

CHEMICAL PROPERTIES OF DIFFERENT SOIL HUMIC ACIDS

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Introduction

Organic substances occur widely in soils, sediments and natural waters. The soil has almost unlimited capacity to accept these organic matters and transform them by biodegradation processes. Organic matter content affects the soil structure, fertility and water holding capacity, the acid-base buffering potential of soils, the adsorption properties, the behavior of micronutrients and heavy metals.

Acidification of the environment increases because of industrial activity, urbanization and intensive soil use. Soil pH influences physical, chemical and biological properties of the soils. The rate of acidification of soils depends on the quality and quantity of the buffer systems present. The main buffer systems operating in the soils are variable charged surfaces of the soil colloids, humic substances, surface of Al(III)- and Fe(III)-hydroxides, break surfaces of clay minerals, polymers of aluminum-hydroxides, -CaCO_3 - $\text{Ca(HCO}_3)_2$ - H_2CO_3 system (Filep and Rédly, 1990). In consequence of soil acidification the solubility of micronutrients and heavy metal ions changes. These soluble metal ions react with organic and mineral constituents of soils. Humic and fulvic acids are the main reactive natural organic polymers in the soils and natural waters they play very complex and important role in the soils. These organic acids are a very reactive part of the transformed organic materials. Their carboxyl and phenolic hydroxyl groups are responsible for the acidic-base properties. They as ligands can interact with metal ions (such as Cu, Mn, Al...) to form metal complexes (van Dijk, 1971 and Zunino, 1979). The aim of the examination is to study acid-base buffering properties of some soils, complexation of natural organic ligands with metal ions.

Natural organic acids consist of a mixture of well- and ill-defined organic acids, the structure and chemical behavior of the ill defined organic acids is very complex.

Methods and materials

Extraction of humic acids (HAc) from soils

Soil samples were collected from Hungary in native state and under grass vegetation. We selected different main types of soils such as chernozem, meadow, alluvial, brown forest and peat soils. We supposed that the humification processes in these soils were different really.

Humic acids were extracted under N_2 by tetrametil-ammonium-hydroxide according to Buzás, 1990. This method is suitable to extract the humic acids in native state. Humic acids were purified by dialysis and then freeze-dried.

Chemical characterization of HAc

Ash content determined by heating air-dry samples at 850°C for 6 hr. The elemental composition of HAc was determined by Elementar Vario El Analyzer.

Total acidity and quantity of carboxyl groups were measured by Ba(OH)_2 and Ca-acetate methods of Schnitzer and Gupta, 1965. Quantities of phenolic OH groups were calculated as difference of total acidity and amount of carboxyl groups. The acid-base properties and metal complexing were studied by pH potentiometry (Gamble, 1970 and Schnitzer, 1976).

Results

Yield of HAc

We didn't find direct correlation between soil humus content and quantity of extractable HAc. Ash content of native HAc increases with increasing silt and clay content of soils (Table 1).

Table 1. Analytical characteristics of soil humic acids

Soil type	<i>Hu</i> % (soil)	Extracted HAc (g/100g soil)	Ash%	C%	N%
Chernozem soil (leached)	3.1	2.10	44.4	21.9	2.29
Chernozem soil (calcareous)	3.8	8.60	55.1	44.1	6.72
Meadow soil	5.6	6.04	46.3	31.23	2.49
Alluvial soil	1.4	1.05	27.0	15.97	2.14
Brown forest soil	1.7	1.04	53.5	22.04	2.41
Peat	28.7	2.80	21.2	50.97	4.63

Chemical analysis

The knowledge of the acid-base properties of studied organic ligands is a basic condition to study of coordination compounds. We studied the acid-base properties of different HAc by potentiometric titration curves. By means of these curves we determined the inflexion points of titration curves. These pH values informed us about the quality of functional groups (Table 2). It was apparent from Table 2 that for each sample the pH of the inflexion point was between 6,3 and 6,9. These pH values confirm that the most important functional groups of HAc are the carboxylic (-COOH) and phenolic -OH groups.

The reactivity of HAs was characterized by determination the quantity of acidic functional groups. According to the value of total acidity (Table 2) the peat HAc was the most acidic compound and it followed the calcareous chernozem HAc and the meadow HAc (Table 2). The quantity of phenolic -OH groups was more than carboxylic groups in each case. So titration curves give information on the acid-base properties of organic acids and the degree of ligand-metal interactions.

Table 2. Acid-base properties of humic acids

Soil type	pH _{infl.}	Total acidity (meq/g)	-COOH (meq/g)	-OH (meq/g)
Chernozem soil (leached)	6.40	5.70	1.72	3.98
Chernozem soil (calcareous)	6.64	4.60	1.00	3.60
Meadow soil	6.41	5.20	1.62	3.58
Alluvial soil	6.90	4.50	1.49	3.01
Brown forest soil	6.30	4.60	1.11	3.49
Peat	6.90	6.30	1.73	4.57

From the potentiometric titration curves we found, that the complex forming ability of the soil humic acids increased in the following order peat > chernozem > meadow soil > alluvial soil > forest soil.

Conclusion

The acid-base ability of the humic acids was characterized by potentiometric titration. From the potentiometric titration curves we determined the acidity and complex forming ability of the HAc extracted from six different soils. Results of the investigation give significant data to know the behavior of metal ions in soil, which is of great importance from agricultural aspect.

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