Potentiometric Study on the Proton Binding of Humic Substances

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The acid-base properties of humic substances (HS) (humic acid (HA) and fulvic acid (FA)) extracted from weathered coal, peat and soils obtained from International Humic Substance Society (IHSS) and Chinese natural samples were investigated by potentiometric titration in 0.050~1.00 M NaClO$_4$ solution. For the purpose of comparison, similar titrations were carried out on the homogeneous polymeric acid, polyacrylic acid (PAA). Titrations were conducted with 0.500 g/L HA or FA solution in the range of pH 3.0 ~ 11.2 under a nitrogen gas atmosphere at 298 K. Based on the conceptual model proposed for the cation-humic interaction considering the heterogeneous composition and polyelectrolyte property of humic substances (HS), the apparent dissociation constant expressed by $pK_{i,app} = pK_i + m_i pcH - b \log [Na^+]$ ($i = 1$ for carboxylic and $i = 2$ for phenolic groups) for $K_{app} = [H^+][R^-]/[HR]$ was applied to the titration results. In the expression, pK_i, m_i, and b are constant parameters depending on the HS. The result indicated that the amount of total carboxylic groups per gram HS decreased in the order of 7.2 meq/g for FA (coal) > 5.1 meq/g for FA (peat) > 4.4 meq/g for HA (peat) > 3.4 ~ 4.5 meq/g for HA (soil), and that the value of $pK_1/(1-m_1)$, which corresponds to $pK_{1,app}$ at α (degree of dissociation) = 0.5, increased in the order of 3.1 ~ 3.3 for FA (coal) < 3.5 for HA (peat) ≈ 3.6 for FA (peat) < 3.7 ~ 4.0 for HA (soil). As compared with the fitted values of $m_1 = 0.45 ~ 0.55$ for PAA, the values were larger for HS (0.54 ~ 0.70) indicating the heterogeneous distribution of the –COOH in HS. The fitted values of b were larger for PAA (0.30 ~ 0.39) than for HS (0.15 ~ 0.29) and higher for HA than for FA, reflecting the structure of the electrical double layer formed around the macromolecule, which in turn depends on the density of the anionic sites, molecular weight and conformation of HS.

1. Introduction

Humic substances (HS) are complex mixtures of refractory high-molecular weight organic materials formed by the decomposition and condensation of plant, animal and microbial materials. They are abundant and persistent in the biosphere and immediate subsurface, being present in particulate and dissolved forms in soils, waters and sediment. Since they contain functional groups such as carboxyls and phenols, they extensively interact with cations (protons and metal ions) and control the acidity of natural waters, speciation and the transport of metal ions.[1-5] However, when we try to estimate their effect on speciation, we are confronted with the problem that a humic substance cannot be treated as a simple complex-forming ligand.[1-8] This is because a HS is not a single well-defined molecule but a mixture of various heterogeneous macromolecules containing a variety of functional groups resulting in polyelectrolyte and polyfunctional properties.

Among the interactions of HS with cations, the interaction with protons (acid-base property) is one of the most important and fundamental because the interaction of HS with metal ions is strongly dependent on pH. Numerous attempts have been carried out to model and describe cation-humic interactions,[8-23] and in many of these cases, to apply the findings to proton-humic interaction.[8, 9, 14-19, 22] The most advanced models are Model V/VI[2, 8] and the NICA-Donnan model[9-14] where the heterogeneous site distribution in HS is described with a collection of discrete simple chemical reactions or with continuous functions. The effect of crowded negative charges on the macromolecules is described by considering the Donnan equilibrium. By considering these models, the following simplified equation was proposed to describe the interaction of cations with HS in our previous paper.[23]

$$\log K_{app} = \log K + a \log \alpha - b \log [Na^+] - m \log [M^{z+}], \quad (1)$$

where

$$M^{z+} + zR^- \rightleftharpoons M^{z+} \cdot zR^- \qquad K_{app} = \frac{[M^{z+} \cdot zR^-]}{[M^{z+}][R^-]} \quad (2)$$

and where $[M^{z+} \cdot zR^-]$ is the concentration of the cation bound to the HS, $[M^{z+}]$ is the concentration of the free cation, and $[R^-] = (C_R - z[M^{z+} \cdot zR^-])\alpha$ (C_R is a total concentration of proton exchanging sites and a is a degree of dissociation). Log K, m, a, and b are constant parameters depending on the cation and HS. $[Na^+]$ is the concentration of the background cation competing with the cation of interest. The objective of the present study is to apply this model to the interaction of HS with protons in order to test the applicability of the model and to discuss the characteristics of HS of various origins. For the proton-binding of HS, eq 1 can be expressed by

$$pK_{app} = pK + m pcH - b \log [Na^+], \quad (3)$$

where $pcH = -\log [H^+]$ and

$$HR \rightleftharpoons H^+ + R^- \qquad K_{app} = \frac{[H^+][R^-]}{[HR]} \quad (4)$$

Potentiometric titrations were conducted for humic (HA) and fulvic acids (FA) extracted from weathered coal, peat and soils obtained from the International Humic Substance Society (IHSS) and from China as well as for polyacrylic acids in 0.050–1.00 M NaClO$_4$ solution. The results were analyzed by applying eq 3 to carboxylic and phenolic groups of these HS samples, and the values of the obtained parameters— C_R^W (the amount of functional groups per unit weight of HS), pK, m,

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and *b*—were discussed in view of the heterogeneity and other properties of HS of various origins.

2. Experimental

Humic substances. Three samples were purchased from the International Humic Substance Society (IHSS): humic acid extracted from soil (Cat. No.1 S102H), abbreviated as HA (soil, IHSS), and humic and fulvic acids extracted from peat (Cat. No.1 R107H and Cat. No.1 R107F), abb. as HA (peat, IHSS) and FA (peat, IHSS), respectively. Other samples were kindly provided by Dr. Tao Zuyi, Lanzhou University (P.R. China), which were extracted according to the IHSS procedure: fulvic acid extracted from coal (Gongxian, Henan province, P.R. China), abb. as FA(coal, Gongxian); and humic acids extracted from the soil of south of China (Daya Bay, Guangdong province, P.R. China) and from the soil of northeast of China (Helongjiang province, P.R. China), abb. as HA(soil, Daya Bay) and HA(soil, Helongjiang), respectively. All three were characterized elsewhere,[24–26] Polyacrylic acids (PAA, [–CH$_2$CH(COOH)–]$_n$) (MW = 2000, 5000 and 450000 Daltons, powder from Aldrich Chemical Co. and MW = 90000 Daltons, 25 wt% aqueous solution) from Polysciences were used as received.

Potentiometric titration. Potentiometric titration was conducted with an automatic titrator (COM-1500, HIRANUMA, Japan) equipped with 50-mL water-jacketed glass vessel at (298.2 ± 0.1) K under a nitrogen atmosphere. A combination electrode (TOA Dempa, GST-5421C) was used for pcH measurement and its reference electrode was filled with 4.0 M NaCl (instead of KCl) to avoid precipitation of KClO$_4$ at the junction of the electrode and the solution. The calibration of the electrode for the conversion of the pH reading into pcH was conducted as described previously.[27] In the titration, the solution in the reaction vessel was bubbled with nitrogen gas that had been passed through a dilute NaOH solution and NaClO$_4$ solution in sequence. The CO$_2$-free NaOH solution of 0.1044 mol/L was used as a titrant. De-ionized water (Milli-Q® Pureline, Yamato, Japan) was used to prepare the solution. The HS concentration of all the stock solution was 1000 mg/L. FA was directly dissolved in the solution. HA was first dissolved into dilute NaOH solution (~pH 11.5) and placed under a nitrogen atmosphere overnight. Then, an equal amount of HClO$_4$ was added to this solution to compensate for the amount of previously added NaOH. Finally, de-ionized water was used to dilute the solution to reach a fixed volume.

3. Results and Discussion

Proton dissociation of polyacrylic acid. The potentiometric titration directly gives the relation of added amount of alkali (NaOH) and the resultant pH. This result can been reorganized to give the total concentration of dissociated functional groups [R$^-$] as a function of [H$^+$] for each titration point by using the following relation:

$$[R^-] = \frac{[H^+] + C_b V_b/(V_0 + V_b) - [OH^-]}{V_0/(V_0 + V_b)} \qquad (5)$$

where C_b and V_b are the concentration of NaOH and the volume of added titrant, respectively, and V_0 is the initial volume before the titration. From this relation, the apparent dissociation constant is calculated as

$$pK_{app} = -\log \frac{[H^+][R^-]}{[HR]} = -\log \frac{[H^+][R^-]}{(C_R - [R^-])} \qquad (6)$$

where C_R is the total concentration of proton-releasing sites. For HS and PAA, K_{app} is not a constant but a function of the

degree of dissociation ($\alpha = [R^-]C_R$). According to our previously proposed model, pK_{app} is described by

$$pK_{app} = pK + m\,pcH - b\log[Na^+], \qquad (7)$$

where $pcH = -\log[H^+]$ and pK, m and b are constant parameters for each PAA. pK is the pK_{app} at $pcH = 0$ and $[Na^+] = 1.0$ M. Chemically, $pK/(1-m)$ is more meaningful since this value gives pK_{app} (or pcH) at $\alpha = 0.5$. Using the pK_{app} given above, the concentration of the dissociated carboxylate groups, [R$^-$], is given by the following equation:

$$[R^-] = C_R\alpha = \frac{C_R}{10^{pK_{app}-pcH}+1} = \frac{C_R}{10^{pK+(m-1)pcH-b\log[Na^+]}+1}, \quad (8)$$

where C_R is also a constant parameter obtained from the titration result.

The titrations of different PAAs (MW from 2000k to 90000) were carried out with a concentration of 0.500 g/L in 0.040 ~ 1.0 M NaClO$_4$ solution and 0.025 ~ 1.0 M NaCl solution. The results were reorganized to give the relation of [R$^-$] calculated by eq 5 versus pcH and were fitted to eq 8 by nonlinear least-squares fittings, and the best set of the parameters pK, m, b, and C_R were obtained. The data (markers) and fitted curves (solid lines) for PAA of MW = 90000 in 0.025 ~ 1.0 M NaCl are shown in Figure 1, and the resultant parameters for various molecular weight PAAs are given in Table 1, where (R$^-$) and C_R^W (expressed in meq/g-PAA) were converted from [R$^-$] and C_R. Note that the five solid lines in Figure 1 were calculated with one set of parameters for MW = 90000 listed in Table 1.
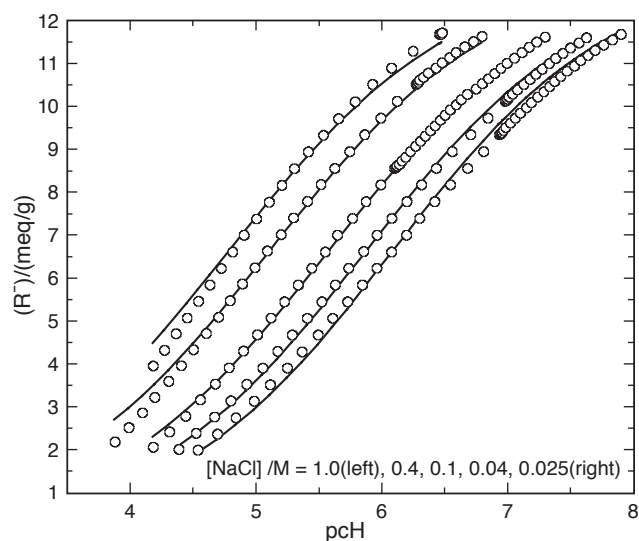

Figure 1. The application of the model to the proton dissociation of polyacrylic acid (MW = 90000) in 0.025, 0.040, 0.1, 0.40 and 1.00 M NaCl. Solid lines are drawn by using $pK_{app} = pK + m\,pcH - b\log[Na^+]$ with the parameters given in Table 1.

TABLE 1: Apparent Acid Dissociation Constants pK_{app} and Site Contents C_R^W (meq/g PAA) of PAA Obtained by Fitting the Titration Data to the Equation, $pK_{app} = pK + m\,pcH - b\log[Na^+]$

	C_R^W	$\frac{pK}{1-m}$	m	b	C_R^W	$\frac{pK}{1-m}$	m	b
MW		NaClO$_4$				NaCl		
450k	13.8(2)	4.78(4)	0.55(1)	0.35(1)	13.7(1)	4.73(3)	0.53(1)	0.37(1)
90k	12.8(1)	4.85(4)	0.48(1)	0.36(1)	13.2(1)	4.78(2)	0.51(1)	0.39(1)
5k	11.7(1)	4.76(4)	0.46(1)	0.34(1)	12.0(1)	4.72(4)	0.47(1)	0.35(1)
2k	10.2(1)	4.74(4)	0.45(1)	0.30(1)	10.3(1)	4.67(5)	0.46(1)	0.33(1)

The digits in the parentheses following numerical values represent the estimated standard deviation (σ) of those values in terms of the final listed digits.

No significant differences in the fitted parameters were observed between $NaClO_4$ and $NaCl$ solution, and the model curves fit the data fairly well. This suggests that, in spite of its homogeneous structure, the energy of deprotonation of the carboxylic functional group smoothly changes with the degree of dissociation due to its polyelectrolyte nature; in other words, the dissociation of the proton from a certain –COOH is affected by the deprotonated or protonated conditions of its neighboring carboxylate groups. Obtained values of $pK/(1-m)$ are only slightly larger than those of monomeric acids (CH_3COOH: 4.60 ± 0.01, C_2H_5COOH: 4.73 ± 0.01, C_3H_7COOH: 4.68 ± 0.012 at $I = 1.0$ M $NaClO_4$),[28] indicating that the value of $4.7 \sim 4.8$ corresponds to the dissociation constant of isolated –COOH in $C_nH_{2n+1}COOH$ for a high n at $I = 1.0$ M. Table 1 also shows that m and b slightly increase with the molecular weight of PAA. This is probably due to the increased interaction of the functional groups in larger molecular weight polymers. Figure 1 shows that the dependences of the experimental data on $\log [Na^+]$ are smaller than the curves predicted by the model at low degrees of dissociation and are larger at high degrees of dissociation. This is reasonable because the formation of the double layer depends on the charge density of the macromolecule, and the model does not take into account this effect.

Proton dissociation of HS. The titrations of various HS were carried out in the same manner as those for PAA. In Figure 2, the results for the titration of various HS in 0.1 M $NaClO_4$ are shown in the form of (R^-) as a function of pcH. Each of the curves showed a dependence on $NaClO_4$ concentration. All the titration results obtained for various concentrations of $NaClO_4$ were reorganized in the form of (R^-) as a function of pcH and analyzed. In the case of HS, two groups of pK_{app} were assumed, each of which follows eq 7. Two groups of pK_{app} were assumed because two kinds of functional groups (carboxylic and phenolic groups) are considered to be contained in HS, and their dissociation properties are affected both by the polyelectrolyte nature and the heterogeneous distribution of the functional groups. The parameter b is taken as common to two acidic groups since this parameter is related to the charge and charge density of the macromolecule and not dependent on the kind of functional group. Thus, the concentration of the dissociated functional (carboxylate and phenolate) groups, $[R^-]$, is given by the following equation:

$$[R^-] = C_{R,1}\alpha_1 + C_{R,2}\alpha_2$$

$$= \frac{C_{R,1}}{10^{pK_1+(m_1-1)pcH-b\log [Na^+]}+1} + \frac{C_{R,2}}{10^{pK_2+(m_2-1)pcH-b\log [Na^+]}+1} \quad (9)$$

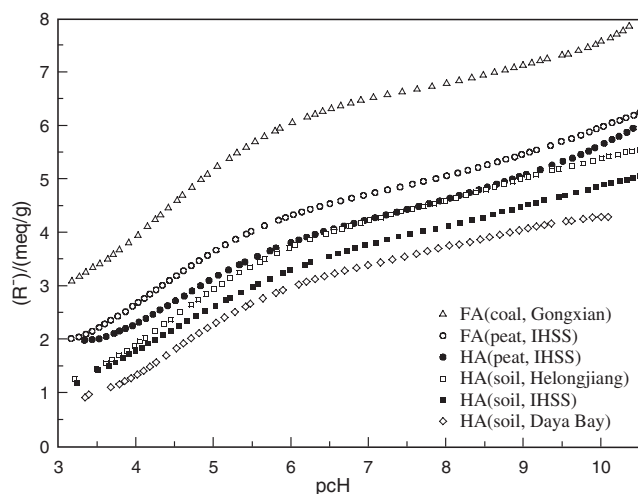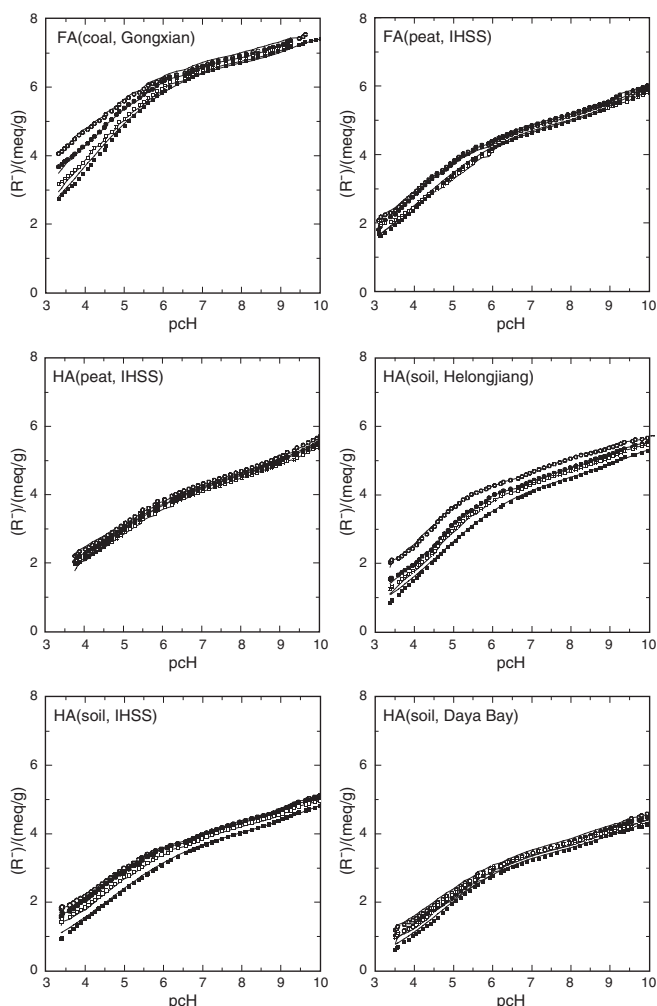**Figure 2.** Plots of dissociated HS (meq/g HS) vs. pcH in 0.10 M $NaClO_4$ solution for FA(coal, Gongxian)($\triangle$); FA(peat, IHSS)($\bigcirc$); HA(peat, IHSS)($\bullet$); HA(soil, Helongjiang)($\square$); HA(soil, IHSS)($\blacksquare$) and HA(soil, Daya Bay)($\diamond$).

To check the effect of the concentration of HS on the dissociation property of HS, titrations of 0.200, 0.500 and 1.00 g/L solutions of FA(coal, Gongxian) were carried out in 0.050 ~1.0 M $NaClO_4$ solution. Although the titrations were conducted to the final pcH of 11.2, the data below pcH 10.5 were taken for the analyses since the data obtained at high pcH contain large experimental uncertainties. Only the obtained parameters are given in Table 2; as shown, there are no significant differences in the results. Thus, the titrations of all HS samples were carried out using 0.500 g/L of HS in 0.050 ~1.0 M $NaClO_4$ solution. The results of the nonlinear fittings are given in Figure 3 and

TABLE 2: Apparent Acid Dissociation Constants pK_{app} and Site Contents C_R^W (meq/g HS) of HS Obtained by Fitting the Titration Data to the Equation, $pK_{app} = pK + mpcH - b\log [Na^+]$

	$C_{R,1}^W$	$\frac{pK_1}{1-m_1}$	m_1	b	$C_{R,2}^W$	$\frac{pK_2}{1-m_2}$	m_2
FA(coal, Gongxian)							
0.250 g/L	7.1(1)	3.34(1)	0.70(1)	0.15(1)	1.5(1)	10.3(1)	0.13(1)
1.000 g/L	7.1(1)	3.07(1)	0.70(1)	0.20(1)	0.8(1)	9.8(1)	0.06(1)
FA(coal, Gongxian)	7.0(1)	3.16(1)	0.70(1)	0.17(1)	0.6(1)	9.89(7)	-0.06(1)
FA(peat, IHSS)	5.1(1)	3.63(2)	0.66(1)	0.11(1)	1.2(6)	9.2(6)	0.34(6)
HA(peat, IHSS)	4.4(1)	3.51(2)	0.67(1)	0.15(1)	3.5(2)	10.4(1)	0.68(1)
HA(soil, Helongjiang)	4.5(1)	3.68(2)	0.60(1)	0.29(1)	1.3(1)	8.76(1)	0.50(2)
HA(soil, IHSS)	4.2(1)	3.81(1)	0.64(1)	0.22(0)	1.2(1)	9.17(1)	0.42(0)
HA(soil, Daya Bay)	3.4(1)	4.02(5)	0.54(2)	0.23(2)	1.4(1)	8.8(4)	0.55(5)

For HS, two groups of pK_{app} are assumed (obtained for 0.500 g/L HS in $NaClO_4$ unless otherwise denoted).

The digits in the parentheses following numerical values represent the estimated standard deviation (σ) of those values in terms of the final listed digits.

Figure 3. Plots of dissociated HS (meq/g HS) vs. pcH: 0.050 ($\blacksquare$); 0.10($\square$); 0.40($\bullet$) and 1.00($\bigcirc$) for $[NaClO_4]$/M; markers are calculated by eq 5 and solid lines are calculated by eq 8 using the parameters given in Table 2. All the HS concentrations used were 0.500 g/L.
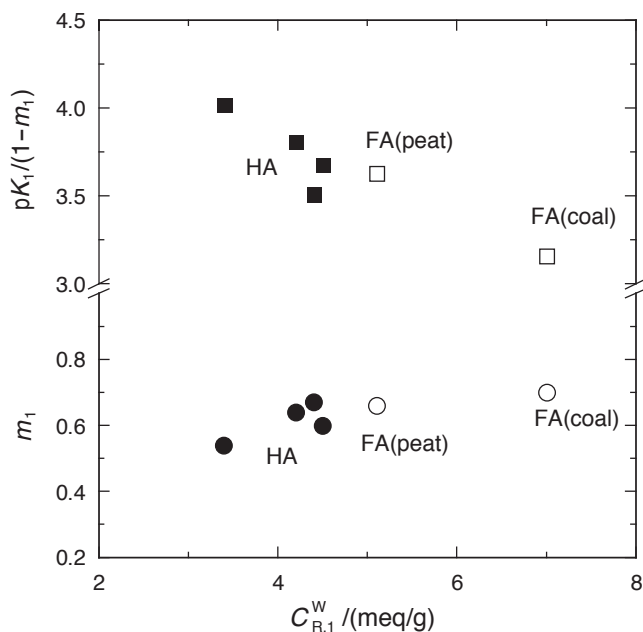
Figure 4. Plots of the fitted heterogeneity parameters m_1 and the mean dissociation constants $pK_1/(1-m_1)$ against the estimated carboxyl contents of HS.

the obtained parameters are listed in Table 2. The results of the fitting shown in Figure 3 indicate that the model equation can be successfully used to reproduce the titration results of various HS samples. The fitted parameters in Table 2 indicate that the amount of total carboxylic groups $C_{R,1}^W$ decreases in the order of 7.2 meq/g for FA (coal) > 5.1 meq/g for FA (peat) > 4.4 meq/g for HA (peat) > 3.4 ~ 4.5 meq/g for HA (soil), and that the value of $pK_1/(1-m_1)$, which corresponds to $pK_{1,app}$ at α (degree of dissociation) = 0.5, increases in the order of 3.1~3.3 for FA (coal) < 3.5 for HA (peat) ≈ 3.6 for FA (peat) < 3.7 ~ 4.0 for HA (soil). The larger $C_{R,1}^W$ for FA than for HA is considered to be due to the fractionation procedure, which separates FA from HA by solubility in acidic solution. The values of $pK_1/(1-m_1)$ are smaller than those of PAA and isolated –COOH. This clearly indicates that –COOH groups are heterogeneously distributed in the HS macromolecule; that is, there should be some pairs with shorter distances to give smaller dissociation constants, or there should be some –COOH groups which are strongly affected by the neighboring atoms or structures such as aromatic rings. The value of m_1 is considered to reflect the heterogeneity of HS since m gives the change of pK_{app} for the unit change of pcH; i.e., $m = \partial pK_{app}/\partial pcH$. As compared with PAA, the larger values of m_1 for HS probably result from the heterogeneous distribution of –COOH. Roughly, m_1 is larger for FA than for HA and larger for HA from peat than for HA from soil. It is interesting to note that it seems that the heterogeneity parameters m_1 and the mean dissociation constant $pK_1/(1-m_1)$ are more or less linearly related to the estimated carboxyl contents $C_{R,1}$ of HS as shown in Figure 3; which in turn indicates that the distribution of –COOH is more heterogeneous for the HS containing a larger amount of acidic functional groups. This can be explained by the fact that, when fulvic acids and humic acids are fractionated, fulvic acids are the fraction that is soluble in acids and bases, and humic acids are the fraction that is soluble in bases but insoluble in acid. Therefore, the humic substances containing a larger number of acidic groups and more-acidic groups are fractioned into a fulvic fraction. Thus, the fraction containing a larger amount of functional groups usually contains a larger amount of more-acidic groups. The parameter b gives the change of pK_{app} for the unit change of log [Na$^+$], $b = -\partial pK_{app}/\partial \log[\mathrm{Na}^+]$. The fitted values for HS are smaller than that for PAA probably due to the larger C_R^W for PAA than HS. However, for HS, the

values of b are larger for HA than for FA in spite of the fact that HAs have smaller $C_{R,1}^W$ values. This is because HAs contain larger amounts of large-molecular-weight components, and the structure of the double layer around the macromolecule is determined not only by the amount of charged sites per unit weight of HS but also by its molecular weight and molecular conformation. As for the phenol groups in HS, the $C_{R,2}^W$ values are usually small except in the case of HA(peat, IHSS). The values of $pK_2/(1-m_2)$ are close to the pK of phenol (9.82 ± 0.02* at $I = 1.0$ M).[28] However, as shown in the results on FA(coal, Gongxian), the experimental uncertainties are fairly large and make further discussion difficult.

4. Conclusions

Equation 1 proposed for the cation-humate interaction constant was successfully applied to the proton dissociation of various humic substances in the form of eq 8. With the parameters listed in Table 2, the dissociated amount of functional groups can be well reproduced as a function of pcH and log [Na$^+$]. Obtained parameter values of C_R^W reflect the fractionation procedure for fulvic and humic acids. The values of $pK/(1-m)$ indicate that there should be heterogeneous distribution of the functional groups in the humic macromolecule. The obtained values of b are considered to be determined by the molecular weights and the molecular conformations of the humic substances.

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