Determination of the protonation enthalpy of humic acid by calorimetric titration technique

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ABSTRACT

In this study, the calorimetric titration technique was used to determine the protonation enthalpy of two reference humic acids and polyacrylic acid. First, we obtained the apparent protonation constant of two kinds of humic acid purchased from IHSS (International Humic Substances Society) and polyacrylic acid by potentiometric titration. Second, we obtained the protonation enthalpy of them by calorimetric titration. The protonation enthalpy of humic acid was affected by pH and the ionic strength of bulk solution. From the comparison of ΔH between humic acid and polyacrylic acid, it was concluded that the pH dependence of ΔH is attributed to the heterogeneity of humic acid. And ΔH of phenolic hydroxyl group in humic acid is strongly influenced by the electric double layer of humic acid's surface. This is considered to be a reason of the ionic strength dependence of ΔH. On the other hand, Gibbs free energy of the protonation of humic acid is affected by the electrostatic attraction with the progress of dissociation of functional groups such as carboxyl group and phenolic hydroxyl group. Consequently, the thermodynamics of the protonation of humic acid is affected by the polyelectrolyte effect and the heterogeneity.

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1. Introduction

Humic Substances (HSs) are heterogeneous mixture of high-molecular-weight organic materials formed by humification of animals, plants and microbes. HSs are believed to play an important role in the transportation of metals in environment, and are confirmed to be present even in the deep underground where radioactive wastes are planned to be disposed. It is commonly recognized that HSs have many functional groups in the macromolecule. Especially, carboxyl group and phenolic hydroxyl group interact strongly with variety of metal cations by forming complexes and affect the migration behavior of radionuclides released from the disposed radioactive wastes [1–3]. Thus, numerous attempts have been carried out to model and describe the interaction of HSs with metal cation [4–10]. In these previous studies, the interaction of humic acid (a kind of HSs which is soluble in basic solution but insoluble in acidic solution) with metal cation and proton under various chemical condition have been investigated. The complexation model has been applied to describe the interaction of HSs with metal cation, and the availability of complexation model have been discussed. Most of studies attempted

thermodynamic interpretation by estimating the result as equilibrium reaction. However, in terms of interaction of humic acid with cation, only a few studies determined the reaction enthalpy (ΔH) and entropy (ΔS) which are necessary for a discussion of reaction thermodynamics, so most of previous studies reported only equilibrium constants corresponding with Gibbs free energy (ΔG) [11,12]. The calorimetric titration technique is a promising for the determination of the reaction enthalpy by a direct measurement in the solution system. Rao et al. [13,14] succeeded to determinate the reaction enthalpy in hydrolysis of Neptunium (V) and complexation of Thorium (IV). In our previous study, we applied potentiometric titration and calorimetric titration to the reactions of dicarboxylic acids with Uranium (VI) and Europium (III), thus cultivated a better understanding of reaction mechanism by accurate determination of ΔG, ΔH, and ΔS [15–18]. Therefore, in this study, we applied calorimetric titration technique which is revealed to be reliable in our previous study for the interaction of humic acid with proton. There are five reports on the application of calorimetric titration to humic acid [19–23], however no report estimates the protonation constant continuously against pH. These reports determined ΔH of carboxyl group from the reaction heat in the range of pH 4 to 7, and ΔH of phenolic hydroxyl group from the reaction heat in the range of pH 9 to 11. However, some phenolic hydroxyl group react with proton even in neutral pH range. Therefore, there is a possibility of overestimation of ΔH of carboxyl group in the neutral pH range. In this study, we attempt more

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accurate determination of ΔG, ΔH, and ΔS by combination of the equilibrium model, potentiometric titration and calorimetric titration. We selected two kinds of humic acids, Waskish Peat and Elliot Soil. Both of them were purchased from International Humic Substances Society (IHSS). We also applied same method to polyacrylic acid which is homogeneous polyelectrolyte having carboxyl group. By comparing the thermodynamic quantities determined by combination of direct measurement of reaction heat by calorimetry and apparent equilibrium constant by potentiometry, we discussed the influence of polyelectrolyte effect and heterogeneity of humic acid in the interaction with proton.

2. Material and methods

2.1. Sample preparation

Two humic acids named as Elliot Soil (Cat. No. 1S102H) and Waskish Peat (Cat. No. 1R107H) were purchased from the IHSS. These humic acids were extracted from the fertile prairie soils and sphagnum bog peat, respectively. Polyacrylic acid, sulfamic acid, perchloric acid, acetic acid, sodium hydroxide, aqueous ammonia and sodium perchlorate, were purchased from Wako Pure Chemical Industries and used without further purification. The molecular weight of polyacrylic acid is 90,000. Each humic acids were dissolved in standardized 0.1 M sodium hydroxide solution, then neutralized with an adequate amount of standardized perchloric acid. The initial concentrations of humic acids and polyacrylic acid are 1.0 g/dm³. The emf reading of the pH electrode was converted to the absolute hydrogen ion concentration by a conversion procedure described in the following section. Sodium hydroxide solution used for the titration of the humic and polyacrylic acids solution were standardized against 0.10 M sulfamic acid. The standardized and de-carbonated 0.1 M NaOH solution was then used for the determination of the concentration of perchloric acid and acetic acid for the calibration of the glass electrode. The standardized 0.1 M HClO₄ solution also used for the determination of the concentration of ammonium solution. The Ionic strengths of all samples were adjusted to (0.1, 0.5, and 1.0) M by adding appropriate amounts of sodium perchlorate as a background electrolyte, respectively.

2.2. Potentiometric titration

Potentiometric titration was carried out at 25 ± 0.2 °C by using an automatic titration system (HIRANUMA, COM-1500) to determine the protonation constants of the humic and polyacrylic acids. The glass-electrode filling solution (saturated KCl) was replaced with a saturated NaCl solution to avoid clogging of the electrode frit glass septum by precipitation of KClO₄. The glass-electrode was calibrated by the standard strong acid (0.1 M HClO₄) vs. standard strong base (0.1 M NaOH) titration and the standard weak acid (0.1 M CH₃COOH) vs. standard weak base (0.1 M NH₃) titration, where ionic strength was kept constant during the titrations as (0.1, 0.5 or 1.0) M by NaClO₄. The absolute hydrogen ion concentration at each titration steps of the above mentioned standard titrations were calculated from the mass balance equations and protonation equilibrium equations using reported protonation constants of hydroxide ion, acetic acid and ammonia in NIST database [24]. Then, the negative logarithm of the calculated absolute hydrogen ion concentration, which is expressed as pcH (=−log[H⁺]abs.) in this paper, were compared with the pH readings of the standard titrations between strong acid vs. strong base and weak acid vs. weak base at each titration steps. This comparison provided linear relation between pH readings of the titrator and pcH in wide pH range at each ionic strengths. As a result, the pH

readings in the potentiometry were always converted to the pcH value for the equilibrium discussion by using this linear relation in the potentiometry. The base titration using sodium hydroxide carried out for the two humic acids and polyacrylic acid, where the glass-electrode potential was monitored at 2-min intervals after each addition of the titrant. The emf of electrode was recorded when its drift was less than 0.1 mV/min.

Beside, N₂ gas was flowed continuously into the titration vessel to prevent the dissolution of carbon dioxide.

2.3. Calorimetric titration

Calorimetric titration was conducted with an isothermal solution calorimeter system (TAM-III, TA Instruments). The titration assembly consists of a reaction vessel (1 cm³ volume, made from hastelloy), a reference vessel, thermoelectric devices, a calibration heater and 18 K gold-stirrer driven by an electric motor. The assembly was immersed in a high precision heat sink of instrument which maintains the temperature at (25 ± 0.000004) °C. The titrant was delivered into the reaction vessel through a titrant tube from syringe, which was also immersed in the heat sink. The titrant volume was controlled constantly by precision syringe pump (P/N 3810-5, TA Instruments). In the measurement for each ligand protonation enthalpy, 1 ml of humic acids and polyacrylic acid solutions were titrated with a 0.1 M sodium hydroxide solution in different ionic strength which is (0.1, 0.5, and 1.0) M respectively. The titrants injections were repeated 12 times with 3 μl of volume and 90 min interval. To check the extent of the dissolution of carbon dioxide from air to the reaction vessel as carbonate anion, a blank calorimetric titration was conducted where 0.1 M sodium hydroxide solution was added to a pH adjusted solution with no humic acid nor polyacrylic acid in the same calorimetric titration manor. After this blank titration, the final concentration of carbonate existing in the vessel was determined by a potentiometric titration with standard perchloric acid. It revealed that the final concentration of carbonate in the calorimetric titration vessel was about 0.20 mM. This concentration was less than 14% of the concentration of the phenolic hydroxyl group (e.g. (1.50 ± 0.14) mM) in the humic acid titration. Since the dissolved carbonate concentration was almost same as the value of estimated standard deviation of the phenolic hydroxyl group concentration, we have regarded the existence of dissolved carbon dioxide as negligible for the determination of thermodynamic quantities in this study.

In each run of the measurement, the reaction heat of protonation at ith step titrant addition ($\Delta Q_{r,i}$) was obtained by subtracting dilution heat from the heat measured by the calorimeter:

$$\Delta Q_{r,i} = \Delta Q_{ex,i} - \Delta Q_{dil,i}, \tag{1}$$

where $\Delta Q_{ex,i}$ is the measured heat by the calorimeter (J) at the ith step addition of titrant and $\Delta Q_{dil,i}$ is the consumed heat of dilution of titrant determined by the separate run. In this paper, the positive heat value means that reaction system obtained the heat of $\Delta Q_{r,i}$ J from the surroundings.

3. Results

3.1. Stability constants of protonation

Since humic substances is not a single well-defined molecule but a mixture of various heterogeneous macromolecules containing a variety of functional groups, the accurate concentration of dissociated functional group cannot be defined unlike a simple organic acid. In our previous study, the logarithm of the apparent