Surface Activity of Humic Substances

MARIS KLAVINS, OSKARS PURMALIS
Department of Environmental Science
University of Latvia
Raina blvd. 19, LV-1586, Riga
LATVIA
maris.klavins@lu.lv

Abstract: - Humic substances are able to reduce the surface tension of their solutions and thus can act as surface-active substances in natural environment and possibly also for industrial applications. The ability to influence the surface tension of humic substance solutions depends on their origin. The objective of this study is a comparison of the ability of humic substances of different origins (soil, water, peat, lignite etc.) to influence the surface tension of their solutions and identification of the structural characteristics of peat humic acids, determining their surfactant properties. Industrially produced humic materials demonstrated no or insignificant impact on the surface tension of their solutions, whereas the humic acids isolated from peat demonstrated significant impact of the surface tension of their solutions – they act as weak surfactants. The surface tension of humic acid solutions decreased with increasing concentration, and it depends on the solution pH. The ability to influence the surface tension of peat humic acids isolated from a well-characterized bog profile demonstrates dependence on age and humification degree. With increase of the humification degree and age of humic acids, their molecular complexity and ability to influence surface tension decreases; even so, the impact of the biological precursor (peat-forming bryophytes and plants) can be identified.

Key-Words: - Surface tension; Humic substances; Humification degree; Peat

1 Introduction
Humic substances (HSs) are the most widely distributed organic substances, and they can be generally described as naturally occurring, biogenic, heterogeneous, yellow to black in colour, of high molecular weight, and refractory. Humic substances can be divided into three fractions: a) humin is the fraction of humic substances that is not soluble in water at any pH; b) humic acid (HA) is the fraction of humic substances that is not soluble in water under acidic conditions (below pH 2), but becomes soluble at greater pH; c) fulvic acid is the fraction of humic substances that is soluble under all pH conditions [1]. Humic substances are the main organic component of soil, peat and natural waters, and they influence the process of formation of fossil fuels, as well as play a major role in the global carbon geochemical cycle. Interaction of humic substances with xenobiotics can modify the uptake and toxicity of these compounds and affect the fate of pollutants in the environment [2,3]. The structure of humic substances is characterised by the presence of numerous aromatic, carboxylic and phenolic functionalities, linked with alkyl moieties, imparting a measure of flexibility to the polymer chains. The molecular weight range commonly quoted for fulvic acids is 500 to 50 000 daltons (Da), while it can extend to values > 1 000 000 Da [1] for humic acids. Surface tension measurements define humic substances as surface-active substances [4-6]. The amphiphilic nature of humic substances has given rise to the micellar model for these compounds [4, 7]. Other studies have indicated that the spontaneous aggregation of aquatic solutions of humic substances can be intramolecular (involving single polymer molecule) or intermolecular (involving multiple chains) [8-10], and the interior of these assemblies is relatively hydrophobic, while the exterior is more hydrophilic. It has been suggested to describe the way of arrangement of humic substances in solutions as pseudomicellar [11, 12]. The objective of this study is a comparison of the ability of humic substances of different origins (soil, water, peat, lignite etc.) to influence the surface tension of their solutions and identification of the structural characteristics of peat humic acids (isolated from a peat profile), determining their surfactant properties.

2 Materials and Methods
2.1. Studied humic samples
Humic substances were isolated from soil, peat, sludge and water in Latvia, representing different environments. Full peat profiles were obtained from an ombrotrophic bog (located in the central part of Latvia) and cut into 5-cm layers for the analysis of peat properties and isolation of humic acids. Humic acids were extracted and purified.
using procedures recommended by the International Humic Substances Society (IHSS) [13]. An industrially produced humic acid (Aldrich) and an IHSS reference humic acid isolated from Pahokee (USA) peat were used for comparison. Analytical quality reagents (Merck Co., Sigma-Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without further purification.

2.2. Analysis of humic acid properties

Carbon, hydrogen, nitrogen and sulphur concentrations in the peat and humic acid samples (elemental analysis of C, H, N, S) were determined by the combustion-gas chromatography technique, using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments). UV/Vis spectra were recorded on a Thermospectronic Helios γ UV (Thermoelectron Co.) spectrophotometer in a 1-cm quartz cuvette. The ratio E\textsubscript{465}/E\textsubscript{665} [15], i.e. the ratio of absorbance at 465 and 665 nm, was determined for 10 mg of humic acid solutions in 100 mL of 0.05 M NaOH. Humification degree (according to [16]). For estimation of carboxylic groups and total acidity, an automatic titrator TitroLine easy (Schott-Geräte GmbH) was used. The known Ca-acetate method [13], based on the formation of acetic acid, was used for determining the total number of carboxylic groups. To estimate the total acidity, Ba(OH)\textsubscript{2} method was used [13].

2.3. Surface tension measurements

Surface tension measurements were taken with a Krüss K6 (Krüss GmbH) tensiometer, fitted with a 19 mm diameter platinum ring. Samples were prepared for measurement by diluting the standard solution in humic substances (1000 mg · L\textsuperscript{-1}) till the appropriate concentration and equilibrated for 24 hours. Solutions were placed in a shallow glass dish of 50 mm diameter, and the platinum ring was inserted in the middle of the container to avoid edge effects and equilibrated for 90 min. The ring was raised through manual operation of the torsion mechanism, and the tension readings at the instant of surface detachment were noted. All measurements were taken in triplicate at a temperature of 22 °C, and the mean results are used with a standard deviation not more than ±0.1 mN · m\textsuperscript{-1}. The surface excess values Γ (mol · cm\textsuperscript{-2}) (which represent the amount of HA molecules at an air-water interface) were calculated from the slope of (dγ/dlnC\textsuperscript{-1}) in a concentration dependence of surface tension. Gibb’s adsorption equation describes these values as follows:

\[ \Gamma = -\frac{1}{RT} \times \frac{d\gamma}{d\ln C}. \]

where R is the gas constant, T is absolute temperature, \( \gamma \) is the surface tension of the HA solution, and C is the concentration of humic substances [17].

2.4. Colloidal stability test

In coagulation tests [18], 0.2 g · L\textsuperscript{-1} of HA were used, increasing the amounts of coagulation electrolyte (NaCl, up to 1 mol · L\textsuperscript{-1}) at constant pH 3. Samples were left for 3 days. The coagulation intensity were determined with a HACH DR/2000 spectrophotometer, measuring turbidity at 450 nm. The coagulation ratio were calculated using the equation:

\[ T = \frac{T_{0.0001} - T_1}{T_{0.01} - T_1}, \]

where T stands for turbidity and the concentration of coagulation electrolyte is 0.0001 – 1 mol · L\textsuperscript{-1}.

3 Results and Discussion

3.1. Ability of humic substances of different origin to influence the surface tension of their solutions

To study the changes in the ability of humic substances to influence surface tension depending on their origin, we have used well-characterised humic substances (Table 1) isolated from soils, peat and aquatic sources as well as industrially produced and reference humic matter. The composition of major elements, atomic ratios and ash contents of the HA samples examined are presented in Table 1.

![Figure 1. Variation of surface tension of the humic acid solutions of different origins depending on their concentration (designation of humic acids as in Table 1).](image)

The studied humic acids demonstrate the ability to influence the surface tension \( \gamma \) of their solutions (Figure 1). In concentration intervals from 50 mg · L\textsuperscript{-1} to 1000 mg · L\textsuperscript{-1}, \( \gamma \) dropped from 56 – 70 mN · m\textsuperscript{-1} to 44 – 64 mN · m\textsuperscript{-1}. The surface tension of humic acid solutions at a fixed concentration can be...
used to describe their surfactant properties, and a comparatively high variability was observed among the studied humic substances.

Table 1. Elemental and functional composition of humic substances of different origin used in the study.

<table>
<thead>
<tr>
<th>Humic substance</th>
<th>Elemental composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial HA (Aldrich-HA)</td>
<td>60.70 3.70 1.50 34.10</td>
</tr>
<tr>
<td>Reference HA (Pahokee-HA)</td>
<td>58.84 3.60 3.74 36.62</td>
</tr>
<tr>
<td>Lignohumate HA</td>
<td>56.34 3.73 0.32 39.61</td>
</tr>
<tr>
<td>TP HA (podsol soil HA)</td>
<td>53.78 5.43 3.04 37.75</td>
</tr>
<tr>
<td>HG HA (glee soil HA)</td>
<td>45.41 4.34 3.34 46.91</td>
</tr>
<tr>
<td>SP HA (sod podsol soil HA)</td>
<td>39.13 4.27 3.41 53.19</td>
</tr>
<tr>
<td>Aquatic HA (River Daugava)</td>
<td>23.19 2.25 0.65 73.91</td>
</tr>
<tr>
<td>Olaine Bog HA</td>
<td>49.12 4.68 2.84 43.36</td>
</tr>
<tr>
<td>Sapropel HA</td>
<td>42.09 4.63 3.55 49.73</td>
</tr>
<tr>
<td>Compost HA</td>
<td>46.29 4.15 3.41 46.15</td>
</tr>
<tr>
<td>Sludge HA (sewage sludge HA)</td>
<td>52.76 6.85 6.48 33.91</td>
</tr>
</tbody>
</table>

3.2. Surface tension of humic acids from a peat profile

To study the impact of humic acid sources on their ability to influence the surface tension of their solutions, we have selected for study the humic acids isolated from an ombrotrophic bog peat profile (Figure 2). Such an approach allows to study how the biological composition of biological material and humification process affect the properties of peat humic acids. The results of paleobotanical investigations indicate the development and diagenesis of peat organic matter and humic substances. The studied bog Eipurs has been formed due to paludification of sandy ground as result of groundwater level increase and wet conditions after the Ice Age. The lowest part of Eipurs Bog is formed by fen woodgrass peat as well as Hypnum and sedge-Hypnum peat (Figure 2), and these layers are covered by transition type wood peat. The upper part is represented by a 3.45 m thick layer of raised bog peat of different types and decomposition degrees. For example, well-decomposed (40-48%) pine-cotton grass peat occurs at the depth of 1.18-1.39 m (Figure 2).

![Figure 2. Peat stratigraphy in Eipurs Bog.](image)

Basic peat humic acid properties were analyzed using peat elemental (C, H, N, O, S) composition and are summarized in Figure 3. The ash content in the studied humic acids range between 0.10 ± 0.02 % and 1.00 ± 0.05 %, with an average content of 0.5 ± 0.05. The C concentrations range from 48 to 56 %, H – from 4.2 to 5.4 %, N – from 1.8 to 2.5 %, S – from 0.5 to 1.8 % and O – from 38 to 44 %. The elemental composition of peat humic acids in Eipurs Bog is comparatively variable and reflects changes in the peat decomposition degree and peat types. C concentration in peat humic acids is increasing starting from the depth of 1 m up to the level of 53 % and then again decreasing. H concentrations demonstrate a significantly higher variability. Changes in N concentrations (increased in the upper and lower horizons of the bog, and also demonstrating increased values coinciding with the changes in the peat composition and formation conditions) could be associated with changes in the peat botanical composition and decomposition degree. S concentrations are significantly lower just in a few upper centimetres of the peat bog and comparatively stable along the peat column.
Figure 3. Elemental composition of peat humic acid in Eipurs Bog.

Figure 4. Variation of the surface tension of humic acid solutions depending on the location depth.

The surface tension of humic acid solutions decreases with increasing depth of location in the peat column (age of the peat and its humification degree). Trend of these changes is yet more evident if analyzing the changes in the ability of humic acid solutions to influence the surface tension depending on the depth of location (and also on the age and humification degree) of the humic acids isolated from a peat profile (Figure 5). Also in this case, it becomes evident that the ability of humic acids to influence surface tension (surfactant properties) decreases with increasing humification. With increasing depth of humic acids within a bog profile, the coagulation ability increases as well, thus supporting the idea regarding their micellar behaviour in solutions. The peat humic substances isolated from consecutively increasing depths in Eipurs Bog do have major differences in their ability to modify the tension of aquatic solutions (Figure 4).

Figure 5. Variation of the surface tension of humic acid solutions from Eipurs Bog and their coagulation ratio depending on the depth of humic acid within a peat profile.

Figure 6. Correlation between the parameters describing the properties and the ability of humic substances to influence the surface tension (surface tension for a solution with the concentration of humic acid at 100 mg · L⁻¹) of their solutions.

The effect of humic substances on surface tension depends on their amphiphilic character and tendency to accumulate at the water-air interface. It is known that the behaviour of humic substances in
aquatic solutions depends on their concentration, pH and, metal ion concentrations [8,9,11], and the same factors determine the influence of humic substances on the surface tension and the formation of pseudomicelles, since both are manifestations of the same solution properties. In the same time, the dependence of the properties of humic substances on their origin is well known [19,20]. Whereas the elemental composition of humic substances from soils and peat is generally similar to that of soil humic substances presented in literature [21], it is different from the composition of commercially available preparations isolated from coal and other sources. The ability of humic substances to influence the surface tension of their solutions largely supports the hypothesis that humic substances behave and can be described as supramolecular associations of relatively small molecules (for example, < 500 Da) rather than macromolecular polymers. This model implies that small and heterogeneous humic molecules self-assemble in supramolecular conformations stabilized mainly by weak forces, such as dispersive interactions (van der Waals, p-p, and CH-p bonds) and hydrogen bonds. These weakly bound conformations have only apparent large molecular dimensions, which can be reversibly disrupted into smaller molecular associations by treating humic solutions with small amounts of organic acids. The resulting reduction in molecular size is explained by the disruption of unstable humic superstructures into smaller-sized associations stabilized by the formation of strong intra- and intermolecular hydrogen bonds among humic molecules. To test the process of destruction of humic suprastructures, we have studied the changes in the ability of humic acids to coagulate in the presence of increasing concentrations of dissolved salt (coagulation test), depending on the depth of humic acid within a peat profile (Figure 5). As far as the ability of humic substances to influence the surface tension of their aquatic solutions significantly depends on their origin (Figure 1, 4), whereas the origin of humic substances influences their properties and structure, we have studied the impact of the basic properties of humic substances on their surfactant properties (Figure 9). There exist definite relations between the properties of humic substances (E_d/E_o, concentrations of functional groups, elemental composition and others), describing them as surfactants, and their basic properties; however, each of the selected parameters does not totally describe their ability to influence the surface tension of their solutions. Evidently, the development of micelles requires the interaction and development of associations of molecules. So, the ability to influence the surface tension of humic solutions cannot be described using the descriptors of molecular properties. The changes in the surface tension of humic acid solutions show that the total acidity and H/C atomic ratio are negatively correlated to the surface tension values. These descriptors of humic properties can be suggested for assessing the ability of humic substances of different origins to influence the surface tension of their solutions. Thus, with the increase of humification, age and peat decomposition, the molecular complexity of humic acids and their ability to influence the surface tension decreases. Γ (size of the humic macromolecule) also decreases with increasing humification degree.

4 Conclusions

The surface tension-pH curves of humic substances featured a minimum for all solutions, declining steeply from higher and lower pH values. The decrease in surface tension with decreasing pH reflects the gradual neutralization of acidic sites, which created amphiphilic species that migrated to the surface. The surface tension of humic substance solutions decreased with an increasing concentration as well as in the presence of metal salts. Many industrially produced humic materials demonstrated no or insignificant impact on the surface tension of their solutions, whereas the humic substances isolated from natural environments (water, soil, peat, sediments) demonstrated a significant impact on the surface tension of their solutions. Thus, there exist direct links between the origin and structure of humic substances on the one hand and their ability to influence the surface tension of aquatic solutions on the other hand. With the increase of humification, age and decomposition degree, the molecular complexity of humic substances and their ability to influence the surface tension decreases. Surface tension reflects the properties of biological precursor molecules, as it can be seen on the character of relations between the surface tension and precursor biological material.

Acknowledgements:

This work has been supported by the National Research program NatRes.

References:


