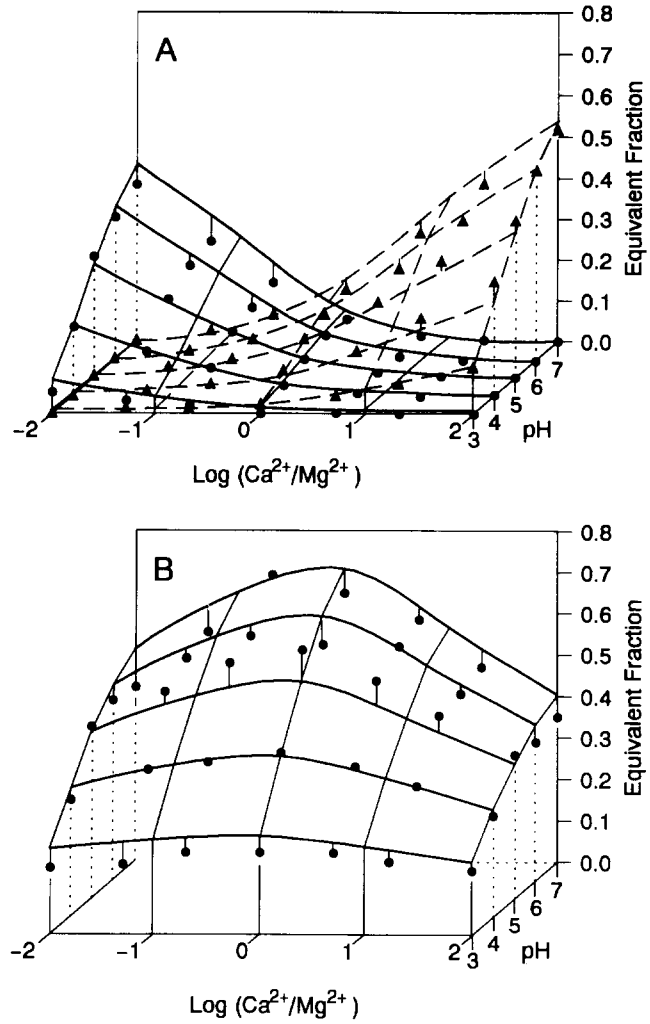

Figure 1 Extent of Ca^{2+}, Mg^{2+}, and K^+ binding to corn bran in 75 mmol/L KCl solution. Panel A: observed equivalent fractions of Ca^{2+} (▲) and Mg^{2+} (●). Dashed and solid lines are model-predicted values for Ca^{2+} and Mg^{2+}, respectively. Panel B: symbols and lines are observed and calculated values for K^+ and $Mono^+$, respectively.

Results

In order to mimic the range of ionic conditions potentially present in the GI tract,[43-51] the cation-binding properties of corn bran were measured in solutions, pH 3–7, containing 75–150 mmol/L K^+ and 0.1-10 mmol/L Ca^{2+} and Mg^{2+}. Although stomach pH can be lower than 3.0, corn bran bound negligible quantities of ions at pH 2.0 or lower (data not shown). At a given K^+ concentration, Ca^{2+} and Mg^{2+} concentrations varied such that solution ionic strength remained essentially constant. Therefore, model parameters could be determined for individual data sets without regard for the influence of ionic strength, except for its effect on solution-phase activity coefficients. A data set constituted 35 different ionic conditions (5 pH values × 7 Ca^{2+}/Mg^{2+} concentration ratios). The K^+, Ca^{2+}, and Mg^{2+} contents of each sample were measured, giving 105 observations. All observations were weighted equally. Model parameters were optimized independently for the four data sets corresponding to 75, 100, 125, and 150 mmol/L KCl solutions.

The total exchange capacity of corn bran was found to be 212 ± 6 (n = 6) mEq per kg dry weight, quite similar to what Rasper[28] determined. *Figure 1* displays the equivalent fractions of K^+, Ca^{2+}, and Mg^{2+} bound for the 75 mmol/L data set. Binding of all three metals increased with pH. At any given pH, with Ca^{2+} and Mg^{2+} at 1.0 mmol/L (log Ca^{2+}/Mg^{2+} = 0), Ca^{2+} bound to a greater extent than Mg^{2+}. This demonstrates the higher selectivity of corn bran for Ca^{2+}. When Ca^{2+}, Mg^{2+}, and H^+ were all 1.0 mmol/L (pH 3.0, log Ca^{2+}/Mg^{2+} = 0), H^+ occupied 77% of the exchange sites, reflecting the preference of corn bran to bind H^+. These ion-binding traits are typical of plant cell wall tissues.[33,34,37]

Close agreement was achieved between experimentally-observed and model-predicted values when the term $e^{\Lambda_H \cdot M_H}$ was substituted for f_H in Equations

Table 1 Model optimized parameter values

Parameter[b]	Data set[a] 75	100	125	150	Mean estimate
K_H^{Mono}	1.7 ± 0.3[c] (1.0–2.3)[d]	1.5 ± 0.4	1.5 ± 0.3	1.3 ± 0.3 (0.6–1.9)	1.5
K_H^{Ca}	4.1 ± 1.7	4.0 ± 1.9	4.3 ± 1.8	4.1 ± 2.2	4.1
K_H^{Mg}	2.1 ± 0.9	2.0 ± 1.0	2.0 ± 0.9	2.1 ± 1.1	2.1
Λ_H	7.9 ± 0.4 (7.1–8.7)	7.8 ± 0.5	7.2 ± 0.4 (6.4–8.0)	7.4 ± 0.5	7.6

[a] Monovalent cation concentration (mmol/L) of solution.
[b] K_H^{Mono} values have been multiplied by 10^5. K_M^{Ca} and K_H^{Mg} values have been multiplied by 10^{10}.
[c] Parameter estimate ± one standard deviation.
[d] Univariable 95% confidence region of parameter.

6–8. The use of an exponential function was derived empirically. The constant Λ_H was optimized along with the K_H^i parameters. Introduction of this expression for f_H resulted in a six-fold reduction in the sum of squared residuals. *Figure 1* shows the experimental and model values for the 75 mmol/L K^+ data set. Introduction of additional f_i terms as functions of M_i for the other resin-phase species resulted in a computationally unstable system of equations. Therefore, the remaining f_i terms were assigned values of one.

Table 1 lists the optimized parameter values for all four data sets. Note that K_H^i values are much less than one, reflecting the higher selectivity of H^+ than other ions for corn bran. K_H^{Ca} was two-fold larger than K_H^{Mg} in all instances, as a consequence of the greater relative affinity of Ca^{2+}. K_H^{Mono} is five orders of magnitude larger than K_H^{Ca} and K_H^{Mg}. This results from the particular formulation of the model. It does not imply that K^+ has greater affinity than Ca^{2+} or Mg^{2+}. This point has been discussed at length by Bush & McColl.[41] A positive valued Λ_H implies that f_H increases as a function of M_H. This is opposite of the solution phase situation where concentration and activity coefficient generally vary inversely. The need for resin-phase activity coefficients greater than one has also been noted by Bush & McColl.[41]

Table 2 presents the goodness-of-fit statistics of the model employing the corresponding parameter estimates. The coefficients of determination (similar to correlation coefficients for linear models) were similar for the four data sets (*Table 2*), indicating that the model has little bias for higher or lower ionic strength conditions. The majority of the residual error (difference between observed and calculated) accumulated in the monovalent cation term (*Table 2*). This occurred for at least two reasons. First, since there were twice as many divalent-cation than monovalent-cation observations, Ca^{2+} and Mg^{2+} values had a proportionally higher impact on the fitting process. Second, there was a greater degree of experimental error in determining the bound K^+ fraction because of the large correction required for unadsorbed K^+. This correction was far less for Ca^{2+} or Mg^{2+}.

Table 2 Summary of goodness-of-fit statistics[a]

Data set[b]	Coefficient of determination	Sum of squared residuals Mono$^+$	Ca^{2+}	Mg^{2+}	Total
75	0.983	0.048	0.010	0.010	0.068
100	0.979	0.065	0.016	0.016	0.098
125	0.986	0.052	0.015	0.015	0.082
150	0.977	0.092	0.018	0.023	0.133

[a] Based on parameters given in *Table 1*.
[b] Monovalent cation concentration (mmol/L) of solution.

Estimates of the model parameters varied little as a function of solution phase ionic strength (*Table 1*). There is some suggestion of a trend towards lower values of K_H^{Mono} and Λ_H as KCl concentration increased. However, the 95% confidence regions of the highest and lowest estimates of the parameters greatly overlapped. This indicates that an ionic strength effect on K_H^{Mono} and/or Λ_H, if present, could not be determined from these data.

To ascertain whether the model and/or parameters could be applied to lower ionic strength solutions, corn bran was tested against solutions containing 5-150 mmol/L K^+ and 5.0 mmol/L Ca^{2+}, at pH 6.0. When Λ_H was allowed to vary as a linear function of ionic strength (i.e., $\Lambda_H = Slope \cdot \sqrt{I} + Intercept$), a fairly good fit of the model to the data was achieved (*Figure 2*). However, the nonrandom deviation of the observed values from the calculated values suggests that the relative affinities of K^+ and Ca^{2+} for corn bran slowly change with solution ionic strength.

There is disagreement on whether plant cell walls display selectivity (binding preference) among monovalent cations. Both selectivity[52] and no selectivity[32,53] have been reported. Therefore, corn bran selectivity between K^+ and Na^+ was tested. Samples were treated with solutions containing K^+ and Na^+ at various concentration ratios (i.e., varying solution phase mole fraction) and total monovalent cation concentrations. With selectivity defined as shown in Equation 10

$$K_{Na}^{K} = \frac{X_{Na} \cdot M_K}{X_K \cdot M_{Na}} \quad (10)$$

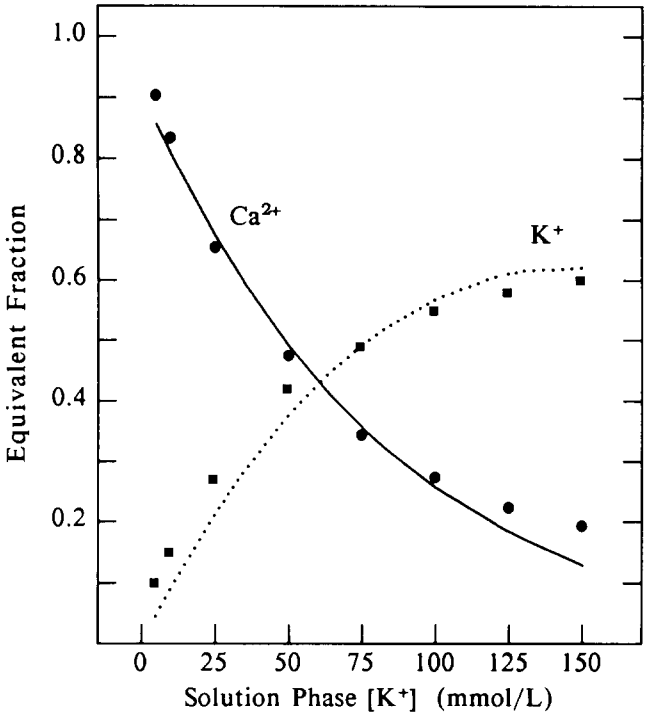

Figure 2 Observed and calculated values of Ca^{2+} and K^+ bound to corn bran with varying solution phase K^+ concentration. Solution Ca^{2+} concentration was held constant at 5.0 mmol/L. Data shown are the means of three separate determinations. Standard deviations of the values are approximately equal to their symbol size. Model parameter values, optimized for these data, are K_H^{Mono} = 1.67×10^{-5}, K_H^{Ca} = 3.65×10^{-10}, *Slope* = −59.3 and *Intercept* = 24.4 (see text for details).

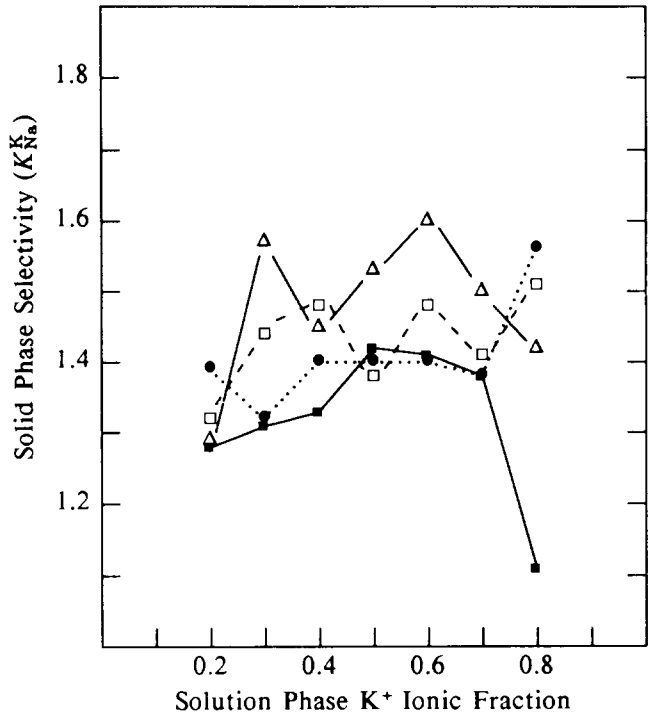

Figure 3 K_{Na}^K selectivity values of corn bran. Corn bran samples were equilibrated with solutions having various K^+ and Na^+ ionic fractions. Solution pH was held constant at 7.0. Solutions also contained 2.0 mmol/L Ca^{2+}. Buffer and Ca^{2+} were not included in the calculation of solution phase ionic fraction values. Total monovalent cation concentrations (not including buffer) were 75 (—■—), 100 (···●···), 125 (--□--) and (—△—) 150 mmol/L.

where X_i and M_i refer to solution and solid phase mole fractions, respectively, K_{Na}^K values greater than one indicate preferential binding of K^+. Within experimental error, K_{Na}^K values were constant over the tested range of X_i (0.2–0.8) and ionic strength (*Figure 3*). The mean K_{Na}^K value was 1.4. Synthetic resins with carboxylate functional groups have a similar preference for K^+.[54] Corn bran selectivity for NH_4^+ would be expected to be between that of Na^+ and K^+. Since K_{Na}^K is equivalent to K_H^K/K_H^{Na}, a value of 1.1×10^{-5} was deduced for K_H^{Na} ($K_H^K = 1.5 \times 10^{-5}$, *Table 1*). Thus, separate relations for K_H^K and K_H^{Na} should be substituted for the K_H^{Mono} exchange relation (Equation 6) of the model.

Discussion

The Sposito model does not require, nor provide, a molecular interpretation of ion binding. This can be both a blessing and a curse. The model has been criticized recently for its insensitivity to solution pH and for its inability to generate information about molecular events.[55] The introduction of the exponential expression for f_H makes the model highly sensitive to pH. Numerous models derived from statistical–mechanical reasoning have been developed to describe ion interactions with plant cell walls.[37,56-59] While they produce an interpretation of ion binding in terms of specific molecular interactions, they generally rely on making estimates of unmeasurable molecular properties and questionable assumptions about the uniformity of distribution of binding sites. The Sposito model does not suffer explicitly from this problem (although one could argue that f_H is not directly measurable either).

One recently proffered statistical–mechanical theory for cell walls, the Constant Capacitance model,[59] bears striking resemblance to the model presented herein. The Constant Capacitance model introduces an exponential term relating the activity coefficients of the COOH and COO^- species to the charge density of the wall. The adjustable parameter of this relationship, the integral capacitance density, is very similar in action and magnitude to the Λ_H parameter. Although the term $e^{\Lambda_H \cdot M_H}$ was introduced to calculate f_H (all other f_i values equal to one), an alternative interpretation would be that this expression actually describes the ratio $(f_H)^{z_i}/f_i$. Thus, Λ_H may be related closely to the surface charge density of corn bran cell walls.

The model presented permits calculation of the extent of cation binding to corn bran under the highly varied conditions of the GI tract. Introduction into the model of a simple expression for the resin phase activity coefficient of the protonated carboxyl exchange site produced a fairly close correlation between mod-

eled and observed values. Under the high ionic strength milieu characteristic of the mammalian, monogastric GI tract,[46-51] all model parameters (i.e., K_H^i and Λ_H) may be treated as constants for corn bran. The model can be extended to an even greater range by allowing Λ_H to vary as a function of ionic strength. These enhancements should permit the application of the model to other insoluble fibers, cell wall preparations, and some synthetic resins under psychological or other real-world conditions.

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