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Calcium Ion Binding to a Soil Fulvic Acid Using a Donnan Potential Model

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Summary

Calcium ion binding to a soil fulvic acid (Armadale Bh Horizon) was evaluated over a range of calcium ion concentrations, from pH 3.8 to 7.3, using potentiometric titrations and calcium ion electrode measurements. Fulvic acid concentration was constant (100 milligrams per liter) and calcium ion concentration varied up to 8×10^{-4} moles per liter. Experiments discussed here included: (1) titrations of fulvic acid-calcium ion containing solutions with sodium hydroxide; and (2) titrations of fully neutralized fulvic acid with calcium chloride solutions. Apparent binding constants (expressed as the logarithm of the value, $\log \beta_{app}$) vary with solution pH, calcium ion concentration, degree of acid dissociation, and ionic strength (from $\log \beta_{app} = 2.5$ to 3.9) and are similar to those reported by others. Fulvic acid charge, and the associated Donnan Potential, influences calcium ion-fulvic acid ion pair formation. A Donnan Potential correction term allowed calculation of intrinsic calcium ion-fulvic acid binding constants. Intrinsic binding constants vary from 1.2 to 2.5 (the average value is about $\log \beta = 1.6$) and are similar to, but somewhat higher than, stability constants for calcium ion-carboxylic acid monodentate complexes.

1. Introduction

Heterogeneous organic materials of intermediate molecular weight (1000–2000) (fulvic acids) [1] are common to terrestrial and aquatic environments [2]. Reactions of these acids with aqueous metal ions and mineral surfaces influence and impact metal ion equilibria in natural waters [3]. Understanding processes controlling metal ion reactions with fulvic acids are critical to geochemical and water quality [4, 5] research areas including nuclear waste disposal [6–8], mineral weathering [9] and metal transport [4]. Fulvic acid binding of radionuclides (for example, strontium(90), barium(133) and radium ions) and measurement of binding parameters for aqueous solution modeling of metal ion-dissolved organic carbon interactions are critical areas of investigation [7, 8, 10, 11].

Two fulvic acid characteristics obstruct interpretation of acid proton and metal ion binding reactivity [12, 13]. The first is the variation of proton and metal binding constants with background electrolyte concentration levels after correcting for ionic strength variations with the Debye-Hückel equation [14]. The second is functional group heterogeneity [15]. Background ion concentration levels modify humic and fulvic acid dissociation. Marinsky and Ephraim [16] (1986) have measured and interpreted the background electrolyte effect on fulvic acid proton and metal ion binding reactions. This approach, based on "polyelectrolyte theory", assumes that high molecular weight fulvic acid ionic charge, and the associated Donnan Potential, causes the background electrolyte effect, as it does with linear polyelectrolyte-simple salt systems [15, 17].

Several approaches to compensate for the electric field associated with ionized polyelectrolyte acid molecules have been proposed [18] to adjust fulvic acid metal binding at different solution ionic strengths. A procedure that has gained acceptance is the use of a Donnan Potential correction term (DP) [19, 20]. Marinsky and co-workers [19] (1995) applied Donnan Potential corrections to fulvic acids and synthetic polyelectrolytes to interpret proton dissociation and ion binding properties of fulvic acid and metal ions.

The Donnan Potential is caused by ion distribution on each side of a membrane separating two portions of an electrolyte solution. On one side of the membrane a polyelectrolyte (e.g., a fulvic acid) is introduced. The fulvic acid molecules and ions associated with them cannot pass through the membrane. Ion distribution on the two sides of the membrane will be unequal and a membrane potential (the Donnan Potential) will be established. Under certain circumstances a single fulvic acid macromolecular ion of sufficient size and charge may have a Donnan Potential [21].

Calcium ion binding to fulvic acid is influenced by a Donnan Potential whenever a fulvic acid solution is separated from a similar solution without fulvic acid even if no membrane is present at the boundary [21]. The Donnan Potential controls the distribution of ions

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between these two solutions or regions of a single solution unless it is minimized by the presence of high salt concentration and applies only to sufficiently high molecular weight fulvic acid molecules. Such high molecular weight molecules exhibit a "polyelectrolyte effect" [22, 23]. We assume fulvic acids approach polyelectrolyte behavior as molecular weights approach about 600 to 800 Daltons [24]. Other approaches to analysis of ionic equilibria of organic macromolecules have been proposed and are discussed by Tanford [21] and Buffle [18]. Apparent and intrinsic binding constants are discussed by Tanford [21].

Polyelectrolyte weak acid proton ionization and metal binding characteristics have been interpreted using a Donnan Model [7−10]. This interpretation suggests that a counterion concentrating region, and an associated "Donnan Volume" exists adjacent to the ionized polyelectrolyte molecule. However, in the case of fulvic acid the Donnan Volume is uncertain because only a portion of the fulvic acid molecules in solution have sufficiently high molecular weight to have a Donnan Potential. Moreover, the complex distribution of molecular weights, functional groups and ionizable groups in fulvic acid render the use of the Donnan Volume concept problematic. Hydrophobic interactions may contribute to the fulvic acid Donnan Volume and will change as fulvic acid ionizes. Charge on ionized fulvic acid causes counter ion accumulation at the site of ion binding. This effect influences ion binding reactions and is incorporated by modification of intrinsic equilibrium constants to incorporate enhanced interaction at discrete binding sites.

The correction term, the Donnan Potential (DP), is determined experimentally from fulvic acid potentiometric titrations as a function of ionic strength

$$\mathrm{DP} = \Delta \log K = \log K_{\mathrm{app}} - \log K_{\mathrm{int}}$$

where K_{app} is the observed acid dissociation constant and K_{int} is the intrinsic acid dissociation constant. $\Delta \log K$ at each ionic strength is obtained from the difference between $\log K_{\mathrm{app}}$ at a particular ionic strength and $\log K_{\mathrm{int}}$ which is determined at I = 1.0 M where the sensitivity of pK_{app} to ionic strength is small [15].

Reduction of Donnan Potential ionization effects by high background electrolyte concentrations (which effectively screen the polyion charge) is used [15] to identify fulvic acid functional groups and their average abundance. Ephraim and coworkers [15] identified four weak acid functional groups with different acidities and similar abundances for the Armadale Bh Horizon soil fulvic acid used in this report [15]. The discrete site-polyelectrolyte approach proposed by Marinsky and others is incorporated into a numerical computational code to describe humic and fulvic interactions in natural waters, soils and sediments [25, 26].

Calcium ion-fulvic acid binding measurements have been reported by several investigators [27−32]. However, variations in natural organic material and in the method of isolation and purification of the fulvic acid from the natural organic material have limited comparison of calcium ion-fulvic acid binding results [13]. Investigators report calcium ion binding to fulvic acid increases with increasing solution pH, and binding constants vary with experimental conditions [13].

The goal of this report is to determine apparent and intrinsic calcium ion-fulvic acid binding constants over a range of solution conditions. A Donnan Potential correction term was used to convert apparent binding constants to intrinsic constants [16]. Our working hypothesis is that the Donnan Potential correction of apparent calcium ion-fulvic acid binding allows for comparison of intrinsic binding constants with binding constant values for calcium ion-carboxylate complexes. We assume that only 1:1 ligand-to-metal ion complexes form in solution and that multidentate binding is absent.

2. Materials and methods

Chemicals, their preparation, the electrochemical apparatus and the procedures used for potentiometric measurements have been described previously [15, 16, 32]. Experimental and computational procedures employed have appeared elsewhere [32]. Characteristics of the Armadale Bh Horizons soil fulvic acid have been published elsewhere [12, 33, 34]. Calcium content of this fulvic acid is less than 0.1 ppm [34]. Titratable acidity for the Armadale sample [12] is 5.60 +/− 0.15 meq/gm. Non-aqueous titrations suggest that this corresponds to 4.15 +/− 0.05 meq/gm as carboxylate acidity and 1.84 +/− 0.06 meq/gm phenolic acidity. The carboxylate acidity is associated with four sites with pK values of 1.8, 3.4, 4.2 and 5.7 having similar abundances [12]. Calcium ion binding to fulvic acid is assumed to occur only to carboxylate groups forming a monodentate calcium ion-fulvate complex.

Two experimental procedures were used to characterize calcium ion fulvic acid interaction. One series of experiments consisted of titrations done with a fixed calcium ion concentration. A second series of experiments used stepwise calcium ion addition. Briefly, calcium ion-Armadale Bh Horizons fulvic acid binding was determined at two background electrolyte concentrations (0.010 and 0.10 M $NaNO_3$) by stepwise neutralization of calcium ion containing fulvic acid solutions with standard base. Both solution pH and calcium ion activity were measured simultaneously after each base addition. Details of calcium ion activity measurements using the specific ion electrode appear elsewhere [12, 32, 35].

At each equilibrium point in the experiments, the amounts, in moles, of the ionized fulvic acid binding site (A^{-n}), unionized fulvic acid site (H_nA), and monodentate calcium ion-fulvic acid complex species (CaA^{-n+2}) were calculated with the following mass

balance equations which give the total moles of each species:

$$\sum A_f^{-n} = b\,V_b + h\,V_{sf} - \sum CaA_f^{-n+2}\,, \quad (1)$$

$$\sum CaA_f^{-n+2} = (Ca_i^{+2})(V_{si}) - (Ca_f^{+2})(V_{sf})\,, \quad (2)$$

$$\sum H_nA_f = \sum H_nA_i - (bV_b + hV_{sf})\,, \quad (3)$$

where the subscript "i" refers to the solution before addition of titrant, subscript "f" refers to the solution after the addition of titrant, "b" corresponds to base concentration, "h" the hydrogen ion concentration after each addition of base, V_b base volume added in each neutralization step, V_{si} the initial solution volume of solution before addition of base, V_{sf} the solution volume after addition of base, $\sum H_nA_i$ is the starting quantity of fulvic acid, and Ca_i^{+2} and Ca_f^{+2} refer respectively to the concentration of calcium ion measured with an ion selective electrode before and after addition of base. Direct measurement of calcium ion concentration before and after addition of base allows determination of calcium ion bound to fulvic acid. Release of hydrogen ion by chelation at multidentate binding sites is not considered.

Equation (1) gives the amount of ionized fulvic acid as the sum of the moles of base added plus the moles of solution hydrogen ion minus the reduction of ionized sites due to calcium ion-fulvic acid complexation. All the terms in the equations represent amounts (moles) obtained from a multiplication of concentration with volume. Equation (2) allows determination of the amount of calcium ion bound to fulvic acid from the change of calcium ion concentration before and after addition of reagent. Equation (3) gives the amount of unionized fulvic acid as a summation of initial fulvic acid, added base and solution hydrogen ion concentration.

The Donnan Potential term used to correct for the background electrolyte effect presumes that charge screening by fulvic acid bound calcium ion ($\sum CaA^{-n+2}$) reduces the Donnan Potential value determined from potentiometric titration in the absence of calcium ion. In the presence of calcium ion, this reduced fulvic acid degree of ionization, called here the effective degree of ionization, "α_{eff}" is defined by Eq. (4):

$$\alpha_{eff} = \frac{\sum A_{eff}^{-n}}{\sum H_nA_i} \quad (4)$$

where

$$\sum A_{eff}^{-n} = \sum A^{-n} - \sum CaA_f^{-n+2}\,. \quad (5)$$

Effective degree of ionization is used (by graphical interpolation) to determine fulvic acid Donnan Potential from published results [15].

3. Results and discussion

Initial solution conditions for the binding experiments are shown in Table 1 [32].

Table 1. Initial conditions for calcium ion-fulvic acid binding experiments with 100 milligrams per liter Armadale Bh Horizon soil fulvic acid at I = 0.01 M[a] and 25 °C by base titration[b] initial solution pH, initial total calcium ion concentration, and the initial equivalent ratio of total calcium ion to total fulvic acid

Experiment	Initial pH_0	Total Ca^{+2} moles/l × 10^4	Total Ca^{+2}/Total fulvic acid equivalents/equivalents
1	4.054	1.00	0.325
2	4.016	2.00	0.65
3	4.003	4.00	1.3
4	4.001	4.00	1.3
5	3.759	4.00	1.3
6	6.764	0.80	0.13
7	6.703	0.8	0.13

[a] Experiment 5, I = 0.1 M.
[b] Experiments 6 and 7 are calcium ion titrations of almost fully neutralized fulvic acid.

Table 2. Ranges of amount of calcium ion bound per gram of Armadale Bh Horizon soil fulvic acid and ranges of free calcium ion concentration at I = 0.01[a], and 25 °C by base titration[b]

Experiment	Range of amount of calcium ion bound per gram of fulvic acid moles/gm of FA × 10^4	Range of solution free calcium ion concentration moles/liter × 10^4
1	0.87−0.32	1.3− 6.8
2	1.71−0.90	2.8−11.0
3	3.24−2.57	7.4−14.0
4	3.40−2.59	5.8−13.8
5	3.78−3.18	1.9− 7.8
6	0.31−6.14	4.9−17.8
7	0.19−6.40	6.1−15.1

[a] Experiment 5, I = 0.1 M.
[b] Experiments 6 and 7 are calcium ion titrations of almost fully neutralized fulvic acid.

Calcium ion-fulvic acid binding measurements, done as a stepwise neutralization of a 100 mg/L fulvic acid solution (6.15×10^{-4} eq/L), exhibited increasing pH values with base addition for each ionic strength and calcium ion concentration. The range of calcium ion bound to fulvic acid (as moles of calcium per gram of fulvic acid) and the range of free calcium ion concentration in solution for each experimental measurement are presented in Table 2. The raw data showing the extent of metal binding as a function of pH and Ca/FA ratio has been presented elsewhere [32].

3.1 Apparent binding constant variation with pH

Fulvic acid complexation with calcium ions can be written as

$$Ca^{+2} + A^{-n} = CaA^{-n+2}, \quad (6)$$

where A^{-n} represent an ionized fulvic acid functional group (eq/L) and "n" is the average number of protons

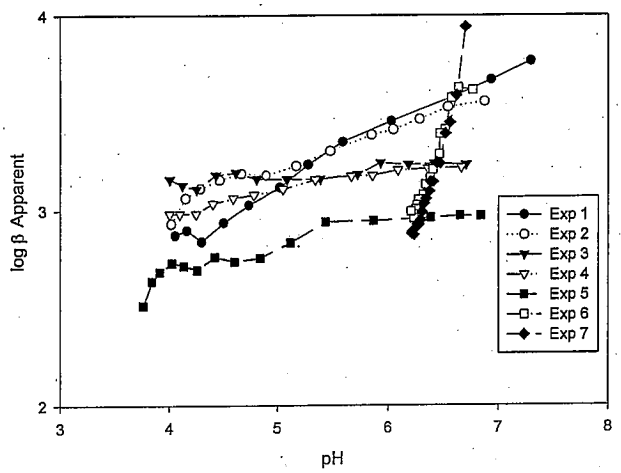


Fig. 1. Apparent calcium ion-fulvic acid binding constant ($Ca^{+2}+A^{-n} = CaA^{-n+2}$; $\log \beta_{app} = \log ([CaA^{-n+2}]/[Ca^{+2}][A^{-n}])$) versus pH.

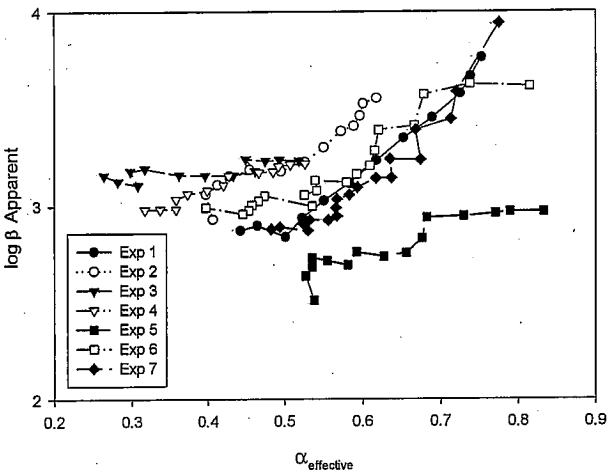
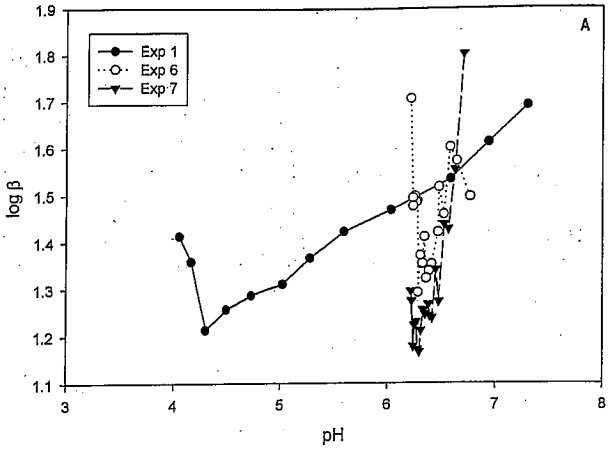


Fig. 2. Apparent calcium ion-fulvic acid binding constant ($\log \beta_{app}$) versus the fulvic acid effective degree of ionization (alpha, effective).



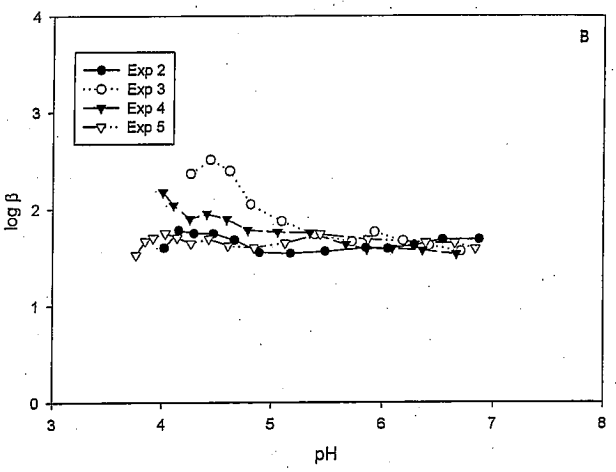


Fig. 3. Plot of Donnan Potential (DP) corrected calcium ion fulvic acid binding constant ($Ca^{+2}+A^{-n} = CaA^{-n+2}$; $\log \beta = \log([CaA^{-n+2}]/[Ca^{+2}][A^{-n}]) - 2 \log (DP)$) as a function of solution pH.

removed from the fulvic acid molecule. The apparent ion-binding constant (β_{app}) is expressed as

$$\beta_{app} = ([CaA^{-n+2}]/[Ca^{+2}][A^{-n}]) \quad (7)$$

where terms in square brackets are solutions concentrations. The binding parameter defined in this way varied with solution composition (Experiments 1, 2, 6 and 7) (Fig. 1).

Duplicate experiments (Experiments 3 and 4) agreed well. Apparent constants measured at different ionic strength (Experiments 3 and 4, I = 0.01, and Experiment 5, I = 0.1) differ by about 0.25 log units over the pH range of the experiments.

Experiments with an initial calcium-to-fulvic acid equivalent ratio greater than 0.7 (hereafter termed high initial calcium experiments) (Experiments 3 to 5) had less variation in β_{app} than other experiments. Apparent constants in duplicate experiments (Experiments 3 and 4) scatter somewhat for solution pH values less than about 5. Base titration experiments (1 to 5) and calcium titration experiments (6 and 7) had different variations in β_{app} with changing solution pH. Calcium titrations of pre-neutralized fulvic acid (Experiments 6 and 7) had more strongly increasing apparent binding constant with increasing solution pH than base titrations (Experiments 1 to 5) and exhibit an increase in the apparent binding constant of more than one log unit with a pH charge of one unit. Base titrations with an initial calcium-to-fulvic acid equivalent ratio less than 0.7 (Experiments 1 and 2) had less rapidly increasing β_{app} with increasing pH than the calcium titration (Experiments 6 and 7). However, both sets of experiments (Experiments 1 and 2, and Experiments 6 and 7) have a more rapidly increasing β_{app} with increasing pH than the high initial calcium experiments (Experiments 3 to 5) (Fig. 1). Apparent binding constants, at a fixed ionic strength, agreed moderately within and among base titration experiments. Variation of β_{app} with solution pH, a common method of fulvic acid-metal ion binding data presentation, is complex. Presentation of calcium ion-fulvic acid apparent binding constants as a function of solution pH gives little insight into the processes controlling interaction.

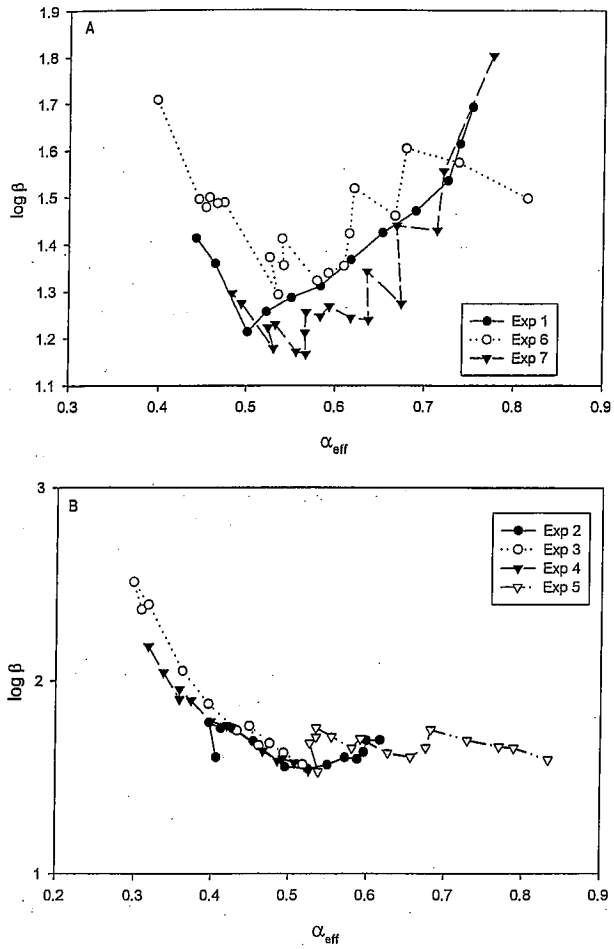


Fig. 4. Plot of Donnan Potential (DP) corrected calcium ion fulvic acid binding constant versus fulvic acid effective degree of ionization (alpha, effective).

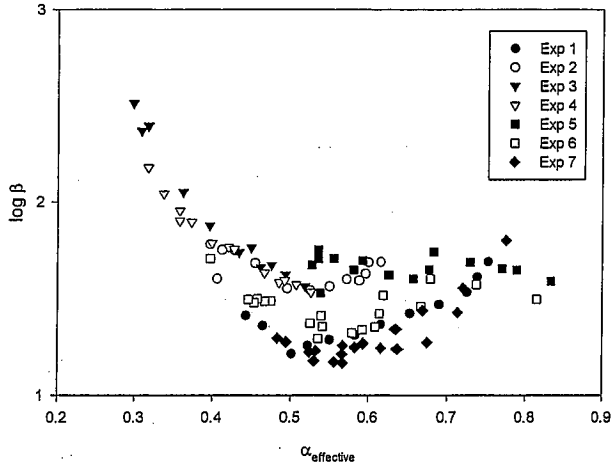


Fig. 5. Donnan Potential (DP) corrected calcium ion-fulvic acid binding constant as a function of the fulvic acid effective degree of ionization (alpha, effective).

3.2 Apparent binding constant variation with effective degree of ionization

Apparent binding constant variation with increasing effective degree of ionization (Fig. 2) is less erratic that the variation associated with changing pH. Apparent binding constants cluster depending on solution ionic strength. There is greater scatter in apparent constants for duplicate experiments (Experiments 3 and 4, Fig. 2) at low effective degree of ionization values (less than 0.4). Otherwise, duplicate experiment β_{app} values agree (Experiments 3 and 4, Fig. 2). Apparent binding constants at ionic strength of 0.01 M are similar (approximately $\beta_{app} = 3.0 \pm 0.2$) up to about $\alpha_{eff} = 0.55$ (Experiments 1 to 4, 6 and 7, Fig. 2) and increase above that value to about $\beta_{app} = 3.7$ (Experiments 1, 6 and 7, Fig. 2). Apparent β's are independent of metal concentration when plotted versus alpha effective (compare Experiments 1 to 4, 6, and 7). Calcium titrations (Experiments 6 and 7) follow the same binding curve when plotted versus α_{eff} as base titrations (Experiment 1) supporting the use of α_{eff} as a master variable. Apparent binding constants shown in Fig. 2 are similar to apparent constants summarized by Paxéus and Wedborg [27] ($\log \beta$ values 1.8 to 3.3) for a number of publications.

3.3 Donnan Potential corrected apparent binding constant variation with pH

Donnan Potential adjustment of fulvic acid apparent binding constants is incorporated into the calcium ion-fulvic acid binding constant binding expression (Eq. (8)) [15]

$$\log \beta = \log ([CaA^{-n+2}]/[Ca^{+2}][A^{-n}]) - 2 \log (DP) = \log \beta_{app} - 2 \log (DP) \quad (8)$$

The Donnan Potential used in Eq. (8) is obtained from the published values [15] of Donnan Potential as a function of degree of fulvic acid ionization. In the case of calcium ion binding the effective degree of ionization (Eq. (4)) is used to determine the Donnan Potential. The Donnan Potential term is squared reflecting the ratio of charges of the calcium ion to the hydrogen ion.

Donnan Potential adjusted calcium ion-fulvic acid binding constants termed "intrinsic binding constants" are about one log unit smaller, and have less scatter when plotted versus solution pH, than the apparent constants (compare Fig. 1 with Fig. 3a and b) and vary less with solution pH and calcium ion concentration. Intrinsic binding constants for low initial calcium ion experiments had a different trend of binding constant versus solution pH (Fig. 3a) than high initial calcium experiments (Fig. 3b). Intrinsic binding constants increased with increasing pH for low initial calcium experiments (Fig. 3a). High initial calcium experiment values were constant, although values scatter somewhat below pH = 4.5.

Intrinsic binding constants for low (from about 1.2 to about 1.8, Fig. 3a) and high (from about 1.5 to 2.5, Fig. 3b), initial calcium experiments cover a similar

range. Moreover, the estimated average binding constant ($\log \beta = 1.6$) is similar to, but somewhat greater than calcium ion-carboxylate monodentate binding constants (calcium ion binding to simple substituted carboxylic acids ($\log \beta$) of about 1) [27].

Similarity of the intrinsic calcium ion-fulvic acid binding constant and the calcium ion-carboxylate monodentate binding constant is a significant result implying that on average the fulvic acid anion reacts with calcium ion in solution as a carboxylate anion. This is evidence against the significant presence of fulvic acid multidentate or phenolic calcium ion complexes. Donnan Potential corrected constants are significantly smaller than apparent binding constants for multidentate calcium ion binding ligands ($\log \beta$ values range from 3 to 5) [36, 37]. However, the calcium ion-fulvic acid binding constant is greater than that for the monocarboxylate complex. This suggests the presence of some bidentate binding sites. We are evaluating the extent of bidentate complexation (unpublished data). Bidentate sites may be most significant at low amounts of bound calcium ion.

3.4 Donnan Potential corrected apparent binding constant variation with effective degree of ionization

Donnan Potential corrected binding constants vary slightly with fulvic acid effective degree of ionization for base titrations and for calcium ion titrations (Fig. 4). In the case of low initial calcium experiment intrinsic binding constants vary from about 1.2 to about 1.8 (Fig. 4a). Higher initial calcium experiments have intrinsic binding constants above two at alpha effective less than 0.3. All other $\log \beta$ values are between 2 and about 1.5 (Fig. 4b). A minimum in the intrinsic binding constant occurs at alpha effective of about 0.6. High calcium ion experiments (Fig. 4b) constants scatter less than low initial calcium experiments (Fig. 4a), values range from 1.5 to 2.5, and ionic strength dependence is absent. Intrinsic binding constant values, over a range of pH, calcium ion concentrations, and ionic strengths, follow a general binding curve when plotted versus the effective degree of neutralization. Intrinsic binding constants (Fig. 5) increase with decreasing alpha effective at low alpha effective values (0.3 to 0.6). At low α_{eff} (more acidic solution), where there is less A^{-n} for binding, the efficiency for binding begins to increase rapidly.

The intrinsic constant increases in magnitude at low effective degree of ionization. This observation, for a soil fulvic acid, may be of importance in understanding calcium ion depletion in acid rain impacted forest soils. In these soils, depleted soil calcium concentrations appear to have an adverse effect on forest health. Higher calcium ion binding by soil fulvic acid at low effective alpha may arise because of calcium binding site heterogeneity. In particular, bident binding with ionized carboxylate and either oxygen may be the source of high calcium affinity at low alpha [36, 37].

4. Summary and conclusions

Calcium ion binding to a soil fulvic acid is modeled assuming formation of a monodentate carboxylate complex. Fulvic acid charge, expressed as the effective degree of ionization, and the Donnan Potential associated with this charge, modifies the binding constant. The Donnan Potential correction term transforms the measured apparent calcium-fulvate binding constants to intrinsic constants. Calculated intrinsic binding constants for all experimental measurements fall on a smooth curve when plotted versus effective fulvic acid charge. Intrinsic constants vary with experimental variables such as solution pH; variation is least with effective degree of ionization. Variation in the intrinsic binding constant suggest a range of calcium ion binding sites in the fulvic acid. The average value of the intrinsic binding constant ($\log \beta = 1.6$) is higher than that of a range of the calcium ion-acetate complex ($\log \beta = 0.5$) and much is less than values of bidentate and multidentate binding. Multidentate calcium ion-fulvate binding sites therefore contribute little to the observed complex formation reaction. Binding of other alkaline earth metal ions of importance in nuclear waste disposal to soil fulvic acid may be similar to that of calcium ion-fulvic acid interaction reported here. If this assumption is valid, approximate alkaline earth-fulvic acid binding constants may be estimated using the simple monodentate, carboxylate-alkaline earth ion binding constants reported in the literature with an appropriate Donnan Potential adjustment.

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