INVESTIGATION OF HUMIC ACIDS AND METAL HUMATES WITH ANALYTICAL ULTRACENTRIFUGE

By

S. SIPOS, I. DÉKÁNY, F. SZÁNTÓ

Institute of Colloid Chemistry, Attila József University, Szeged

and

É. SIPOS

Chemical Department, Pedagogical High School, Szeged

The molecular weight of humic acids and metal humates of different origin was determined as a function of pH, time and electrolyte concentration. The molecular weights, particle radii and shape factors unequivocally indicate the presence of aggregates of molecules in the solution at lower pH values; at higher pH, this aggregates disintegrate. The molecular weight increases also with time. The changes in molecular weight of the humic acids of different ages and origin, and the fact of their pH dependent behaviour point to the circumstance that in assessing the formation of the structure, in addition to the age of the samples, also the geological conditions prevailing during the formation are to be taken into account.

Introduction

The first investigations concerning sedimentation of humic acids were performed by WELTE [1], however, without providing unequivocal results about the polydispersity characteristics of the system; this was partly due to the difficulties arising from the colouredness of the solution. Later on the evaluation of measurements became possible with the optical system devised and developed by PHILPOT and SVENSON.

Several workers, e.g. KERN [2] pointed out that there are important differences between molecular weights determined with classical methods and with ultracentrifuge, respectively. FLAIG [3] determined the molecular weight of humic acids and their morphologic parameters under different conditions with ultracentrifuge method.

The contradictory values of molecular weights found in literature show that the determination of the molecular weight of humic acids is a complex problem. In addition to the origin of the humic acid, several influencing factors are to be taken into account, such as pH, solvent-effects, temperature, concentration, ionic effects, etc. These factors, as well as the method of extraction may exert a decisive influence on the size and shape of the molecule and on the distribution of molecular weights.

In our investigations, the molecular weights of humic acids and metal humates of different origin were determined with ultracentrifuge method. Further, the aggregation state of the samples as a function of pH and time was studied, and some morphological parameters were calculated from sedimentation experiments. The influence of metal ions on humic acids was also investigated. The samples used consisted of humic acids extracted partly from peat, partly from coal of different degrees of carbonification, using appropriate processes for extraction, purification and fractionation.

Materials and methods

Sample No. 1. Humic acid obtained from Ecséd lignite with NaOH. The ligneous
product came from surface mining of a pleistocene formation.
Sample No. 2. Humic acid extracted with NaOH from a miocene Herend lignite
of ligneous-earthy structure, obtained by deep-mining.
Sample No. 3. Humic acid extracted with NaOH from lower eocene Tatabánya
brown coal.
Sample No. 4. Brown humic acid extracted by pyrophosphate process from Keszt-
hely peat.
Sample No. 5. Proteo-humic acid, extracted with NaOH from Keszthely peat.

The molecular weights of the samples were determined with an analytical ultra-centrifuge Mod. G-120 of the Hungarian Optical Works (MOM) Budapest, using the sedimentation equilibrium method.

Results and discussion

The results of our investigations are summarised in Tables I to IV.

Table I

*Dependence on pH of molecular weight, particle radius and shape
factor of the humic acid sample No. 1*

	pH			
	5.0	5.5	6.0	6.6
mol. wt. (equilibrium)	7650	5610	3340	2150
r (Å)	60	45	39	27
f/f$_0$	1.25	1.17	1.10	1.05

As can be seen from Table I, the molecular weight decreases with increasing pH. The shape factor f/f_0, characteristic for the shape of the molecule, suggests that at lower pH values, where the molecules may form relatively larger aggregates, an asymmetrical shape of the molecule is more probable. On the basis of SIMHA-s formula [4] the shape factor 1.25 corresponds to a ratio 1:5 of the axes, whereas

the shape factor 1.05 would correspond to a ratio 1:2. At this pH the aggregates of molecules begin to disaggregate, the particle radius also decreases to about to the half of its value.

It is to be remarked, that the samples have to be desalted for investigations on aggregation; namely, rather much salt gets into the solution during peptization and precipitation. According to FLAIG [3] 0.2 M NaCl given to a humic acid fraction of about 5000 molecular weight at pH 4.5 increases the molecular weight by a factor of about 15. We had similar experiences; our investigations were, however, not extended in this direction.

Table II

Changes in molecular weight of humic acid obtained from coals and peats of different ages, as a function of pH

Sample	pH			
	5.0	5.5	6.0	6.5
1	7650	5610	3340	2150
2	6200	5400	4500	3700
3	8350	7900	7200	5300
4	4400	4100	3900	3600

Inspection of the dependence of the molecular weight of humic acids obtained from coals and peat of different ages as a function of pH shows that the sample 1. is subjected to intensive disaggregation with increasing pH. Similar changes, though less expressed, are found with humic acids extracted from coals of higher ages. Sample 4, extracted from a peat of more recent period than the coals mentioned, shows relatively slight changes in molecular weight in the pH interval investigated.

Measurements in other pH intervals were hindered by the shortcomings of the ultracentrifuge method. Namely, at lower pH values of the solution, big aggregates are formed, which quickly sediment on the action of the centrifugal forces; whereas at higher pH the particles are totaly disaggregated.

These results point to the circumstance that, regarding the formation of the structure of the humic acid, not only the age of the material subjected to extraction has to be taken into account, but also other complex changes (microbiological or geochemical) occurring during the carbonification.

Table III

Changes in molecular weight of Keszthely peat humic acids as a function of time (pH $= 2.7$).

Sample	Time (in days)			
	0	24	56	80
4	3100	3100	4500	8700
5	3300	3400	5000	8000

Furthermore, besides the forces connecting the molecule aggregates, also impurities remaining after purification and hindering the disaggregation (*e.g.* bitumen), may play a certain role. This opinion is supported by the more or less lipophilic character of our coal-humic acid samples.

From the data of Table III, it can be seen that during the first 3 weeks there was no significant change in molecular weight, whereas in 2 months the molecular weight increased to the 1.5 fold of the original, and in 80 days by a factor of about 3.

The results of further investigations concerning the action of different metal ions on humic acids are summarised in Table IV. The dependence on electrolyte concentration of the molecular weight of different metal humates was investigated. The same anion (chloride) was used with all metal ions. The molecular weight was determined in a concentration range where no flocculation occurred; the solution was of colloidal state. The optimal range of electrolyte concentration was found by turbidity measurements, using a Zeiss "Specol" spectrophotometer.

Table IV

Molecular weight of metal humates, determined with sedimentation equilibrium method, independence on electrolyte concentration. Humic acid sample 4. Basic mol. wt.: 2200 (aqueous solution); basic concentration 0.1 g/100 ml; temperature: 25 °C; pH: 2.7

Metal ion	Electrolyte concentration (mmol/lit.)	Molecular weight
—	0.00	2200
Cu(II)	0.35	3100
	0.50	3400
	0.75	5700
	0.82	6700
	0.90	precipitated
Fe(III)	0.13	3400
	0.26	3700
	0.32	4300
	0.50	precipitated
Fe(II)	1.18	3800
	1.50	4000
	1.66	4200
	1.94	precipitated
Co(II)	0.90	3000
	2.10	4000
	2.85	4700
	3.66	precipitated
Mg(II)	3.60	2100
	5.00	2000
	9.00	precipitated

As a result of our measurements, it can be stated that different metal ions exert different effects on the humic acids. From the metal ions used, the strongest aggregating action was found with Cu(II) and Fe(III) ions. The action of Fe(II) and

Co(II) ions proved to be less pronounced. Mg(II) ions, on the other hand, had no aggregating effect, even with electrolyte concentrations which were higher by an order of magnitude. It would be justified to extend such investigations to different anions, too.

The sequence of the aggregating effect of different metal ions is in very good accordance with the sequence of stability of humic acid complexes found by OVTCHA-RENKO and et al. [5].

Investigations on the structure of humic acids are becoming of more and more increasing importance, as humic acids and metal humates play a significant role in pedology and recently find application as biologically active compounds in pharmacology, as well as components of drilling fluids of oil wells.

References

[1] *Welte, E.:* Pflanzenernährung Düng. Bodenkunde **1952**, 101.
[2] *Kern, W., S. Classen:* Makromolekulare Chemie **7**, 46 (1951).
[3] *Flaig, W. A. J.:* In: Isotopes and Radiation in Soil Organic-Matter Studies, p. 23. International Atomic Energy Agency, Vienna, 1968.
[4] *Simha, R.:* J. Chem. Phys. **13**, 1881 (1945).
[5] *Ovcsarenko, F. D.:* Agrokémia és Talajtan **20**, No. 1—2. (1971).

ИССЛЕДОВАНИЕ ГУМИНОВЫХ КИСЛОТ И ИХ СОЛЕЙ МЕТОДОМ АНАЛИТИЧЕСКОГО УЛЬТРАЦЕНТРИФУГИРОВАНИЯ

Ш. Шипош, И. Декань, Ф. Санто и Е. Шипош

Были определены молекулярные веса образцов гуминовых кислот и их солей различного происхождения в зависимости от времени, pH и концентрации электролита. Величины молекулярных весов, размеров частиц и фактора формы однозначно показывают, что при низких pH в растворах присутствуют ассоциаты молекул, эти ассоциаты распадаются с повышением pH. Молекулярный вес нарастает со времением.

Изменения молекулярных весов гуминовых кислот различного происхождения и возраста, а также разное их поведение при изменениях pH среды, повидимому, подтверждают те представления, что при характеристике образования структур необходимо принять во внимание всю предысторию образцов.