

Impact of an Anionic Surfactant Addition on Solubility of Humic Acid in Acid-Alkaline Solutions

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The solubility of humic acid (HA) is a very important factor in the study of its interaction with metal ions and radionuclides. The solubility of HA as a function of hydrogen ion concentration was studied. It has been found that chemical behaviour of HA is similar to other polyelectrolytes. Solubility depends on pH, ionic strength, and many other factors. Unmonotonous character of the solubility curve in relationship with pH may be connected with conformation changes of HA saturated solutions. The results show that the addition of anionic surfactant to HA saturated solution can influence the solubility curve of HA.

A large fraction of soil organic carbon and water-dissolved organic carbon is constituted by humic substances. Humic substances are complex, heterogeneous molecules which are operationally defined on the basis of solubility: fulvic acid is completely soluble in aqueous solution, while humic acid is soluble in alkali but precipitates in acid solutions. A knowledge of the solubility characteristics of HA is important for understanding the behaviour of and relationship between humic substances in soil and natural waters [1]. In solution, HA behaves as micellar colloids. The colloid particles have a negative charge and this isoelectric point is in the acid region. It has been found that chemical properties of HA are similar to the other acidic polyelectrolytes. The solubility of HA depends on pH, ionic strength, and many other factors [2]. In view of the fact that HA is a relatively high-molecular-mass species containing polar and nonpolar moieties [3], we speculate that there occurs a partition-like interaction of the surfactants with the soil HA. The purpose of the present work is to study the solubility of HA at different pH values and influence of an anionic surfactant addition on its solubility curve.

EXPERIMENTAL

HA used in our experiment was obtained from peat Hroboňová, Slovakia (gift of Professor Kandráč, Department of Analytical Chemistry of this Faculty) in H⁺ form. The ratio of absorbances at $\lambda = 465$ and 665 nm referred to as E4/E6 ratio has been widely used in literature for characterization of humic substances. The E4/E6 ratio for used HA was 3.5 and such ratio corresponds to the Chernozem in soil classification [4].

All used chemicals were of anal. grade (Lachema, Brno, Czech Republic). The solubility of HA in dependence on pH was determined in 0.1 M-NaCl as electrolyte solution. The influence of an anionic surfactant on the solubility curve was followed by using of 0.01 M-SDS (sodium dodecyl sulfate) and this solution was prepared in 0.1 M-NaCl. According to the aforementioned concentration the ionic strength would provide the constant value during the time of experiment. The pH was measured with a combined glass-calomel electrode (digital pH-meter OP-211/1 Radelkis, Hungary) at 25°C under aerobic conditions.

Air-dried HA (500 mg) was placed in a titration cell containing the pH electrode and 30 cm³ of electrolyte solution were added. Solutions were stirred with magnetic follower. Equilibrium between two phases (solid and aquatic HA) was assumed when the pH remained constant for at least 30 min; the pH was then raised by addition of 0.1 M-NaOH (or lowered by addition of 0.1 M-HCl). At each selected pH value a 2 cm³ sample was removed and centrifugation followed for 10 min at 4000 min⁻¹, the supernatant solution was removed and analyzed whereas the residue was returned to the working solution by washing with 2 cm³ of electrolyte solution. This procedure was repeated in the presence of 0.01 M-SDS solution. The relationship of HA solubility with different sample concentration of SDS (10^{-3} – 10^{-2} mol dm⁻³) was evaluated by using the same mentioned procedure at pH 4.10. Saturated solutions with various values of pH were obtained and measured by UV VIS spectrophotometry (Specord UV VIS Zeiss, Jena) in 1 cm quartz cuvettes. Concentration of HA in each sample was determined from standard calibration curve at $\lambda = 400$ nm.

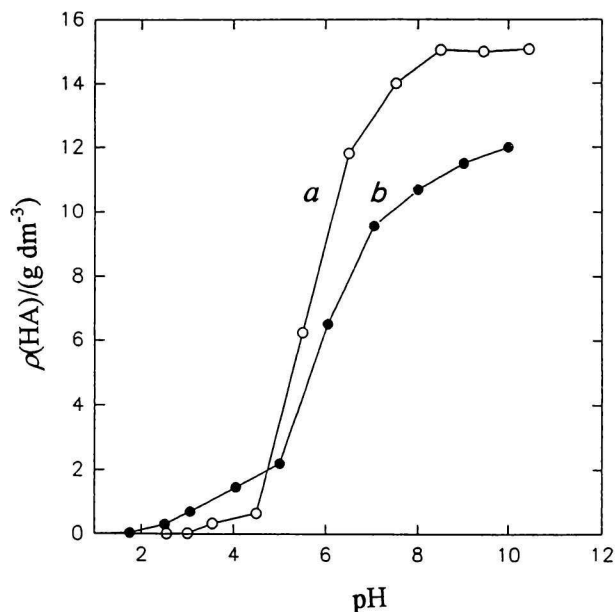


Fig. 1. Dependence of humic acid concentration on pH value (a); in the presence of 0.01 M sodium dodecyl sulfate (b).

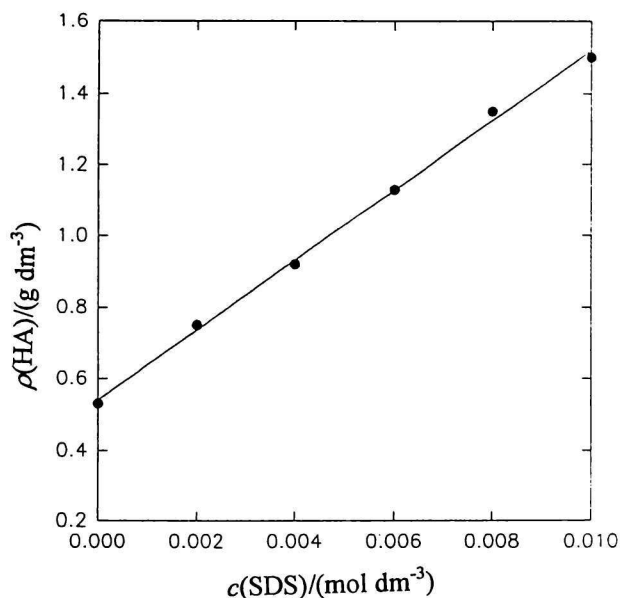


Fig. 2. Relationship between humic acid solubility and various concentrations of sodium dodecyl sulfate at pH 4.10.

RESULTS AND DISCUSSION

The solubility of HA as a function of pH in 0.1 M-NaCl media and influence of SDS on the solubility curve is summarized in Fig. 1. Unmonotonous character of solubility curve in relationship with pH (Fig. 1a) may be connected with conformation changes of HA molecules in saturated solution and colloidal properties at the same time. Research conducted by *Ghosh* and *Schnitzer* [5] indicates that HA molecules behave like rigid "spherocolloids" at high sample concentration, low pH, or the presence of high amounts of neutral electrolyte. On the other hand, at low concentration, neutral pH, or low ionic strengths they behave like "flexible linear colloids". From Ref. [6] it is known that the surfactants can influence the conformation of polyelectrolytes molecules as HA. The effect of surfactant on HA solubility was studied by using of 0.01 M-SDS solution (Fig. 1b). The HA solubility curve *vs.* pH was increased at pH < 5 and decreased at pH > 5 in contrast with the first position. The increase of solubility in the presence of SDS in the range of pH < 5 can be attributed to the effect of SDS on the structure of HA and by such a way the solubility of HA could be changed, otherwise the process of solubilization can also be observed. In agreement with *Ghosh* and *Schnitzer* [5] who have shown that HA can exist in two types of particles forming spherical and linear colloids in dependence on the pH, ionic strength, and HA concentration, the SDS molecules should be miscible with the linear form of HA particles. Due to the high electric charge which can be formed in the range of pH < 5

the HA solubility could be enhanced. Moreover, they are complex mixtures of natural polyelectrolytes exhibiting strongly varying molecular mass distribution [7]. The case of decreasing solubility curve at pH > 5 may be connected with convertible behaviour of HA in saturated solution. It has been recognized for some time that the addition of HA to an alkaline aqueous solution will lower the surface tension of that solution. It has also been shown that saturated HA solution in an alkaline aqueous solution will form a micelle [8] (at mass concentration > 7.4 g dm⁻³). This may indicate that HA in saturated solutions had some properties of surfactants, and at pH > 5 the solubility or the concentration of HA should be increased, therefore the HA particles stepwise will attain spherical structure, where the surfactant molecules may form the aggregates with hydrophobic interior of bulky HA micelles. Another explanation of decreasing solubility curve at pH > 5 may be related with changes in HA pattern micelles and their quantity in SDS molecular solution. The effect of the concentration of SDS on the solubility of HA was investigated in the range of SDS concentration of 10⁻³–10⁻² mol dm⁻³ at pH 4.1 (Fig. 2). It can be seen that the solubility of HA at this pH remained constant with no SDS addition and increased with increasing SDS concentration. Therefore, it was concluded that an anionic surfactant increases the HA solubility at pH < 5 and decreases it at pH > 5.

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