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## Modeling Electrostatic and Heterogeneity Effects on Proton Dissociation from Humic Substances

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■ The apparent acid dissociation constant of humic substances increases by 2–4 pK units as ionization of the humic carboxylate groups proceeds. This change in apparent acid strength is due in part to the increase in electrical charge on the humic molecules as protons are shed. In addition, proton dissociation reactions are complicated because humic substances are heterogeneous with respect to proton dissociating groups and molecular size. In this paper, we use the Debye–Hückel theory to describe the effects of electrostatic interactions on proton dissociation of humic substances. Simulations show that, for a size-heterogeneous system of molecules, the weight-average molecular weight is preferable to the number-average value for averaging the effects of electrostatic interactions. Analysis of published data on the proton dissociation of fulvic acid from the Suwannee River shows that the electrostatic interactions can be satisfactorily described by a hypothetical homogeneous compound having a molecular weight of 1000 (similar to the experimentally determined weight-average value). Titration data at three ionic strengths, for several fulvic acid concentrations, and in the pH range from 2.9 to 6.4 can be fitted with three adjustable parameters ( $pK_{int}^0$  values), given information on molecular size and carboxylate group content.

### Introduction

Characterization of ionic equilibria in surface water and groundwater remains an important task in a variety of scientific disciplines including aquatic science, low-temperature geochemistry, and environmental science. A continuing area of uncertainty pertaining to ionic equilibria in natural waters involves protonation and ion-binding reactions of natural organic matter. Natural organic matter is composed of a complex mixture of compounds. As a result of this complexity, there has yet to be developed a single recognized approach to the treatment of ionic equilibria of these compounds in natural waters and a variety of conceptual and computational procedures has been used (1–10). Even the dissociation of protons remains a controversial issue. Marinsky and Ephraim (8) described the following four types of models used to account for the increase in apparent pK as humic carboxylate groups are titrated: (1) discrete-site models in which the humic substances are treated as if they were a collection of monoprotic acids (7, 9); (2) models in which a continuum of binding sites having varying pK values is assumed (4); (3) "pure electrostatic" models in which all sites are assumed to be chemically the same, and variations in apparent pK are ascribed to effects of electrostatic interactions resulting

from the variable humic charge (3); (4) discrete-site/electrostatic models in which the humic molecules are assumed to have more than one kind of binding site and binding is affected by electrostatic interactions (8, 10).

In attempting to calculate the extents of ion-binding reactions in natural systems, the discrete-site models have the advantage that competition effects involving hydrogen ion and metal cations can readily be taken into account; it is not clear how this can be done with continuum models. To describe the effects of ionic strength on ion-binding reactions, an electrostatic model is required. However, the "pure electrostatic" model overestimates the effects of electrostatic interactions and neglects completely the chemical heterogeneity in binding sites that is evident from structural and titration studies (11). Therefore, we consider models of the discrete-site/electrostatic type to offer the most promising approach.

The object of the research described herein was to apply the Debye–Hückel theory, as developed for macromolecules by Tanford (12), to humic substances in order to describe quantitatively effects of electrostatic interactions on the basis of molecular properties. A difficulty with this approach is that the magnitude of the effects of electrostatic interactions varies with molecular size, even for a constant-weight-based content of proton-dissociating groups. Simulations were made to investigate how to take this variation into account in an attempt to define (model) hypothetical homogeneous humic substances, the properties of which match the average properties of real humic samples. The analysis is restricted to proton dissociation at pH ≤ 7. A test of the applicability of the approach is made by analyzing the data of Ephraim (13), obtained from titrations of fulvic acid from the Suwannee River, a material that has received intensive study from many standpoints (14).

### Model Formulation

The electrostatic interaction adjustment of the dissociation equilibria for humic substances follows the method used for globular proteins by Tanford (12). This embodies the following assumptions: (1) the humic molecules are impermeable spheres; (2) the charge originating from ionization of each functional group is spread uniformly over the surface of the sphere; (3) the charge on the molecules is directly related to the degree of proton dissociation, i.e., there is no counterion binding; and (4) ionization of a group affects that of another only by electrostatic interactions. The electrostatic free energy of a molecule is calculated from the Debye–Hückel theory (12):

$$W_{el} = \frac{Z^2 e^2}{2DR} \left\{ 1 - \frac{\kappa R}{1 + \kappa a} \right\} \quad (1)$$

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where

$$\kappa = \left( \frac{8\pi e^2}{DkT} \right)^{1/2} I^{1/2} = 3.29 \times 10^9 I^{1/2} m^{-1} \quad \text{at } 25^\circ \text{C} \quad (2)$$

Ion activity coefficients are defined in the standard way; by definition,  $RT \ln \gamma$  is the difference between the electrostatic contribution to the chemical potential at a given  $I$ , and at  $I = 0$ . Equation 1 gives the electrostatic free energy,  $W_{el}$ , per molecule; therefore

$$\gamma = \exp \left[ -\frac{Z^2 e^2}{2DkT} \left( \frac{\kappa}{1 + \kappa a} \right) \right] \quad (3)$$

In addition to electrostatic interactions between simple ions in solution and the ionized humic molecule, electrostatic interactions between sites on each molecule need to be considered. At a given ionic strength we define the intrinsic equilibrium constant, which describes dissociation from an uncharged molecule. In general, the actual equilibrium constant is related to the intrinsic one by

$$K = K_{int} \exp(2wzZ) \quad (4)$$

The  $K$ 's can be either mixed or thermodynamic constants. From Tanford (12), we obtain

$$w = \frac{e^2}{2DRkT} \left( 1 - \frac{\kappa R}{1 + \kappa a} \right) \quad (5)$$

Equation 3 allows computation of the effect of the ionic strength at a given humic charge. Equation 5 allows computation of the effect of the humic charge at a given ionic strength. These expressions are next incorporated into equations describing the proton dissociation reactions of humic substances in an aqueous solution.

The dissociation of polyprotic acids was analyzed by Bjerrum (15). The progressive dissociation of protons from a polyprotic acid can be written as



In principle,  $n$  equilibrium constants can be determined experimentally, having the form

$$K_x^{M,E} = \frac{[RH_{n-x}^{x-}]a_{H^+}}{[RH_{n-x+1}^{(x-1)-}]} \quad (6)$$

The degree of deprotonation, i.e., moles of hydrogen ion dissociated per mole of polyprotic acid, is given by

$$r = \frac{\sum_{x=1}^{x=n} \left[ x \prod_{y=1}^{y=x} (K_y^{M,E}/a_{H^+}) \right]}{1 + \sum_{x=1}^{x=n} \left[ \prod_{y=1}^{y=x} (K_y^{M,E}/a_{H^+}) \right]} \quad (7)$$

The experimentally determined mixed dissociation constants are now expressed in terms of intrinsic dissociation constants at zero ionic strength. To do this we need to consider the following: (1) statistical effects, which result because a given general species,  $RH_{n-x}^{x-}$ , consists of more than one component, each with the same degree of molecular deprotonation, but with different functional groups deprotonated; (2) the effect of ionic strength on proton dissociation; and (3) the effect of molecular charge on proton dissociation.

Considering only the statistical effects first, it can be shown that

for  $x = 1$

$$\prod_{y=1}^{y=x} (*K_y^{M,E}/a_{H^+}) = \sum_{i=1}^{i=n} *K_{int,i}^M/a_{H^+} \quad (8)$$

for  $x = 2$

$$\prod_{y=1}^{y=x} (*K_y^{M,E}/a_{H^+}) = \sum_{i=1}^{i=n-1} \sum_{j=i+1}^{j=n} *K_{int,i}^M *K_{int,j}^M/a_{H^+}^2 \quad (9)$$

for  $x = 3$

$$\prod_{y=1}^{y=x} (*K_y^{M,E}/a_{H^+}) = \sum_{i=1}^{i=n-2} \sum_{j=i+1}^{j=n-1} \sum_{k=j+1}^{k=n} *K_{int,i}^M *K_{int,j}^M *K_{int,k}^M/a_{H^+}^3 \quad (10)$$

and so on. (The \* indicates that effects of electrostatic interactions are not yet considered.) For brevity we define the expression  $\langle K \rangle_n^p$  to mean the sum of all products containing  $K_1, K_2, \dots, K_p$ , where each product consists of  $p$  components. For example:

$$\langle K \rangle_4^2 = K_1K_2 + K_1K_3 + K_1K_4 + K_2K_3 + K_2K_4 + K_3K_4 \quad (11)$$

$$\langle K \rangle_5^3 = K_1K_2K_3 + K_1K_2K_4 + K_1K_2K_5 + K_1K_3K_4 + K_1K_3K_5 + K_1K_4K_5 + K_2K_3K_4 + K_2K_3K_5 + K_3K_4K_5 \quad (12)$$

Thus eq 7 becomes

$$r^* = \frac{\sum_{x=1}^{x=n} x \langle *K_{int}^M \rangle_n^x / a_{H^+}^x}{1 + \sum_{x=1}^{x=n} \langle *K_{int}^M \rangle_n^x / a_{H^+}^x} \quad (13)$$

The effect of ionic strength on the proton dissociation reaction is taken into account by the use of activity coefficients; thus, for the experimentally determined dissociation constants

$$K_y^{M,E} = K_y^{0,E} (\gamma_{y-1}/\gamma_y) \quad (14)$$

and

$$\prod_{y=1}^{y=x} K_y^{M,E} = \frac{1}{\gamma_x} \prod_{y=1}^{y=x} K_y^{0,E} \quad (15)$$

(Note that when successive  $K_y^{M,E}$  terms are multiplied together, activity coefficients in the numerator and denominator cancel, except for the final term.) Thus eq 13 becomes

$$r^* = \frac{\sum_{x=1}^{x=n} \frac{x}{\gamma_x} \langle *K_{int}^0 \rangle_n^x / a_{H^+}^x}{1 + \sum_{x=1}^{x=n} \frac{1}{\gamma_x} \langle *K_{int}^0 \rangle_n^x / a_{H^+}^x} \quad (16)$$

where the \* signifies that the effect of molecular charge on  $K_{int}^0$  has not yet been considered.

To take account of molecular charge effects, we replace  $*K_{int,i}^0$  by  $K_{int,i}^0 \exp[-2w_0(i-1)]$  where  $w_0$  is the  $\kappa$ -independent part of the expression for  $w$  in eq 5, i.e.

$$w_0 = e^2/2DRkT \quad (17)$$

This gives

$$r = \frac{\sum_{x=1}^{x=n} \frac{x}{\gamma_x} \langle K_{int}^0 \rangle_n^x \prod_{i=1}^x \exp[-2w_0(i-1)] / a_{H^+}^x}{1 + \sum_{x=1}^{x=n} \frac{1}{\gamma_x} \langle K_{int}^0 \rangle_n^x \prod_{i=1}^x \exp[-2w_0(i-1)] / a_{H^+}^x} \quad (18)$$

Equation 18 describes proton dissociation as a function of pH and ionic strength. The parameters are the  $n$  intrinsic acid-dissociation constants, the number of carboxylate groups per molecule, and the radius of the molecule (i.e.,  $K_{int,1}^0, K_{int,2}^0, \dots, K_{int,n}^0$ ;  $n$ ; and  $R$ ). Tanford (12) showed that the above derivation could be simplified. In the absence

of effects of electrostatic interactions, eq 13 can be expressed as

$$r^* = \sum_{x=1}^{x=n} \frac{{}^*K_{\text{int},x}^M / a_{\text{H}^+}}{1 + {}^*K_{\text{int},x}^M / a_{\text{H}^+}} \quad (19)$$

If the approximation is now made that the average free energy per molecule can be replaced by the free energy of the average molecule (12), then we can use eq 4 to write

$$r = \sum_{x=1}^{x=n} \frac{K_{\text{int},x}^M \exp(2w\bar{Z}) / a_{\text{H}^+}}{1 + K_{\text{int},x}^M \exp(2w\bar{Z}) / a_{\text{H}^+}} \quad (20)$$

where  $\bar{Z}$  is the average charge per molecule. Thus

$$r = \sum_{x=1}^{x=n} \frac{K_{\text{int},x}^P \exp(2w\bar{Z}) / a_{\text{H}^+} / \gamma_1}{1 + K_{\text{int},x}^P \exp(2w\bar{Z}) / a_{\text{H}^+} / \gamma_1} \quad (21)$$

$r =$

$$\sum_{x=1}^{x=n} \frac{K_{\text{int},x}^P \exp \left[ \frac{e^2}{2DRkT} \left[ 2\bar{Z} + \frac{(1-2\bar{Z})\kappa R}{1+\kappa a} \right] \right] / a_{\text{H}^+}}{1 + K_{\text{int},x}^P \exp \left[ \frac{e^2}{2DRkT} \left[ 2\bar{Z} + \frac{(1-2\bar{Z})\kappa R}{1+\kappa a} \right] \right] / a_{\text{H}^+}} \quad (22)$$

For deprotonation only, and with no counterion binding we have  $\bar{Z} = -r$ , thus

$$r = \sum_{x=1}^{x=n} \frac{K_{\text{int},x}^P \exp \left[ \frac{e^2}{2DRkT} \left[ -2r + \frac{(1+2r)\kappa R}{1+\kappa a} \right] \right] / a_{\text{H}^+}}{1 + K_{\text{int},x}^P \exp \left[ \frac{e^2}{2DRkT} \left[ -2r + \frac{(1+2r)\kappa R}{1+\kappa a} \right] \right] / a_{\text{H}^+}} \quad (23)$$

Equation 23 is an approximation of eq 18, which is exact within the assumptions of the model. Equation 23 has the same parameters used with eq 18. The advantage of eq 23 compared to eq 18 is its much greater ease of evaluation, because it does not involve the combinatorial terms in  $K_{\text{int}}$ . This becomes significant when  $n$  is large, and/or where competition for binding among many cations is being considered.

Equation 23 applies least well to small molecules because the approximation made regarding average properties becomes less valid when  $n$  is small. This is because the proper average should be over molecules that are able to shed a proton, not for all molecules. The average used includes molecules with all  $n$  protons dissociated and, therefore, always overestimates the effects of electrostatic interactions. Thus, in the extreme, if  $n = 1$ , the only effect of electrostatic interactions is via the activity coefficient of the product of proton dissociation, whereas eq 23 would give an effect ascribed to the increase in charge, i.e.,  $Z = -r$ . As a result of  $\text{pK}$  for a monoprotic acid would vary with the degree of dissociation, an obvious impossibility. The problem diminishes as  $n$  increases, until eq 18 and 23 give nearly identical results at  $n = 20$ .

In order to simulate effects of electrostatic interactions on proton binding and the effect of size heterogeneity, we consider the following hypothetical system. "Humic molecules" of different molecular size are generated from units each of molecular weight 200 and density  $1.5 \text{ g cm}^{-3}$  (see below). For each unit, one carboxylate group is contributed. The resulting molecules are all spherical. The size of a given molecule is denoted by  $x$ -mer where  $x$  is the

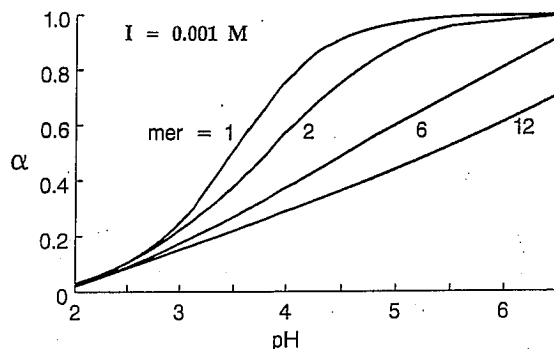


Figure 1. Plots of degree of dissociation ( $\alpha$ ) vs pH for hypothetical humic substances of molecular weight 200 (mer = 1), 400 (mer = 2), 1200 (mer = 6), and 2400 (mer = 12). The plots were calculated with eq 18. Ionic strength 0.001 M.

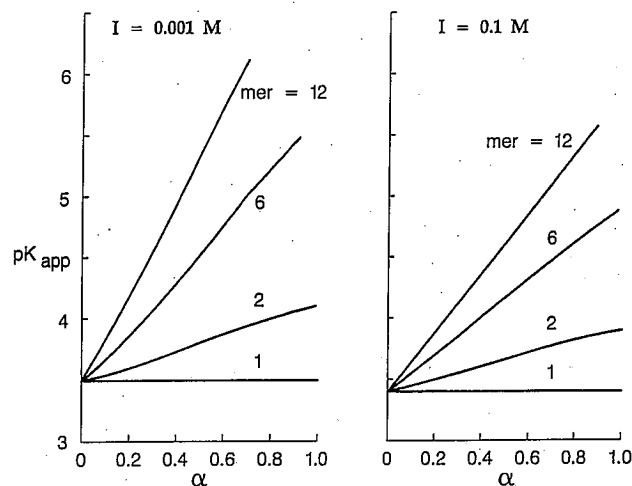


Figure 2. Dependence of apparent  $\text{pK}$  ( $\text{pK}_{\text{app}}$ ) on degree of dissociation ( $\alpha$ ) for hypothetical humic substances of molecular weight 200 (mer = 1), 400 (mer = 2), 1200 (mer = 6), and 2400 (mer = 12). The plots were calculated with eq 18. Left panel: ionic strength 0.001 M. Right panel: ionic strength 0.1 M.

number of units. For example, a 3-mer would have a molecular weight of 600, a molecular radius of 0.54 nm, and three carboxylate groups. To avoid complications due to chemical heterogeneity of the carboxylate groups, they are all assigned a fixed intrinsic  $\text{pK}$  of 3.5. It is emphasized that this system is simply used to generate hypothetical molecules of different sizes. We are not suggesting that real humic substances comprise identifiable subunits.

Figure 1 shows how proton dissociation depends upon molecular weight. The higher is the molecular weight, the greater is the possibility for buildup of charge and consequent hindrance of proton dissociation. This is also illustrated by the dependence on  $\alpha$  of the apparent acid dissociation constant, defined by

$$\text{pK}_{\text{app}} = \text{pH} - \log_{10} (\alpha / 1 - \alpha) \quad (24)$$

As shown in Figure 2, when there are no electrostatic effects (mer = 1), the value of  $\text{pK}_{\text{app}}$  is constant, but when significant charge buildup can occur (mer = 12),  $\text{pK}_{\text{app}}$  can vary more than 2  $\text{pK}$  units. The electrostatic effect diminishes with ionic strength (Figure 2).

**Effect of Molecular Size Heterogeneity on Proton Dissociation.** In addition to electrostatic perturbations (with their molecular weight dependence) affecting proton dissociation of humic substances, molecular heterogeneity may also be significant. We now consider proton dissociation for samples consisting of mixtures of molecules. Each type of molecule in a mixture is generated as described above.

Table I. Molecular Weight Distributions of Hypothetical Humic Substances, Used for Simulation Calculations<sup>a</sup>

mer	distribn A		distribn B		distribn C		distribn D		distribn E	
	no. fractn	wt fractn	no. fractn	wt fractn	no. fractn	wt fractn	no. fractn	wt fractn	no. fractn	wt fractn
1	0	0	0	0	0.1429	0.0357	0.3145	0.0769	0.3535	0.1111
2	0	0	0	0	0.1429	0.0714	0.1572	0.0769	0.1767	0.1111
3	0	0	0	0	0.1429	0.1071	0.1048	0.0769	0.1178	0.1111
4	1	1	0	0	0.1429	0.1428	0.0786	0.0769	0.0884	0.1111
5	0	0	1	1	0.1429	0.1785	0.0629	0.0769	0.0707	0.1111
6	0	0	0	0	0.1429	0.2142	0.0924	0.0769	0.0589	0.1111
7	0	0	0	0	0.1429	0.2499	0.0449	0.0769	0.0505	0.1111
8	0	0	0	0	0	0	0.0393	0.0769	0.0442	0.1111
9	0	0	0	0	0	0	0.0349	0.0769	0.0392	0.1111
10	0	0	0	0	0	0	0.0315	0.0769	0	0
11	0	0	0	0	0	0	0.0286	0.0769	0	0
12	0	0	0	0	0	0	0.0262	0.0769	0	0
13	0	0	0	0	0	0	0.0242	0.0769	0	0
$\bar{M}_n$	800		1000		800		800		636	
$\bar{M}_w$	800		1000		1000		1400		1000	

<sup>a</sup>The molecular weight of a given type of humic molecule is  $200 \times \text{mer}$ .  $\bar{M}_n$  and  $\bar{M}_w$  are number- and weight-average molecular weights, respectively.

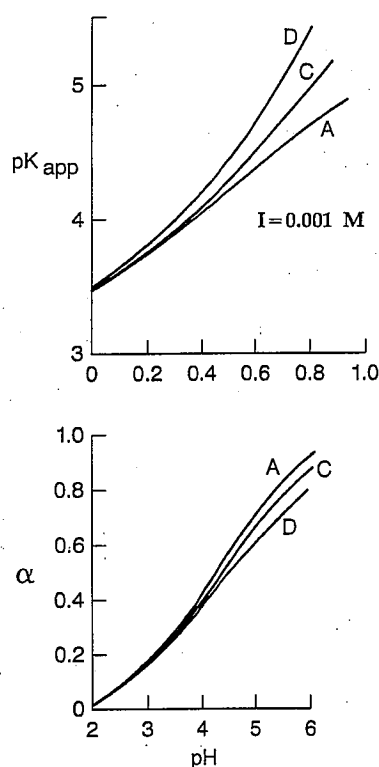


Figure 3. Effect of molecular heterogeneity on proton dissociation from hypothetical humic substances. Curves were calculated by using eq 18 for molecular weight distributions A, C, and D (see Table I). In each case the number-average weight is 800.

Three hypothetical molecular weight distributions are considered. In the first, a monodisperse system, all molecules have the same molecular weight. The second is defined such that the weight fraction of each type of molecule is proportional to the molecular weight of that molecule; in this distribution the number fraction of each type of molecule is constant. In the third distribution the weight fraction of each type of molecule is constant. Table I summarizes the distributions employed for simulation.

Figure 3 shows simulations for a fixed number-average molecular weight ( $\bar{M}_n$ ) of 800, with weight-average molecular weights ( $\bar{M}_w$ ) of 800, 1000, and 1400 (cf. Table I). It is seen that increasing polydispersity leads to progressive divergence of the plots of  $pK_{app}$  vs  $\alpha$  and  $\alpha$  vs pH. Con-

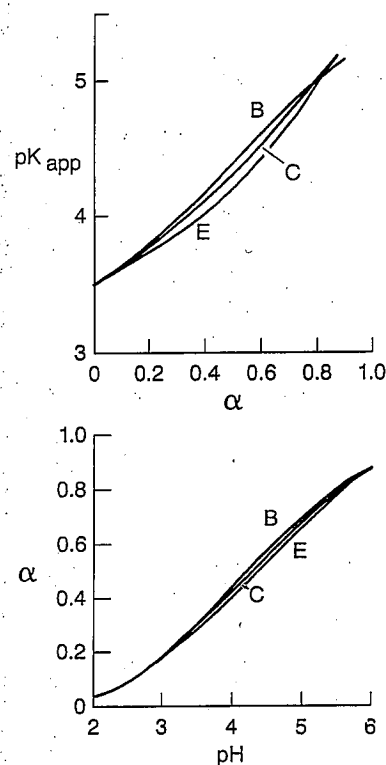


Figure 4. Effect of molecular heterogeneity on proton dissociation from hypothetical humic substances. Curves were calculated by using eq 18 for molecular weight distributions B, C, and E (see Table I). In each case the weight-average molecular weight is 1000.

trasting results are obtained for a fixed  $\bar{M}_w$  (Figure 4). In this case the plots for different  $\bar{M}_n$  diverge initially, but converge as proton dissociation increases. In the light of these results, we propose that  $\bar{M}_w$  is preferable to  $\bar{M}_n$  as a basis for modeling proton dissociation from humic substances; i.e., if it is desired to represent a heterogeneous humic sample by a hypothetical homogeneous material, then the latter should have a molecular weight equal or near to the weight-average molecular weight of the real sample.

It should be noted that, in the above simulations, we have assumed that the number of carboxylate groups per gram of humic substance is constant. A further complication might be that this is not the case; for example, there

**Table II. Summary of Fitting Proton Titration Data for Fulvic Acid from the Suwannee River (11), Using eqs 18 and 23 and Assuming Three Pairs of Carboxylate Groups per Molecule (See Text)<sup>a</sup>**

	eq 18	eq 23
$pK_{int,1}^0$	2.53 (0.16)	2.39 (0.04)
$pK_{int,2}^0$	3.75 (0.04)	3.50 (0.02)
$pK_{int,3}^0$	5.65 (0.05)	5.54 (0.03)
RMSD in pH	0.067	0.070

<sup>a</sup>RMSD, root mean square deviation. Values in brackets are standard errors.

is a general tendency for the number of oxygen-containing functional groups to be less for aquatic humic acids than for aquatic fulvic acids, and for the humic acids to be of greater molecular weight (16). On the other hand, the fractionation study of Leenheer et al. (17) showed no systematic dependence of carboxylate group content with either number-average or weight-average molecular weight for 15 fractions of fulvic acid from the Suwannee River separated on silica gel. At present, therefore, it is not clear how carboxylate group content depends on molecular weight. The approach described in this paper would, however, allow simulation calculations to be performed for hypothetical relations.

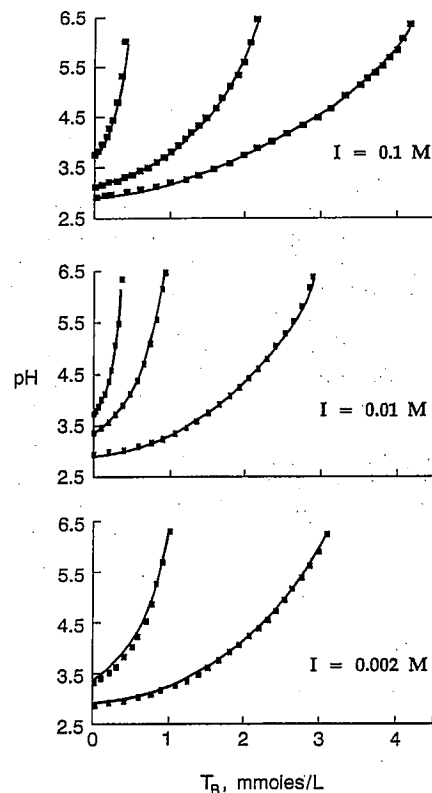
**Fitting Experimental Data for Fulvic Acid from the Suwannee River.** Values of  $\bar{M}_n$  and  $\bar{M}_w$  for fulvic acid from the Suwannee River are in the ranges 600–1000 and 900–1500, respectively (18–21). The carboxylate group content is  $(6.0\text{--}6.2) \times 10^{-3} \text{ mol g}^{-1}$  (22). The partial specific volume in aqueous solution is in the range 0.465–0.69  $\text{cm}^3 \text{ g}^{-1}$ , depending upon concentration (21, 23). On the basis of these data we propose a hypothetical homogeneous material anticipated to exhibit electrostatic interaction properties similar to those of the real material; the model substance has a molecular weight of 1000, six carboxylate groups per molecule, and a density of 1.5  $\text{g cm}^{-3}$ . The molecular weight and density correspond to a molecular radius of 0.64 nm. Only carboxylate groups are assumed to ionize in the pH range considered ( $\text{pH} < 7$ ).

The experimental data used for fitting were those of Ephraim (13). The data sets consist of 138 points covering a pH range of 2.9–6.4, a range of concentration of fulvic acid of 0.1–1  $\text{g dm}^{-3}$  and an ionic strength range of 0.0015–0.1  $\text{mol dm}^{-3}$ . Referring to eqs 18 and 23, the available adjustable parameters are just the  $pK_{int}^0$  values. Four possibilities were considered as follows: (1) a single  $pK_{int}^0$  value, i.e., six identical COOH groups; (2) two  $pK_{int}^0$  values, each applying to three COOH groups; (3) three  $pK_{int}^0$  values, each applying to two COOH groups; and (4) six  $pK_{int}^0$  values, i.e., six different COOH groups. Parameter optimization was performed by minimizing  $\sum (\text{pH}_{\text{meas}} - \text{pH}_{\text{calc}})^2$ , where the subscripts refer to measured and calculated pH, respectively.

Poor fits were obtained with a single value of  $pK_{int}^0$ . The three- $pK_{int}^0$  model gave significantly better fits than the two- $pK_{int}^0$  version. When six different values of  $pK_{int}^0$  were tried, the optimization algorithm failed to give convergence, but it was clear that the fit would not have been significantly better than that for three  $pK_{int}^0$  values. Optimized parameter values for the three- $pK_{int}^0$  case are presented in Table II. Plots of measured and calculated titration data are shown in Figure 5.

#### Discussion and Conclusions

Given knowledge of average molecular dimensions of humic substances, application of the Debye–Hückel theory provides a straightforward way to separate electrostatic



**Figure 5.** Solution pH values plotted as a function of total base added ( $T_B$ ) for titrations of fulvic acid from the Suwannee River. Solid lines are calculated by using eq 18 with three  $pK_{int}$  values (Table II); points are experimental values from Ephraim (13).

effects on proton dissociation from the effects of heterogeneity in dissociating groups. The successful fitting of titration data for fulvic acid from the Suwannee River, especially bearing in mind the wide ionic strength range covered, suggests that the electrostatic effects are described reasonably quantitatively. However, it is clearly desirable to test the model further, by analyzing titration data obtained over wider ranges of pH for humic substances with different (known) average molecular weights. With regard to size heterogeneity within a given humic sample, the present results suggest that it can be ignored in modeling ion binding, as long as an appropriate average molecular size is adopted for computing electrostatic effects. Studies on humic preparations of greater polydispersity might indicate circumstances under which size heterogeneity needs to be explicitly accounted for. Should a need arise, the present modeling approach could readily be adapted to simulate the influence of such heterogeneity.

#### Glossary

$r$	moles of protons dissociated per mole of humic substance
$n$	total moles of carboxylate group per mole of humic substance
$R$	radius of the humic molecule
$a$	sum of the radius of the humic molecule ( $R$ ) and distance of closest approach of counterion
$Z$	charge on the humic molecule
$z$	charge on combining ion (+1 in the case of $\text{H}^+$ ion)
$e$	proton charge
$D$	dielectric constant of water
$k$	Boltzmann constant
$\kappa$	Debye parameter ( $\text{m}^{-1}$ )
$\gamma_x$	activity coefficient of species $x$
$w$	electrostatic interaction factor
$T$	temperature (K)
$W_{el}$	electrostatic free energy
$I$	ionic strength ( $\text{mol dm}^{-3}$ )

$\alpha$	$r/n$ , i.e., the degree of dissociation of the humic substance
$K_x^M$	mixed dissociation constant (function of $I$ ); $[RH_{n-i}]a_{H^+}/[RH_{n-i+1}]$
$K_x^0$	dissociation constant in terms of activities; $a_{RH_{n-i}}a_{H^+}/a_{RH_{n-i+1}}$
$K_{int,x}^M$	intrinsic dissociation constants, i.e., referring to dissociation from species with a charge of zero
$K_{int,x}^0$	
$K_{x,E}^{M,E}$	experimentally determined mixed dissociation constant

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#### Literature Cited

- Buffle, J. *Complexation Reactions in Aquatic Systems*; John Wiley and Sons: New York, 1988.
- Posner, A. M. Titration curves of humic acid. In *Proceedings of the 8th International Congress of Soil Science*, Part II; Bucharest, Romania, 1964.
- Wilson, D. E.; Kinney, P. *Limnol. Oceanogr.* 1977, 22, 281-289.
- Perdue, E. M.; Lytle, C. R. A distribution model for binding of protons and metal ions by humic substances. *Environ. Sci. Technol.* 1983, 17, 654-660.
- Cabaniss, S. E.; Shuman, M. S.; Collins, B. J. Metal-organic binding: A comparison of models. In *Complexation of Trace Metals in Natural Waters*; Kramer, C. J. M., Dunker, J. C., Eds.; Martinus Nijhoff/Dr. J. W. Junk Publishers: Boston, MA, 1984; pp 165-179.
- Perdue, E. M. Acidic functional groups of humic substances. In *Humic Substances, in Soil, Sediment, and Water—Geochemistry, Isolation, and Characterization*; Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; John Wiley and Sons, Inc.: New York, 1985; pp 493-526.
- Paxeus, N.; Wedborg, M. *Anal. Chim. Acta* 1985, 169, 87-98.
- Marinsky, J. A.; Ephraim, J. *Environ. Sci. Technol.* 1986, 20, 349-354.
- Gregor, J. E.; Powell, H. K. J. *J. Soil Sci.* 1988, 39, 1-10.
- Tipping, E.; Backes, C. A.; Hurley, M. A. *Water Res.* 1988, 22, 597-611.
- Ephraim, J.; Alegret, S.; Mathuthu, A.; Becking, M.; Malcom, R. L.; Marinsky, J. A. *Environ. Sci. Technol.* 1986, 20, 354-366.
- Tanford, C. *Physical Chemistry of Macromolecules*; Wiley: New York, 1961.
- Ephraim, J. H. Studies of the protonation and metal ion complexation equilibria of natural organic acids: fulvic acids. Ph.D. Thesis, State University of New York at Buffalo, Buffalo, NY, 1986.
- Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures*; Averett, R. C., Leenheer, J. A., McKnight, D. M., Thorn, K. A., Eds.; U.S. Geological Survey Open-File Report 87-557, 1989.
- Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*; Hoase: Copenhagen, Denmark, 1941.
- Thurman, E. M. *Organic Geochemistry of Natural Waters*; Nijhoff/Junk: Dordrecht, The Netherlands, 1985.
- Leenheer, J. A.; Brown, P. A.; Noyes, T. I. Implications of mixture characteristics on humic-substance chemistry. In *Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants*; Suffet, I. H., MacCarthy, P., Eds.; Advances in Chemistry Series 219; American Chemical Society: Washington, DC, 1989; pp 25-39.
- Thurman, E. M.; Wershaw, R. L.; Malcolm, R. L.; Pinckney, D. *Org. Geochem.* 1982, 4, 27-35.
- Aiken, G. R.; Malcolm, R. L. *Geochim. Cosmochim. Acta* 1988, 55, 2177-2184.
- Aiken, G. R.; Brown, P. A.; Noyes, T. I.; Pinckney, D. J. Molecular size and weight of fulvic and humic acids from the Suwannee River. In *Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures*; Averett, R. C., Leenheer, J. A., McKnight, D. M., Thorn, K. A., Eds.; U.S. Geological Survey Open-File Report 87-557, 1989; pp 163-178.
- Reid, P. M.; Wilkinson, A. E.; Tipping, E.; Jones, M. N. *Geochim. Cosmochim. Acta* 1990, 54, 131-138.
- Thurman, E. M.; Malcolm, R. L. In *Aquatic and Terrestrial Humic Materials*; Christman, R. F., Gjessing, E. T., Eds.; Ann Arbor Science Publishers: Stoneham, MA, 1983.
- Brown, P. A.; Leenheer, J. A. Significance of density determination in molecular structures comprising fulvic acid from the Suwannee River. In *Humic Substances in the Suwannee River, Georgia: Interactions, Properties, and Proposed Structures*; Averett, R. C., Leenheer, J. A., McKnight, D. M., Thorn, K. A., Eds.; U.S. Geological Survey Open-File Report 87-557, 1989; p 311-330.

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