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Proton and metal ion binding to natural organic polyelectrolytes—II. Preliminary investigation with a peat and a humic acid*

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Abstract—We summarize here experimental studies of proton and metal ion binding to a peat and a humic acid. Data analysis is based on a unified physico-chemical model for reaction of simple ions with polyelectrolytes employing a modified Henderson–Hasselbalch equation. Peat exhibited an apparent intrinsic acid dissociation constant of $10^{-4.05}$, and an apparent intrinsic metal ion binding constant of: 400 for cadmium ion; 600 for zinc ion; 4000 for copper ion; 20000 for lead ion. A humic acid was found to have an apparent intrinsic proton binding constant of $10^{-2.6}$. Copper ion binding to this humic acid sample occurred at two types of sites. The first site exhibited reaction characteristics which were independent of solution pH and required the interaction of two ligands on the humic acid matrix to simultaneously complex with each copper ion. The second complex species is assumed to be a simple monodentate copper ion–carboxylate species with a stability constant of 18.

Key words: Donnan potential, heterogeneity, 2-dimensional, 3-dimensional aggregate (gel), polyelectrolyte, complexation, electrostatic potential.

INTRODUCTION

Natural weak-acid organic polyelectrolytes may exist in surface and groundwaters as two phase systems, an aqueous phase and a water containing organic gel phase. The distribution of ionic species between these two phases is regulated by chemical and membrane equilibriums. Previous investigations of proton and metal ion binding to these materials have attempted to use simple chemical equilibrium models employing aqueous phase concentrations with standard mass action and mass balance equations. Several studies have neglected the Donnan membrane potential term, and polyelectrolyte effects. Because of these omissions proton and metal ion binding constants for weak acid functional groups present in natural samples appeared to be strongly dependent on experimental conditions such as solution ionic strength, total ligand concentration, pH, and degree of neutralization. Such behavior is opposite to that exhibited by simple electrolytes, and in a practical sense limits attempts to mathematically model the metal ion complexation behavior of naturally occurring organic polyelectrolytes. To quote a recent observation on this subject by Stevenson (1982, p. 372):

> "*Serious problems are encountered in the determination of stability constants of metal complexes with humic and fulvic acids. A variety of methods have been applied, and considerable progress has been made, but agreement has not yet been reached as to how the data can best be analyzed and interpreted. The need for future research in this area is evident.*"

Solution electrochemical properties of high molecular weight natural organic materials may be regulated by their intrinsic electrolyte properties or by their structural heterogeneity. Structural heterogeneity arises because humic materials consist of three dimensional arrays having numerous side chains and functional groups. Chemical properties of these materials are similar to weak acid polyelectrolytes having a range of apparent molecular weights, solubilities, and acid strengths.

The first paper in this series (Marinsky and Reddy, 1984) presented an experimental method to characterize chemical equilibrium at reaction sites of organic weak-acid polyelectrolytes in a single or two phase system. This technique, which utilizes potentiometric titrations of weakly acidic organic polyelectrolytes in the presence and absence of metal ions, provides reliable data for ion binding reactions in these complex systems. Applied to the analysis of proton or metal ion binding by natural high molecular weight organic polyelectrolytes, this approach allows quantification of the apparent ion binding constants associated with polyion–cation interaction. Our objective in this paper is to demonstrate experimentally this approach for the accurate assessment of stability constants characterizing the complexed species formed by metal ions with repeating ligands of natural polyelectrolytes. These results provide unambiguous, quantitative evidence for the role of functional group heterogeneity in the ion binding reactions of natural materials.

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MATERIALS AND METHODS

Analytical reagent grade chemicals and grade A glassware were used in all experiments. Special precautions were taken to prevent carbon dioxide contamination of the standard sodium hydroxide used in the investigation. Peat, characterized previously (Bunzl, 1974), was transformed to the acid form by successive treatment with one normal hydrochloric acid, followed by distilled water washing. Cation exchange capacity of the peat for lead ions at pH 4 was 1.7 m-equiv/dry g; peat dissolution was reported to be negligible (Bunzl and Schultz, 1980).

Potentiometric and metal ion binding studies with peat were performed by equilibrating 0.15 g of peat (with a water content of 0.137 g) with 20 ml of a stock solution containing the metal ion of interest and the background electrolyte (sodium chloride). Hydrogen ion associated with the peat was neutralized by successive additions of a standard sodium hydroxide solution. Calcium ion, cadmium ion, lead ion, and zinc ion concentrations were monitored with appropriate radioisotopes. Copper ion concentrations were determined using the procedure of Schmidt and Dietl (1981). Potentiometric titrations of peat in the absence of metal ion and in the presence of copper ion were done with peat and solution amounts 10 times those indicated above to facilitate analytical precision. Samples were equilibrated for six hours with continuous shaking. After standing overnight, supernatant solution was assayed for pH and metal ion concentration. Each experiment was in duplicate.

Humic acid was prepared by the method of Schnitzer and Kahn (1972), and details are given by Gupta *et al.* (1980). After purification the humic acid contained 55% carbon and 2% nitrogen. Its equivalent capacity was found to be 3.5 m-equiv/g.

Detailed characterization of the humic acid sample was performed employing a suite of physical and chemical techniques. Organic material extractable from the humic acid sample was determined as a function of solution pH and electrolyte composition. For pure water less than 3% of the carbon present was extracted by a single extraction, while less than a total of 4% of the carbon was solubilized with four successive extractions. Humic acid solubilization in a 0.2 M sodium nitrate solution was 9.25% carbon extracted at pH 4.8 and 16.1 % carbon extracted at pH 5.97 (Gupta and Schindler, 1977).

Potentiometric titrations were performed by adding 100 mg of humic acid to 36 ml of background electrolyte (sodium nitrate) in a stirred cell with a nitrogen atmosphere. Following a standardized base–acid cycling procedure, titration of the humic acid was done by adding small amounts of standard sodium hydroxide solution. The end point for the potentiometric titration was defined as the titrant volume associated with the maximum of the second derivative of the change in pH with titrant volume.

Copper ion binding to humic acid was examined in a batch type experiment. One hundred milligrams of humic acid was added to 36 ml of background electrolyte in a polyethylene bottle. After an appropriate base-acid cycle, humic acid titration was accomplished by addition of a standard sodium hydroxide solution (with the appropriate background electrolyte). Subsequently, copper ion was introduced into the solution by addition of fixed amounts of a 0.005 Molar copper nitrate solution in the background electrolyte. Each sample was blanketed with nitrogen gas, sealed, and shaken for a period of thirty days to attain equilibrium.

Hydrogen and copper ion selective electrodes were employed in measurement of their solution concentrations at several fixed ionic strengths (Marinsky *et al.*, 1982).

RESULTS AND DISCUSSION

Potentiometric titration data obtained during the neutralization of synthetic (monofunctional) weak-acid polyelectrolytes have been interpreted with a modified form of the Henderson–Hasselbalch equation (equation 1)

$$\mathrm{pH} - \log(\alpha/1-\alpha) = \mathrm{p}K_a - 0.4343\, e\psi/kT = \mathrm{p}K_a\ (\mathrm{app}) \qquad (1)$$

where K_a is the intrinsic acid dissociation constant of the ionizable functional groups on the polyion, e is the electrical charge of the mobile ion, ψ is the electrical potential at the surface of the polyion, k is the Boltzmann constant, and T is the absolute temperature. The left hand side of this equation plotted versus the degree of polyion dissociation, alpha (α), extrapolated to zero degree of dissociation, yields as the ordinate intercept the intrinsic microscopic acid dissociation constant, K_a, of the repeating functional group in the synthetic polyelectrolyte. Graphical resolution of pK_a in this manner is valid since e/kT approaches zero in value as alpha approaches zero and

$$\lim(\mathrm{pH} - \log(\alpha/1-\alpha))_{\alpha\to 0} = \mathrm{p}K_a \qquad (2)$$

the variation of the apparent dissociation constant during the titration of a synthetic weak acid polyelectrolyte is thus attributable to the changing electrostatic potential of the polyion. As shown in equation (1) and illustrated in the previous paper (Marinsky and Reddy, 1984) the apparent proton dissociation constant (i.e. pK_a (app)) will, even when there is no functional group heterogeneity, exhibit a marked pH dependence due to the so-called "polyelectrolyte effect". The polyelectrolyte effect is composed of two terms, a constant representing the intrinsic proton binding properties of the repeating functional group (i.e. pK_a), and a variable representing the increased work need to be done to remove a proton from a charged moiety, the $-0.4343e\psi/kT$ term in equation (1), hereafter termed ΔpK.

In a two phase system containing an aqueous phase and a polyelectrolyte gel phase application of the modified Henderson–Hasselbalch equation (equation 1) is appropriate only for the gel phase. Since gel phase pH is inaccessible to direct measurement, potentiometry of this phase must be based on the pH of the solution phase in (Donnan membrane) equilibrium with the gel.

Potentiometric properties of a peat

The apparent acid dissociation constant for peat, calculated at three different bulk electrolyte concentrations using the measured solution pH with equation (1) varies dramatically over the course of each titration. Plots do not extrapolate to a single value independent of ionic strength (Fig. 1). The Donnan membrane potential term that prevails in these systems (Marinsky *et al.*, 1980) was used to estimate gel phase pH values for use in the Henderson–Hasselbalch equation. The results that were obtained in this way are presented in Fig. 2.

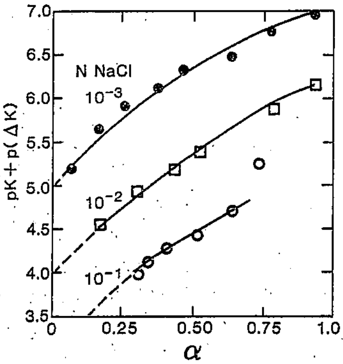

Fig. 1. A potentiometric titration of a peat in three different ionic strength solutions. The Henderson–Hasselbalch function has been calculated using the measured solution pH values. Note the ten-fold increase in the apparent ($pK + P(\Delta K)$) and the intrinsic (pK, the ordinate intercept) acid dissociation constant with a corresponding 10-fold increase in ionic strength (Marinsky *et al.*, 1980).

The marked improvement in the correlation of the potentiometric data over the course of the titration is noteworthy; the points merge and extrapolate to a single, unique value of 4.05 for the apparent intrinsic acid dissociation constant. The inflexible peat matrix maintains the volume of the gel phase fixed and independent of the external solution ionic strength over the complete neutralization range.

Variation in the Henderson–Hasselbalch function over the course of the titration is presumed to arise exclusively from the changing charge on the organic polyion, as was the case for synthetic polyelectrolytes (Marinsky and Reddy, 1984). This assumption, while valid for synthetic organic polyelectrolytes, must be critically examined for natural materials. Natural organic polyacids are heterogeneous compounds containing functional groups with a range of acid strengths. Since marked carboxylic acid functional group heterogeneity can exist in peat samples this factor certainly could have contributed to the observed variation in the Henderson–Hasselbalch function over the course of the polyacid titration.

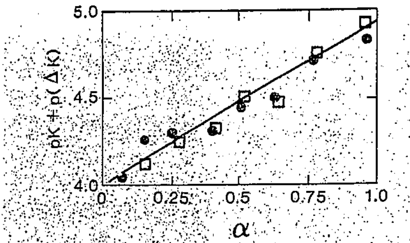

Fig. 2. A modified Henderson–Hasselbalch plot of a peat potentiometric titration at two different ionic strengths, symbols have the same meaning as shown in Fig. 1. The apparent acid dissociation constant at each experimental point has been determined with a calculated gel phase pH (Marinsky *et al.*, 1980).

Divalent metal ion–peat complex formation

The value of the free metal ion concentration within the gel phase ($M^{+}{}_{g}$), like the value of the gel phase hydrogen ion concentration, is not amenable to direct measurement. However, its value can be computed (Marinsky and Reddy, 1984).

Complexation of divalent metal ions by coordinating sites within the sphagnum peat gel has been expressed as shown below by comparing their competition with hydrogen ion for the cation binding sites (Marinsky *et al.*, 1980).

$$\mathrm{M}_b * a_{\mathrm{H}}/a_{\mathrm{M}} \times [\mathrm{HA}] = D \qquad (3)$$

In this equation all terms refer to the gel phase; M_b and [HA] refer to gel bound metal and hydrogen ions, respectively. Free metal (a_{M}) and hydrogen ion concentrations (a_{H}) within the gel were computed from the solution concentrations with equation (3) assuming a Donnan equilibrium exists between the solution and the gel.

Metal ion binding processes for peat should be similar to those occurring in synthetic polyelectrolytes. The predominant ion processes that occur in metal ion–carboxylate containing weak acid polyelectrolyte systems are ion condensation, due to the high charge density adjacent to the polyanion (Oosawa, 1957; Manning, 1969), and complex formation (Marinsky, 1973). Functional groups in peat and humic materials which are likely to bind to metal ions include hydroxyl and carbonyl groups and the aromatic carboxylates and phenolics. We sought first to establish whether binding of metal ion to peat was independent of solution pH (over the range 3–7). The apparent absence of pH independent interactions in this pH range eliminated the hydroxyl and carbonyl groups from consideration. The phenolic units and the second carboxylic moieties in any dibasic functional group had to be fully protonated in the solution pH range examined in this study as well, and it seemed unlikely that they would be involved in metal ion binding except through chelation. Thus only ion complexation of the divalent ion by the repeating monofunctional carboxylic unit (i.e. formation of a monodentate complex) was presumed to occur.

Equation (3) may be rewritten as

$$D = \beta_{M(II)}/\beta_H \tag{4}$$

where $\beta_{M(II)}$ and β_H represent the overall gel metal ion and proton binding constants, respectively. Deviation of β_H and $\beta_{M(II)}$ from their respective intrinsic values can originate in one of two ways: from the electric field due to the charged polyion at the site of reaction (i.e. the polyelectrolyte effect), or from the structural heterogeneity of the monofunctional carboxylic units in the natural material.

Variation in the experimental D value with changing polyacid neutralization should parallel the variation in the proton binding constant if electrostatic effects dominate the reaction. A plot of log D against the Henderson–Hasselbalch function should then give a straight line with a non-zero slope. On the other hand, if the characteristic shape of the Henderson–Hasselbalch function plotted versus degree of polyacid neutralization is due primarily to functional group heterogeneity, then its influence on the observed binding constant will be independent of the charge on the metal ion, since it should influence both metal ion and proton binding similarly. The value of D in this case would be expected to remain relatively constant over the range of polyacid neutralization examined. Indeed, the values of the divalent metal–hydrogen ion competition functions so measured were relatively constant over the pH and neutralization range examined here (Marinsky *et al.*, 1980). It seems that variation of the Henderson–Hasselbalch function during peat neutralization is primarily a manifestation of functional group heterogeneity.

Our data interpretation suggesting that polyelectrolyte effects do not regulate metal ion distribution in a peat–aqueous solution system is consistent with ion binding measurements of a synthetic polyelectrolyte gel. For a crosslinked polymethacrylic acid (PMA) gel (Marinsky and Reddy, 1984) the variation of ΔpK $(-0.4343e\psi/kT)$ did not exceed 0.2 pK units over the neutralization range (0.0–0.8). Gel crosslinking was sufficient to leave an inflexible resin product. As a consequence the gel volume was small and the counterion concentration was high. High counterion concentrations within the gel phase effectively screened the electric field of the charged polyion matrix. This in turn reduced the electrical potential at the complexation site and thus the electrostatic correction term. The inflexible matrix of the peat behaves in much the same way. The effective shielding by counterions within the peat gel reducing electric field effect.

The ion binding reaction shown to predominate in the peat–metal-ion systems examined here is

$$M(II) + A^- = M(II)A^+ \tag{5}$$

with all species referring to gel phase concentrations. The metal ion binding functions, $\beta_{M(II)}$, can be estimated by multiplying the computed D value by β_H. These values extrapolated to zero degree of polyacid neutralization (for 0.01 and 0.001 equiv/l ionic strength) are for cadmium, 4×10^2; zinc, 6×10^2; copper, 4×10^3; and lead, 2×10^4.

Potentiometric properties of a humic acid

Potentiometric titration data for a humic acid in sodium nitrate solutions of different concentrations (0.02, 0.2 and 2.0 M) have been interpreted using the Henderson–Hasselbalch equation. Results of this analysis, the apparent pK as a function of alpha, are plotted for the three different background electrolyte concentrations in Fig. 3. Each point corresponds to an equilibrium pH of the solution phase during each step of the humic acid neutralization. This plot yields two curves that parallel each other and differ by 0.9 pK_a units.

The superposition of the two lower curves in Fig. 3 suggests that the Donnan membrane potential term, pNa−pNa_s, is nearly the same at both solution ionic strengths. This can only happen if the water content of the humic acid gel is such that the ratio of the concentration of sodium ion in the gel and solution is about the same at both ionic strengths. An estimate of the Donnan membrane potential term is approximately 0.3 for both 0.2 and 2.0 molar sodium nitrate background electrolyte concentrations. With the most dilute sodium nitrate solution (0.02 M) the Donnan membrane potential term is estimated to be approximately 0.9. The predicted separation of the curves on this basis is approximately 0 and 0.6 in reasonable agreement with observation.

The assignment of a value of 2.25–2.3 to the apparent intrinsic acid dissociation constant of the

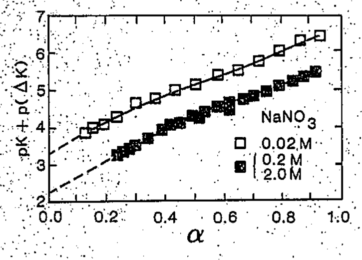

Fig. 3. Potentiometric titration of a humic acid in three different sodium nitrate solution ionic strengths (Marinsky *et al.*, 1982).

humic acid functional groups, by extrapolation of the lowest curve in Fig. 3 until it intercepts the ordinate axis, disregards the Donnan membrane potential term of approximately 0.3 and a pK_a value of 2.55–2.6 may be more correct. Also, if heterogeneity in the humic acid sample is most responsible for the shape of the curve the linear extrapolation in Fig. 3 may provide an exaggeration of the potentiometric behavior. With heterogeneity the major factor, the curve has to flatten in the lower (0.0–0.2) and the higher alpha ranges (0.9–1.0). We have synthesized a potentiometric titration curve by presuming three different acidic groups with pK values of 3, 4, and 6, respectively, to be present at a molecular ratio of 3 to 2 to 5 in a weak acidic molecular aggregate (Fig. 4). The computed points, on this basis, fall on an experimental potentiometric curve similar to that shown in Fig. 3.

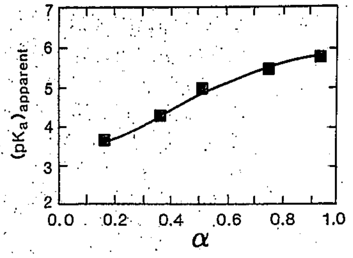

Fig. 4. A synthesized potentiometric titration curve selected to mimic the potentiometric titration behavior of the humic acid sample shown in Fig. 3. The apparent pK_a as a function of alpha was calculated assuming the acid functional groups attached to the polymer were in the ratio 3 to 2 to 5, and exhibited intrinsic pK_a's of 3, 4, and 6, respectively.

Divalent metal ion binding to a humic acid

The two functional groups most likely to be involved in the binding of metal ions by organic acid soil are aromatic carboxylates and phenolics. Their arrangement in repeating functionality units accessible to metal ion resembles most closely the two monomer units salicyclic and phthalic acids (Schnitzer and Kahn, 1972). Marinsky *et al.* (1982) in their approach to the analysis of divalent metal binding in humic acid therefore presumed that a monodentate complex, MHA^+, involving the divalent metal ion was the dominant species formed at the reaction sites of the humic acid gel. The reaction was expressed as shown:

$$[M^{+2}] + 2\,[H_2A] \rightleftharpoons [MHA^+] + [HA^-] + 2\,[H^+] \tag{6}$$

By writing equation (6) in this manner, the source of the ΔK_a term in the numerator and denominator, if predominantly due to the electric field of the charged gel matrix, will cancel, giving

$$D_1 = [MHA^+][HA^-][H^+]/[M^{+2}][H_2A] \tag{7}$$

With relatively small amounts of copper ion added to the solution the value of D_1 decreased as the copper ion concentration increased, until a constant value for D_1 was found independent of the amount of copper ion added to the system. Variation in D_1 appeared to be due to the presence of a copper ion binding site other than the assumed monodentate site. Incorporation of a second binding site into the proposed reaction model was accomplished by first forcing the resolution of a constant value for D_1. Additional copper ion bound to the humic acid gel over and above that calculated from the forced value of D_1 was assumed to be complexed at the second complexation site. This hypothetical site had to have a much stronger interaction with copper ion than carboxylic acid sites, and its interaction with copper ion did not depend on the solution pH value. A plot of the logarithm of copper bound to these energetic sites versus the logarithm of the free copper ion in solution yielded straight lines whose slopes were uniquely defined by: (1) the initial humic acid degree of neutralization prior to addition of copper ion, and (2) the ionic strength of the solution. In each case the same degree of site saturation was eventually reached (Fig. 5). The saturation capacity corresponded to 4.6% of the hydrogen ion capacity of the carboxylic acid component of the humic acid sample.

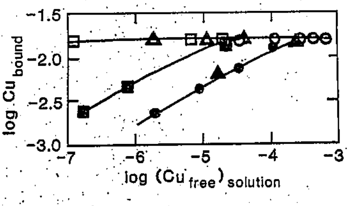

Fig. 5. Copper ion binding to a humic acid expressed as the log of copper ion bound to humic acid versus the log of the free copper ion concentration in solution. Solid symbols are for alpha = 0.2, and open symbols are for alpha = 0.8; ○—represents 2.0 M; △—represents 0.2 M; and □—represents 0.02 M sodium nitrate solution (Marinsky *et al.*, 1982).

The family of curves obtained by this data treatment merge into one when the free copper ion concentration at the site of binding within the gel is assumed to depend exclusively on the electrical field emanating from the charged surface of the humic acid gel (Fig. 6). As we have already pointed out the bulk concentration of the free mobile counterions in the solution and gel phases were about equal when the sodium nitrate background electrolyte concentration was 0.2 or 2.0 M. The bulk solution copper ion concentration could be thus multiplied by the square of the ΔK_a term defined at each alpha value by the vertical displacement of the potentiometric curve from the intercept value of 2.25–2.3 at alpha = 0 to compute this parameter.

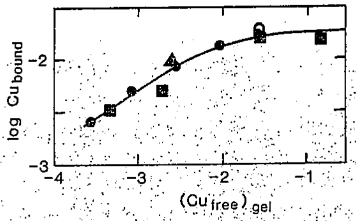

Fig. 6. Copper ion binding to a humic acid when the binding site in the gel is assumed to mimic the free-hydrogen ion behavior in the 0.2 and 2.0 molar sodium nitrate solutions. As in Fig. 5 solid symbols signify alpha = 0.2 and open symbols signify alpha = 0.8; ○—represents 2.0 M; △—represents 0.2 M; and □—represents 0.02 M sodium nitrate solution (Marinsky *et al.*, 1982).

The Freundlich isotherm that this treatment of the data resolves (Fig. 6) can be interpreted with the hypothetical reaction between copper ion and unidentified site, S, in the humic acid gel matrix

$$\mathrm{Cu} + 2\mathrm{S} = \mathrm{CuS_2} \qquad (8)$$

With copper ion binding to two independent sites (saturation capacity of these sites being twice that determined by presuming a one-to-one binding of the copper), the above reaction is consistent with the isotherm in Fig. 6. Stability constants for the proposed reaction has been estimated by interpolating points from the smooth curve in this Figure (Marinsky *et al.*, 1982).

Values of $\bar{D}$ obtained with equation (7) by forcing this approach at each ionic strength were: $D_1 = 1.6 \times 10^{-4}$ in 2.0 M sodium nitrate solution; $D_1 = 3.3 \times 10^{-4}$ in 0.2 M sodium nitrate solution; and $D_1 = 3.4 \times 10^{-4}$ in 0.03 M sodium nitrate solution. The fluctuation observed in D_1 at constant ionic strength was not felt to be significant while the D_1 value dependence on ionic strength could be attributed to the absence of activity coefficient values for the copper ion at the three ionic strengths used.

Estimate of the formation constant of the copper ion–humic acid complex, $\mathrm{CuHA^+}$, can be made by dividing D_1 by the square of the intrinsic proton dissociation constant (i.e. $\mathrm{p}K_a = 2.3$). This yields a value of 1.8×10^1 for the copper ion–humic acid complex. The magnitude of this constant is of the same order as for other monodentate carboxylate complexes with copper ion. For example, the salicylic acid–copper ion stability constant is 2.4×10^1 (Sillen and Martell, 1964).

Interaction of copper ion with a humic acid appears to result in the formation of two separate species within the gel matrix. The first species formed exhibits reaction characteristics which are independent of solution pH and which require the interaction of two sites on the humic acid matrix simultaneously with each copper ion. The number of such sites is approximately 9% of the accessible hydrogen capacity. The second complexation reaction proposed is less selective than the first, and is attributed to the formation of a complex of copper ion with monodentate carboxylate functional groups within the humic acid gel matrix. The formation constant for this species is similar to that observed for other copper monodentate complexes with carboxylate containing ligands.

RECAPITULATION

Acid dissociation constant variability has two possible sources in the gel. First the humic acid sample may be expected to have a number of different molecular combinations of carbon, hydrogen, and oxygen atoms attached to the repeating carboxylic acid units with different intrinsic dissociation constant behavior characterizing each particular assemblage. Inability to quantify this aspect has required the combination of all carboxylic acid groups in applying the Henderson–Hasselbalch equation. The variation of the $\mathrm{p}K_a$ for each unique carboxylic functionality is thus potentially attributable to a statistical parameter which arises from the treatment of all carboxylic functional groups in an equivalent manner whether or not they are in fact equivalent. In practice alpha is equal to $A_1 + A_2 + A_3 + (\ldots) + A_i$ but the ratios $A_1/1 - A_1$, $A_2/1 - A_2$, $A_3/1 - A_3$ and so on are not equivalent. Each of the individual ratios differ one from another as K_1, K_2, K_3, and so on. The variability of each unique constant, K_i, arising from this perturbation source.

The second possible source of deviation in the potentiometric plots is electrostatic in nature. In this case the increase in $\mathrm{p}K_a$ with alpha is due to the increasing electric field as the charge of the gel surface increases and enhances the concentration of mobile ions at the site of reaction.

With heterogeneity as the primary source of $\mathrm{p}K_a$ diversity in humic acid, the equilibrium between binding sites and ions other than hydrogen ion should be independent of electrostatic factors. Stability constants for the competing equilibria should as a consequence be independent of the charge of the ion, and should mimic the pattern observed for the acid equilibrium. If however, the deviation term in the apparent acid dissociation constant has to be squared the source of deviation is primarily electrostatic in nature, and the enhancement of ion concentration at the reaction site will be a function of its valence.

Copper complexation by the humic acid gel was successfully modelled by incorporation of an electrostatic correction term based on the "polyelectrolyte effect". This result was unexpected since data for peat suggested that functional group heterogeneity would be the primary source of diversity in ion binding constants. This leads to a final aspect to be examined concerning the differences in proton and metal ion binding between peat and humic acid: (1) it is possible that the peat and the humic acid have developed significant differences between carboxylate functionalities present in each sample because of source material differences and/or formation conditions, and (2) sample preparation and pretreatment may also have introduced differences in the chemical properties of carboxylate functional groups present in peat and the humic acid. Resolution of this question will be possible with the availability of standard reference humic and fulvic acids through the International Humic Substances Society.

It should be pointed out that binding site heterogeneity may have been minimized by the exhaustive acid–base cycling techniques and extensive equilibration times used in the humic acid investigation. The implications of such exhaustive sample manipulation in interpreting or extrapolating laboratory studies to humic materials as they exist in the environment is unclear.

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