



Dissociation properties and behavior of active humic fractions dissolved in aqueous systems



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ABSTRACT

The function of humic acids in nature is strongly affected by their solubility and their ability to dissociate. This work is focused on the fraction of humic acids which is dissolved in water or rather the aqueous phase in humic-containing systems. This fraction can be rich in acidic functional groups which are the most active ones. The amount of the dissolved humic fraction can be considered to be the result of equilibrium between dissolved and undissolved humic substances. In this study, the concentration dependence of the dissociation constants was determined and analyzed.

A maximum was observed for the dependence of the degree of dissociation on the concentration. In less concentrated leachates, less soluble humic particles with weaker functional groups were able to be dissolved. The weak functional groups have lower dissociation ability and they were able to remain in non-dissociated forms. The increase of humic contents in leachates caused smaller amounts of soluble fractions with the weakest functional groups to remain in an undissolved form, which led to the increase in the degree of dissociation. The increase in concentration of humic acids in the leachates caused the degree of dissociation decrease as a result of interactions between dissolved particles.

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1. Introduction

Humic acids in soils and natural waters constitute a significant fraction of dissolved organic carbon. The polyfunctional nature of dissolved humic particles, their polyelectrolyte character, and their conformational variability are responsible for their complexing and buffering abilities. Dissolved organic matter is one of the decisive factors affecting the mobility of pollutants in soils receiving waste amendments. The behavior of humic acids in soils and aquatic systems is strongly affected by their solubility and dissociation ability. The dynamics of dissolved fractions with negative charges is related to the absorbing capacity of the soil solid phase and the contents of organo-mineral compounds and acidic functional groups [1–3]. The amounts and properties of ionizable acidic groups as well as the colloidal character of these substances are important for their functioning in natural environments. Because dissolved organic matter, as the most active organic fraction in nature, plays many significant roles, it is necessary to understand their complexation behavior and proton binding properties [1,2,4,5].

Dissolved humic acids are polydisperse mixtures that have different functional groups. Their acid-base behavior is influenced by many factors such as pH and ionic strength, which can affect the dissociation degree, their polarity and their intra- or inter-molecular interactions [5–11]. Complexation between dissolved organic matter containing

humic acids and metal ions can lead to non-equilibrium conditions and the risk of leaching into soil and natural aquatic systems [12–14]. The acquisition of detailed information on acidic functional groups is a primary task in the study of cation-humic interactions [15–19]. Many studies on dissolved organic matter focus on the dynamics and fates of soils [14,20]. The charge of functional groups of soil compounds, which plays a decisive role in their sorption and desorption, is known to be greatly affected not only by pH but also by the type and concentration of the electrolyte, especially multivalent cations and anions in soil solution [14,21–25]. At constant pH, an increase in electrolyte concentration, i.e. ionic strength, affects the surface charge, whereas, depending on the electrolyte type, an increase or decrease in surface charge is possible [14,26].

The most widely used methods for determining the dissociation constants of humic substances are acid–base titrations [27–31]. Many authors determined apparent dissociation constants on the basis of potentiometric titration data and the Henderson-Hasselbach equation [31–35]. However, the use of potentiometric data for the determination of pK_a is connected with several problems [33,38,39]. The results of many studies have shown that the dissociation behavior of humic acids cannot be characterized sufficiently by one value of dissociation constant. Therefore more complex models such as one with a continuous distribution of dissociation constants, with acidic functional groups having two centers [6,28,38,39], or the NICA-Donnan model [39–42], are often used. Results published by Masini [27] indicated that the acid-base behavior of humic acids can be characterized by five kinds

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of titratable groups (including two or three kinds of carboxylic groups), which have concentration and pK_a values few affected by changes in the ionic strength. Campitelli et al. [43] identified from five to seven different pK_a values for humic acids extracted from soil and compost. Fernandes et al. [37] concluded that their results were strongly dependent on both the choice of mathematical model for fitting the experimental data points as well as the experimental conditions employed (e.g. titration rate). Khil'ko et al. [31] showed that the results depend on the method of titration, the concentration of humic substances in the system, and the time taken to establish the equilibrium value of pH in the titrated system. A common complication associated with the interpretation of titration data is the presence of hysteresis when the path that the forward titration with a base follows does not coincide with that followed by the backward titration [42]. Chemical heterogeneity among groups with the same chemical nature is the major factor governing the acid-base properties of humic acids [21,22,27,44,45]. Humic acids are not a single well-defined molecule but a mixture of various heterogeneous macromolecules containing a variety of functional groups, which give rise to polyelectrolyte and polyfunctional properties [39].

With regard to the above-mentioned problems with the measurement and interpretation of titration data, new alternative methods for the study and characterization of the acid-base properties of humic acids have been developed. Tan et al. [30] used a polyelectrolyte titration technique in order to obtain the charge density of humic substances in simple 1-1 electrolyte solutions. Janot et al. [46] used spectrophotometric titrations as a viable alternative to traditional potentiometric titration in order to obtain proton binding data for concentrations closer to environmental values. Goldberg et al. [47] calculated the dissociation constants of humic acids on the basis of isosbestic points in their fluorescence spectra. Salma and coworkers [48,49] studied atmospheric humic-like substances (HULIS) and their acidic functional groups and dissociation behavior using conductometric measurements. They used the concentration dependence of molar conductivity (Kolrausch's equation) for the determination of the dissociation constants of the substances.

Our approach was different. We focused on the fraction of humic acids which was dissolved in water or rather the aqueous phase in humic containing systems. This fraction can be rich in acidic functional groups and (also) the most active one in environmental systems. The content of the dissolved humic fraction can be considered as the result of equilibrium between dissolved and undissolved humic substances. This equilibrium is affected by many factors including the total amount of humic substances in the system. If their amount is low, fractions less rich in acidic functional groups can be dissolved and weaker functional groups can dissociate. The strength and properties of the dissolved functional groups are thus strongly dependent on the total amount of humic substances in the studied system and various other parameters (pH, ionic strength) [10,21,22,50,51]. The dissociation of acidic functional groups of humic acids supports their dissolution in water therefore the presence of stronger (easily dissociable) functional groups results in higher solubility. On the other hand, the dissolution is connected with a gradual saturation of the forming solution. The dissolution of a substance in its highly concentrated solution is more difficult. Humic acids are the mixture of many different molecules with functional groups of different acidity. If the small amount of humic acids is dissolved in water, fractions containing less acidic functional groups have a possibility to dissolve and dissociate because the surrounding solution is not saturated. Since humic acids are mixture, the different amount of humic acids in the same volume of water means the different quality of their dissolved fraction. The different quality of dissolved humic fractions is a logical conclusion of the definition of humic acids. This is based on their solubility (similarly as the definition of fulvic acids or humins). The solubility of humic substances and these three groups is strongly affected by their structure and functional groups. The high content of acidic groups with lower pK_a values is (together with lower

aromaticity and molecular size) the necessary conditions of their good solubility in aqueous solution. In this work we used the method of flow-through coulometry [10] for the determination of the total amount of ionizable functional groups in aqueous leachates of humic acids and the method of potentiometry for the determination of dissociated acidic groups. We used these data as the basis for the calculation of the dissociation constants of humic acids and their concentration dependence.

2. Materials and methods

2.1. Humic acids

Five different humic acids were used in this work. Samples were extracted from lignite mined in the Czech Republic (Mikulčice in South Moravia) and purchased from the International Humic Substances Society (IHSS).

Sample HA-I was extracted in the ratio of 20 g of lignite to 1 dm³ of a mixture of 0.5 M NaOH and 0.1 M Na₄P₂O₇ (1:1). The obtained suspension was stirred at laboratory temperature (25 °C) overnight. The solid part was removed by centrifugation and humic acids were precipitated by a concentrated HCl solution up to a pH of less than 2, washed repeatedly with deionized water until free from chlorides and dried in the oven at 50 °C.

Sample HA-II was extracted in the ratio of 60 g of lignite to 1 dm³ of a mixture of 0.5 M NaOH and 0.1 M Na₄P₂O₇ (1:1). The solid residue was extracted again for 60 min. Both leaches were mixed and acidified by 20% HCl solution up to a pH of less than 2. The precipitate was dissolved in 1 M NaOH (0.9 dm³) and the solution was acidified again by 20% HCl solution up to a pH of less than 2. The reprecipitated humic acids were washed repeatedly with deionized water until free from chlorides and dried in the oven at 50 °C. The obtained sample was purified using an HCl/HF mixture (48 h), washed repeatedly with deionized water until free from chlorides, and dried in the oven at 50 °C.

Sample HA-III was extracted in the ratio of 50 g of lignite to 1 dm³ of a mixture of 0.5 M NaOH and 0.1 M Na₄P₂O₇ (1:1). The solid residue was extracted again for 60 min. Both leaches were mixed and acidified by 20% HCl solution up to a pH of less than 2. The precipitate was dissolved in 1 M NaOH solution (0.9 dm³) and acidified again by 20% HCl solution up to a pH of less than 2. The reprecipitated humic acids were washed repeatedly with deionized water until free from chlorides and purified using an HCl/HF mixture (48 h), washed repeatedly with deionized water until free from chlorides and dried in the oven at 50 °C.

Sample HA-IV was extracted in the ratio of 50 g of lignite to 1 dm³ of a mixture of 0.5 M NaOH and 0.1 M Na₄P₂O₇ (1:1). The solid residue was extracted again for 60 min. Both leaches were mixed and acidified by 20% HCl solution up to a pH of less than 2. The precipitate was dissolved in 1 M NaOH solution (0.9 dm³) and acidified again by 20% HCl solution up to a pH of less than 2. The obtained sample was purified using an HCl/HF mixture overnight, dialyzed using a SpectraPor 3500 MWCO membrane (for 1 week) and freeze-dried at -15 °C.

Sample HA-V was a leonardite standard from the International Humic Substances Society (1S104H).

2.2. Characterization of humic acids

All humic samples were characterized by their elemental composition using CHNSO Microanalyzer Flash 1112 (see Table 1). The total acidity and content of carboxylic groups were determined by standard methods [12,15,21,22,36]. The results of titration methods, including pK_a values based on the Henderson-Hasselbach model [33,34,36], are listed in Table 2.

2.3. Humic leachates

Suspensions of humic acids with humic contents from 0.01 g dm⁻³ to 20 g dm⁻³ were prepared by mixing powdered samples with a

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