Potentiometric Study on the Proton Binding of Humic Substances

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Received: November 15, 2004; In Final Form: April 21, 2005

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 NaClO₄ 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 pKₐpp = pKᵢ + mᵢpCH − b log [Na⁺] (i = 1 for carboxyl and i = 2 for phenolic groups) for Kₐpp = [H⁺][R⁻]/[HR] was applied to the titration results. In the expression, pKᵢ, mᵢ, 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 pKᵢ(i(1 − mᵢ)), which corresponds to pKᵢ,app at α (degree of dissociation) = 0.5, increased in the order of 3.1 ~ 3.3 for FA (coal) < 3.5 for HA (coal) < 3.6 for HA (peat) < 3.7 ~ 4.0 for HA (soil). As compared with the fitted values of mᵢ = 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 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 polyelectrolytic 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,5,23 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/VI5,14 and the NICA-Donnan model10,14,15 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

\[ \log K_{\text{app}} = \log K + a \log [Na^+] - b \log [M^{n+}] \]

where

\[ M^{n+} + zR^- \rightleftharpoons M^{n+}\cdot zR^- \]

\[ K_{\text{app}} = \frac{[M^{n+}\cdot zR^-]}{[M^{n+}][R^-]} \]

and where [M⁺⁺·zR⁻] is the concentration of the cation bound to the HS, [M⁺⁺] is the concentration of the free cation, and [R⁻] = (C₀ − [M⁺⁺·zR⁻])/z (C₀ is a total concentration of proton exchanging sites and z 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

\[ pK_{\text{app}} = pK + mCH - b \log [Na^+] \]

where pH = −log [H⁺] and

\[ HR \rightleftharpoons H^+ + R^- \]

\[ K_{\text{app}} = \frac{[H^+][R^-]}{[HR]} \]

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 NaClO₄ 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—C₀K (the amount of functional groups per unit weight of HS), pK, m,
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. S102H), abbreviated as HA (soil, IHSS), and humic and fulvic acids extracted from peat (Cat. No.1 R107H and Cat. No.1 R107F), abbreviated 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), abbreviated as FA(coal, Gongxian); and humic acid extracted from coal (Gongxian, Henan province, P.R. China), which were extracted according to the IHSS procedure. Fulvic acid extracted from coal (Gongxian, Henan province, P.R. China) was used to prepare the solution. The HS and PAA, polyacrylic acid (MW = 90000) in 0.025, 0.040, 0.1, 0.40 and 1.00 M NaClO4 solution and 0.025 ~ 1.0 M NaCl solution. The results were reorganized to give the relation of $[R\textsuperscript{-}]$ 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 $C\textsubscript{B}$ 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 $(R\textsuperscript{-})$ and $C\textsubscript{B}$ (expressed in meq/g-PAA) were converted from $[R\textsuperscript{-}]$ and $C\textsubscript{B}$, respectively. Note that the five solid lines in Figure 1 were calculated with one set of parameters for MW = 90000 listed in Table 1.

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 be reorganized to give the total concentration of dissociated functional groups $[R\textsuperscript{-}]$ as a function of $[H\textsuperscript{+}]$ for each titration point by using the following relation:

$$[R\textsuperscript{-}] = \frac{[H\textsuperscript{+}] + C\textsubscript{B}V\textsubscript{i}/(V\textsubscript{f} + V\textsubscript{i}) - [OH\textsuperscript{-}]}{V\textsubscript{f}/(V\textsubscript{f} + V\textsubscript{i})}$$

where $C\textsubscript{B}$ and $V\textsubscript{i}$ are the concentration of NaOH and the volume of added titrant, respectively, and $V\textsubscript{f}$ is the initial volume before the titration. From this relation, the apparent dissociation constant is calculated as

$$pK\textsubscript{app} = -\log \frac{[H\textsuperscript{+}][R\textsuperscript{-}]}{[HR]} = -\log \frac{[H\textsuperscript{+}][R\textsuperscript{-}]}{(C\textsubscript{B} - [R\textsuperscript{-}] )}$$

where $C\textsubscript{B}$ is the total concentration of proton-releasing sites. For HS and PAA, $K\textsubscript{app}$ is not a constant but a function of the degree of dissociation ($\alpha = [R\textsuperscript{-}]C\textsubscript{B}$). According to our previously proposed model, $pK\textsubscript{app}$ is described by

$$pK\textsubscript{app} = pK + m(pCH - b \log [Na\textsuperscript{+}])$$

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

$$[R\textsuperscript{-}] = C\textsubscript{B}\alpha \frac{C\textsubscript{B}}{[10^{pK/(1 - m)} - 10^{-pCH} \log [Na\textsuperscript{+}] + 1]} = C\textsubscript{B}$$

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 NaClO4 solution and 0.025 ~ 1.0 M NaCl solution. The results were reorganized to give the relation of $[R\textsuperscript{-}]$ 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 $C\textsubscript{B}$ 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 $(R\textsuperscript{-})$ and $C\textsubscript{B}$ (expressed in meq/g-PAA) were converted from $[R\textsuperscript{-}]$ and $C\textsubscript{B}$.

![Figure 1](image-url)
No significant differences in the fitted parameters were observed between NaClO₄ 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 constants of its neighboring carboxylic groups. Obtained values of pK/a(1 – m) are only slightly larger than those of monomeric acids (CH₃COOH: 4.60 ± 0.01, C₂H₅COOH: 4.73 ± 0.01, C₃H₇COOH: 4.68 ± 0.012 at I = 1.0 M NaClO₄).²⁸ indicating that the value of 4.7 ~ 4.8 corresponds to the dissociation constant of isolated –COOH groups (carboxylic and phenolic groups) are considered to be functional groups in larger molecular weight polymers. Figure 2. Plots of dissociated HS (meq/g HS) vs. pH in 0.10 M NaClO₄ solution. Each of the curves showed a dependence on NaClO₄ concentration. This is probably due to the increased interaction of the molecule, 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 NaClO₄ are shown in the form of (R⁻) as a function of pH. Each of the curves showed a dependence on NaClO₄ concentration. All the titration results obtained for various concentrations of NaClO₄ were reorganized in the form of (R⁻) as a function of pH and analyzed. In the case of HS, two groups of pK/a app were assumed, each of which follows eq 7. Two groups of pK/a 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 (carboxylic and phenol) groups, [R⁻], is given by the following equation:

\[
[R^-] = C_{R,1}c_1 + C_{R,2}c_2 = \frac{1}{10^{pK_{R,1} + m_1(pH - log[Na^+]^+)} + 1} + \frac{1}{10^{pK_{R,2} + m_2(pH - log[Na^+]^+)} + 1}
\]  

(9)

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 NaClO₄ solution. Although the titrations were conducted to the final pH of 11.2, the data below pH 10.5 were taken for the analyses since the data obtained at high pH 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 NaClO₄ solution. The results of the nonlinear fittings are given in Figure 3 and Table 2.

Table 2: Apparent Acid Dissociation Constants pK/a app and Site Contents C/W (meq/g HS) of HS Obtained by Fitting the Titration Data to the Equation, pK/a app = pK + mpcH - bpcH [Na+]

<table>
<thead>
<tr>
<th>Site Contents</th>
<th>C_W</th>
<th>pK_1 - m_1</th>
<th>m_1</th>
<th>b</th>
<th>pK_2 - m_2</th>
<th>m_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA(coal, Gongxian)</td>
<td>7.1(1)</td>
<td>3.34(1)</td>
<td>0.70(1)</td>
<td>0.15(1)</td>
<td>1.5(1)</td>
<td>10.3(1)</td>
</tr>
<tr>
<td>0.06(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA(coal, IHSS)</td>
<td>5.1(1)</td>
<td>3.63(2)</td>
<td>0.60(1)</td>
<td>0.11(1)</td>
<td>1.2(1)</td>
<td>9.2(6)</td>
</tr>
<tr>
<td>FA(peat, IHSS)</td>
<td>4.4(1)</td>
<td>3.51(2)</td>
<td>0.67(1)</td>
<td>0.15(1)</td>
<td>3.5(2)</td>
<td>10.4(1)</td>
</tr>
<tr>
<td>HA(peat, IHSS)</td>
<td>4.5(1)</td>
<td>3.68(2)</td>
<td>0.60(1)</td>
<td>0.29(1)</td>
<td>1.3(1)</td>
<td>8.7(6)</td>
</tr>
<tr>
<td>FA(soil, Helongjiang)</td>
<td>4.2(1)</td>
<td>3.81(1)</td>
<td>0.64(1)</td>
<td>0.22(0)</td>
<td>1.2(1)</td>
<td>9.17(1)</td>
</tr>
<tr>
<td>HA(soil, Helongjiang)</td>
<td>3.4(1)</td>
<td>4.02(5)</td>
<td>0.54(2)</td>
<td>0.23(2)</td>
<td>1.4(1)</td>
<td>8.8(4)</td>
</tr>
</tbody>
</table>

For HS, two groups of pK/a app are assumed (obtained for 0.500 g/L HS in NaClO₄, 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.
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 $C_{W1}^*$ 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 $pK_i/(1−m_i)$, which corresponds to $pK_{app}$ 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 $C_{W1}^*$ 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 $pK_i/(1−m_i)$ 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 $m_i$ is considered to reflect the heterogeneity of HS since $m_i$ gives the change of $pK_{app}$ for the unit change of $pH$; i.e., $m_i = \partial pK_{app}/\partial pH$. As compared with PAA, the larger values of $m_i$ for HS probably result from the heterogeneous distribution of –COOH. Roughly, $m_i$ is larger for FA than for HA and larger for FA from peat than for HA from soil. It is interesting to note that it seems that the heterogeneity parameters $m_i$ and the mean dissociation constant $pK_i/(1−m_i)$ are more or less linearly related to the estimated carboxyl contents $C_{W1}$ 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 $\log [Na^+]$, $b = \partial pK_{app}/\partial \log [Na^+]$. The fitted values for HS are smaller than that for PAA probably due to the larger $C_{W1}^*$ 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 $C_{W1}^*$ 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 $C_{W2}^*$ values are usually small except in the case of HA(peat, IHSS). The values of $pK_i/(1−m_i)$ are close to the $pK$ of phenol (9.82 ± 0.02* at $I = 1.0$ M). 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–humic 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 $pH$ and $\log [Na^+]$. Obtained parameter values of $C_{W1}^*$ reflect the fractionation procedure for fulvic and humic acids. The values of $pK_i/(1−m_i)$ 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.

Acknowledgment. The present work was supported by a research grant from the Japanese Society for the Promotion of Science.

References


Figure 4. Plots of the fitted heterogeneity parameters $m_i$ and the mean dissociation constants $pK_i/(1−m_i)$ against the estimated carboxyl contents of HS.