

SURFACE ACTIVITY OF HUMIC ACIDS DEPENDING ON THEIR ORIGIN AND HUMIFICATION DEGREE

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Humic substances are able to reduce the surface tension of their solutions and thus can act as surface-active substances in the natural environment, which may have industrial application. The ability to influence the surface tension of humic acid solutions depends on the origin of the humic acids. The objective of this study was comparison of the ability of humic acids of different origin (soil, water, peat, lignite etc.) to influence the surface tension of their solutions, and identification of the structural characteristics of peat humic acids that determine their surfactant properties. Industrially produced humic materials demonstrated no or insignificant impact on the surface tension of their solutions. However, humic acids isolated from peat had significant impact of the surface tension of their solutions, acting as weak surfactants. The surface tension of humic acid solutions decreased with increasing concentration, and depended on solution pH. Using a well-characterised bog profile, the ability to influence the surface tension of peat humic acids was shown to depend on age and humification degree. With increase of the humification degree and age, molecular complexity of humic acids and their ability to influence surface tension decreased; but nevertheless, the impact of the biological precursor (peat-forming bryophytes and plants) could be identified.

Key words: surface tension, humic acids, humification degree, peat.

INTRODUCTION

Humic substances (HSs) are the most common organic substances. They can be generally described as naturally occurring, biogenic, heterogeneous, yellow to black in colour, of high molecular weight, and refractory substances. 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 (Stevenson, 1994). 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 (Steinberg, 2003; Simpson *et al.*, 2004). 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 (Stevenson, 1994) for humic acids. Aqueous solutions of humic substances are

generally polydisperse, with size ranges differing according to the origin (aqueous, terrestrial, or marine) of the material in question and also depending on the isolation procedure.

Surface tension measurements define humic substances as surface-active substances (Guetzloff and Rice, 1994; Gašparovic and Cosovic, 2003; Salati *et al.*, 2011). The amphiphilic nature of humic substances has given rise to the micellar model for these compounds (Guetzloff and Rice, 1994; Piccolo, 2001). 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) (Engelbreton and von Wandruszka, 1996; Yates and von Wandruszka, 1999; Čtvrtničková *et al.*, 2011), 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 (Engelbreton and von Wandruszka, 1994; Schaumann, 2006).

The objective of this study was to compare the ability of humic substances of different origin (soil, water, peat, lignite etc.) to influence the surface tension of their solutions, and to identify the structural characteristics of peat humic acids (isolated from a peat profile) that determine their surfactant properties.

MATERIAL AND METHODS

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) (Tan, 2005). Briefly, 20 g of air-dried and finely ground samples were extracted under N_2 with 1 l of 1 M NaOH and stirred for 24 h. The suspension was filtered, and the solution was acidified with concentrated HCl to pH < 2 to precipitate humic acids. The obtained humic acids were further purified by repeated dissolving and precipitating, as well as dialysing against Millipore water with final drying. An industrially produced humic acid (Aldrich) and an IHSS reference humic acid isolated from Pahokee (USA) peat were used for comparison. The analysis of botanical composition of peat was performed microscopically, using a Carl-Zeiss binocular microscope for determining the decomposition degree (Lishtvan and Korol, 1975).

Analytical quality reagents (Merck Co., Sigma-Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without further purification.

Analysis of humic acid properties. ^{14}C dating was performed at the Institute of Geology of the Tallinn Technical University (Estonia). 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). Ash content was measured after heating 50 mg of each peat sample at 750 °C for 8 h. Elemental composition was corrected considering the ash content, and the oxygen amount was calculated as a difference.

UV/Vis spectra were recorded on a Thermospectronic Helios γ UV (Thermoelectron Co.) spectrophotometer in a 1-cm quartz cuvette. The ratio E_4/E_6 (Chen *et al.*, 1977), 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 (Borgmark, 2005) was estimated as absorption at 540 nm after treatment of 1.00 g of peat sample for 1½ hrs with 25 ml of 8% NaOH in a 25 ml plastic tube in a boiling water bath (95 °C) and filtration. For estimation of carboxylic groups and total acidity, an automatic titrator TitroLine easy (Schott-Geräte GmbH) was used. The known Ca-acetate method (Tan, 2005), based on the formation of acetic acid, was used for determining the total number of carboxylic groups. To estimate the total acidity, the $Ba(OH)_2$ method was used (Tan, 2005). Hydrophobicity of humic substances was characterised by their distribution between the water and polyethylene glycol (PEG) phases (PEG 20000, Fluka) (Zavarzina *et al.*, 2002) as the distribution coefficient $K_{PEG/W}$ (analogous to the octanol/water distribution coefficient K_{ow}).

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⁻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 minutes. The ring was raised through manual operation of the torsion mechanism, and the tension readings at the instant surface detachment was noted. All measurements were taken in triplicate at a temperature of 22 °C, and the mean results were used (standard deviation was less than ± 0.1 mN m⁻¹). The surface excess value Γ (mol cm⁻²) (which represents the amount of HA molecules at the air-water interface) was calculated from the slope of $dg \ln C^{-1}$, assuming dependence of surface tension on concentration. 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, γ is the surface tension of the HA solution, and C is the concentration of humic substances (Terashima *et al.*, 2004).

The slope $\Delta\gamma \Delta C^{-1}$ is the change in surface tension (mN m⁻¹) per unit change of dissolved organic carbon concentration (mgC l⁻¹) (Anderson *et al.*, 1995) for the concentration interval of 150–250 mg l⁻¹.

Colloidal stability test. In coagulation tests (Tombićz, 1999), 0.2 g l⁻¹ of HA were used, increasing the amounts of coagulation electrolyte (NaCl, up to 1 mol l⁻¹) at constant pH 3. Samples were left for three days. The coagulation intensity was determined with a HACH DR/2000 spectrophotometer, measuring turbidity at 450 nm. The coagulation ratio was calculated using the equation:

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

where T is turbidity and the concentration of coagulation electrolyte is 0.0001 – 1 mol l⁻¹.

RESULTS

Ability of humic substances of different origin to influence the surface tension of their solutions. To study the changes in the ability of humic acids to influence surface tension depending on their origin, we 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.

The studied humic acids demonstrates the ability to influence the surface tension γ of their solutions (Fig. 1, Table 2). In concentration intervals from 50 mg l⁻¹ to 1000 mg l⁻¹, γ dropped from 56–70 mN m⁻¹ to 44–64 mN m⁻¹. Regard-

Table 1

ELEMENTAL AND FUNCTIONAL COMPOSITION OF HUMIC SUBSTANCES OF DIFFERENT ORIGIN USED IN THE STUDY

Humic substance	Elemental composition, %				-COOH, mmol g ⁻¹	ArOH, mmol g ⁻¹	Aromaticity, %	E ₄ /E ₆
	C	H	N	O				
Commercial HA (Aldrich-HA)	60.70	3.70	1.50	34.10	2.15	1.17	16.3	4.51
Reference HA (Pahokee-HA)	58.84	3.60	3.74	36.62	8.1	1.8	21.6	3.93
Lignohumate HA (Lignohumate HA)	56.34	3.73	0.32	39.61	-	-	-	4.0
TP HA (HA from typical podsol soil)	53.78	5.43	3.04	37.75	5.5	0.57	22.9	3.83
HG HA (HA from humus gley soil)	45.41	4.34	3.34	46.91	4.9	0.52	19.9	3.73
SP HA (HA from sod podsol soil)	39.13	4.27	3.41	53.19	4.4	0.84	17.8	3.71
Aquatic HA (HA from the River Daugava)	23.19	2.25	0.65	73.91	1.0	4.39	9.5	8.97
Olaine HA (peat HA from Olaine Bog)	49.12	4.68	2.84	43.36	4.2	3.82	20.2	5.95
Sapropel HA (Spigu Bog sapropel)	42.09	4.63	3.55	49.73	3.5	1.7	11.4	2.51
Compost HA	46.29	4.15	3.41	46.15	5.7	1.22	9.7	4.12
Sludge HA (sewage sludge HA)	52.76	6.85	6.48	33.91	2.5	2.68	16.2	3.22

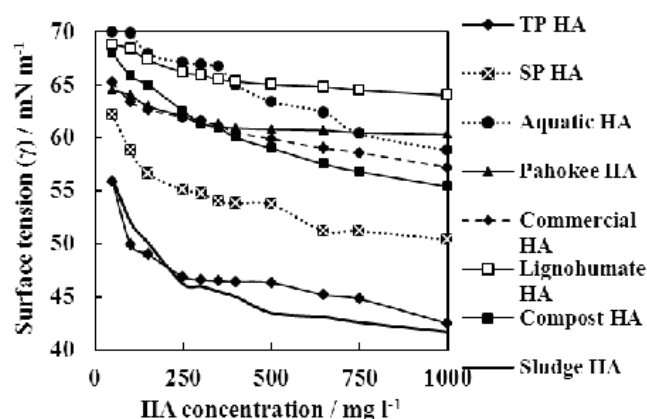


Fig. 1. Surface tension of the humic acid solutions of different origin, depending on their concentration (designation of humic acids as in Table 1).

ing the use of surface tension of humic acid solutions at a fixed concentration to describe their surfactant properties, a comparatively high variability was observed among the studied humic substances. The relative ability to influence surface tension can also be characterised by the slope $\Delta\gamma/\Delta C^{-1}$, as the change in surface tension (mN m⁻¹) in respect to dissolved organic carbon concentration (mgC l⁻¹) (Anderson *et al.*, 1995) for the concentration interval of 150–250 mg l⁻¹.

The surface excess values Γ represent the concentration of HA molecules at the air-water interface (Table 2). The surface excess values, which depend on the concentration of HA in the solution, demonstrate the ability of humic substances to form micellar structures at a distinct threshold micelle concentration — the concentration at which HAs develop organised structures on the interfaces. Surface excess values are higher for HAs isolated from soil and water than from peat, and they can be used in describing the supramolecular properties of HAs.

Surface tension of humic acids from a peat profile. To determine the impact of humic acid sources on their ability to influence the surface tension of their solutions, we selected humic acids isolated from an ombrotrophic bog peat profile (Fig. 2). Such an approach allows to determine how

Table 2

PROPERTIES OF HUMIC SUBSTANCES (designation of humic substances as in Table 1)

Humic substance	K _{PEGW}	$\Delta\gamma/\Delta C^{-1}$	Γ , mol cm ⁻²	Surface tension (100 mg l ⁻¹ HA), mN m ⁻¹
Commercial HA	6.70	-0.006	7.42 · 10 ⁻⁵	63.4
Reference HA	1.98	-0.010	2.47 · 10 ⁻⁵	64.0
Lignohumate HA	31.20	-0.013	4.53 · 10 ⁻⁵	68.4
TP HA	8.21	-0.021	1.21 · 10 ⁻⁴	50.0
HG HA	4.39	-0.028	1.61 · 10 ⁻⁴	64.0
SP HA	5.47	-0.015	1.04 · 10 ⁻⁴	58.8
Water HA	0.69	-0.001	1.02 · 10 ⁻⁴	69.9
Olaine HA	13.20	-0.012	5.44 · 10 ⁻⁵	62.4
Sapropel HA	4.39	-0.002	4.51 · 10 ⁻⁵	61.0
Compost HA	2.96	-0.025	1.04 · 10 ⁻⁴	65.8
Sludge HA	14.00	-0.039	1.20 · 10 ⁻⁴	52.1

the biological composition of biological material and the humification process affect the properties of peat humic acids.

The results of paleobotanical investigations (botanical composition, pollen analysis) indicate the development and diagenesis of peat organic matter and humic substances. The studied bog Eipurs developed by paludification of sandy ground as result of a groundwater level increase and wet conditions after the Ice Age. The lowest part of Eipurs Bog is formed by fen wood-grass peat as well as *Hypnum* and sedge-*Hypnum* peat (Fig. 2); 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 interval of 1.18–1.39 m (Fig. 2).

Basic peat humic acid properties were described using peat elemental (C, H, N, O, S) composition and are summarised in Fig. 3. The ash content in the studied humic acids ranged between 0.10 ± 0.02% and 1.00 ± 0.05%, with an average

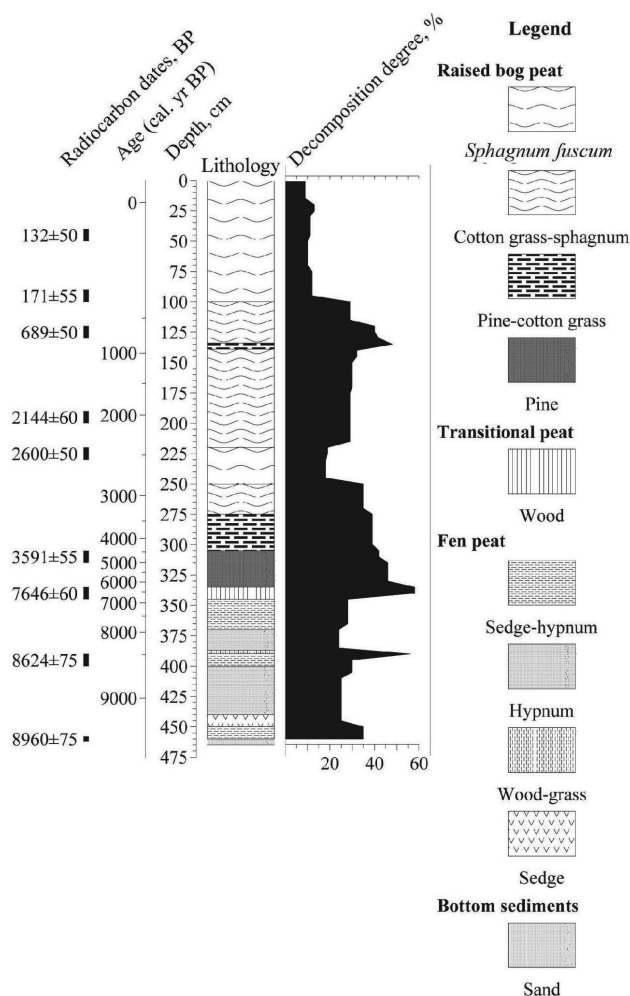


Fig. 2. Peat stratigraphy in Eipurs Bog.

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 increases in younger peat starting from a depth of 1 m up to the level of 53% and then again decreases. H concentrations demonstrate significantly higher variability. Changes in N concentrations (higher in the upper and lower horizons of the bog, in relation to peat composition and formation conditions) could be associated with changes in the peat botanical composition and decomposition degree. S concentrations are significantly lower in a few upper centimetres of the peat bog, but otherwise comparatively stable along the peat column.

Absorption at 540 nm in the visible spectra of peat alkaline extracts can be used as a simple indicator of the humification process, as suggested by (Milori *et al.*, 2002). The changes in the humification index in the peat profile of Eipurs Bog were associated with both the peat decomposition degree and the differences in peat composition (Fig. 4).

Changes in the concentrations of acidic functional groups in peat humic acids (Fig. 5) illustrate the character of peat

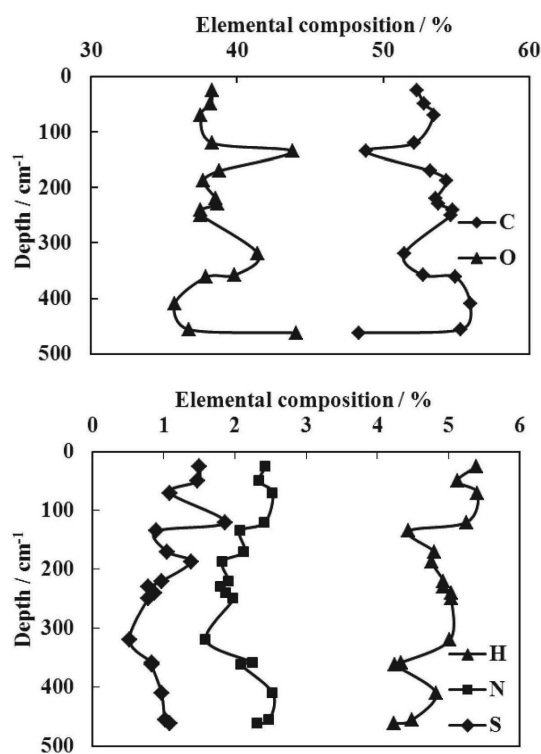


Fig. 3. Elemental composition of peat humic acid in Eipurs Bog.

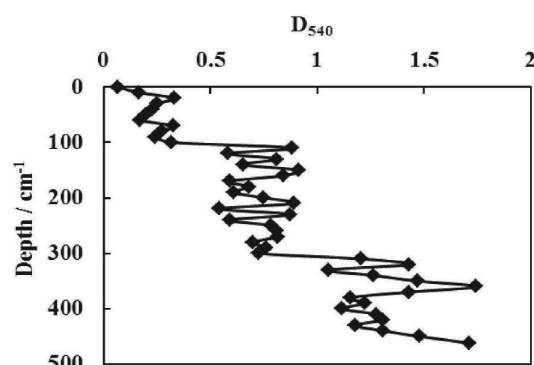


Fig. 4. Humification index (adsorption of peat extract at 540 nm) versus depth in peat from Eipurs Bog.

humic matter diagenesis: a relatively rapid increase in concentrations of carboxylic groups due to microbial decay of living organic matter. Humification is also characterised by a decrease of phenolic acidity in the structure of humic acids.

The peat humic substances isolated from consecutively increasing depths in Eipurs Bog had major differences in their ability to modify the tension of aquatic solutions (Fig. 6). The surface tension of humic acid solutions decreased with increasing concentration, and with increasing depth in the peat column (age of the peat and its humification degree) (Fig. 7).

The trend of these changes is yet more evident in 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 (Fig. 8). Also in this case, it be-

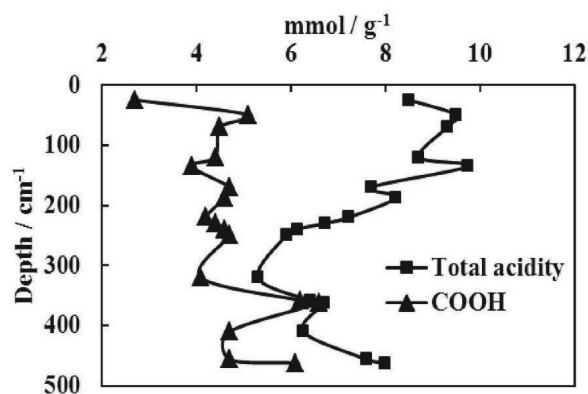


Fig. 5. Concentration of acidic functional groups versus depth in peat from Eipurs Bog.

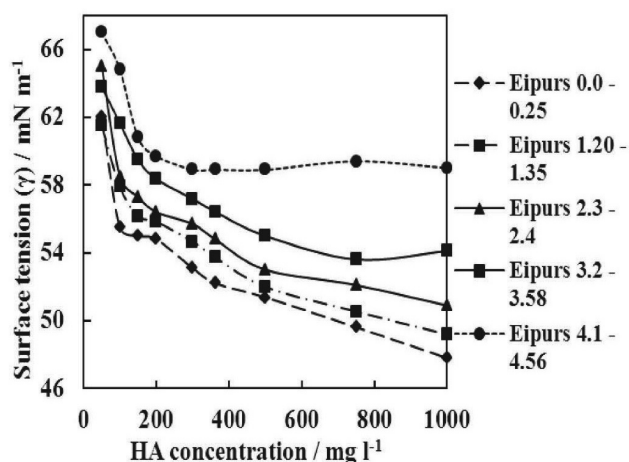


Fig. 6. Surface tension of humic acid (isolated from Eipurs Bog) solutions depending on the location depth.

comes 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 surface tension-pH curves featured a minimum for all solutions, declining steeply from higher and lower pH values (Fig. 7). The measured surface tension was greatest at high pH (>8) in all cases, since the humic solute was highly anionic (and therefore very hydrophilic) under those conditions.

The decrease in surface tension with decreasing pH reflects the gradual neutralisation of acidic sites, which creates amphiphilic species that migrate to the surface. The degree to which this occurred differed for different humic substances. This may be attributed to the high functional group density on these relatively small molecules, which allowed fairly extensive H bonding with the aqueous solvent throughout the pH range and hindered the development of a strong amphiphilic character. In all cases, the surface tension increased again in the low pH ranges, where continued neutralization produced increasingly hydrophobic molecules with low surface activity.

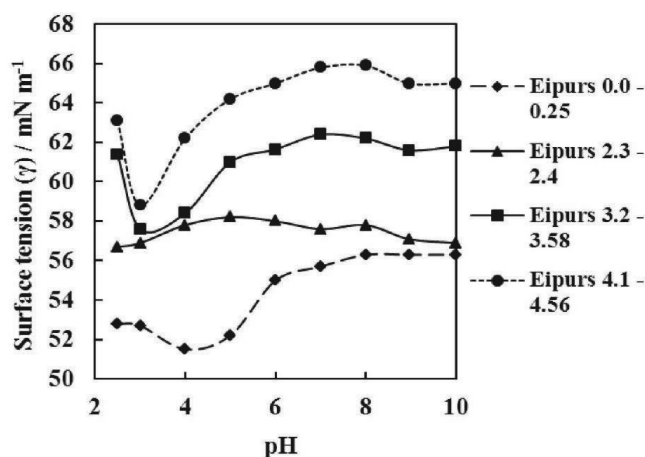


Fig. 7. Surface tension with pH for 100 mg l⁻¹ humic acid (isolated from Eipurs Bog at different depths) solutions.

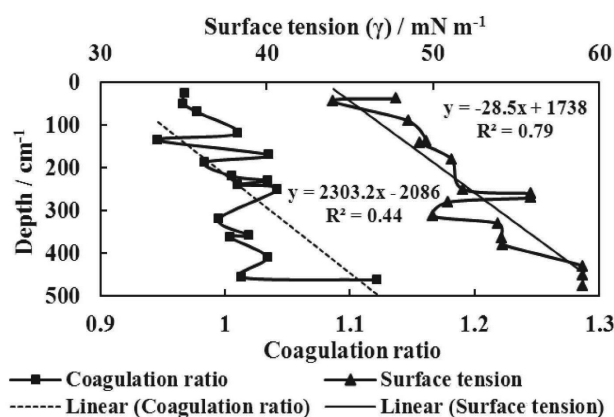


Fig. 8. Surface tension of humic acid solutions from Eipurs Bog and their coagulation ratio depending on the depth of humic acid within a peat profile.

DISCUSSION

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 (Engebretson and von Wandruszka, 1994; Engebretson and von Wandruszka, 1996; Yates and von Wandruszka, 1999; Conte *et al.*, 2005) 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. The dependence of properties of humic substances on their origin is also well known (Klavins, 1998). While the elemental composition of humic substances from soils and peat is generally similar to that of soil humic substances described in literature (Barančikova *et al.*, 1997; Lu *et al.*, 2000; Rozenbaha *et al.*, 2002), it does differ from the composition of commercially available preparations isolated from coal and other sources.

The surfactant properties of the studied humic substances (expressed as $\Delta\gamma/\Delta C^{-1}$) are higher for HAs from soil (Table 2) and lowest for industrially produced HAs (Fig. 1, Table

2). The reason for such significant differences is likely due to the ability of humic substances to interact and form large clusters. Industrially produced humic substances are usually extracted from low-rank coal, and significant destruction during the isolation procedure can take place. These much differ from humic material precursor living organisms, as in the case of soil, aquatic or sewage sludge humic acids. 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) had significant effect on the surface tension of their solutions.

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 rather than macromolecular polymers. This model implies that small and heterogeneous humic molecules self-assemble in supramolecular conformations stabilised mainly by weak forces, such as dispersive interactions (van der Waals, π - π , and CH- π 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 stabilised by the formation of strong intra- and intermolecular hydrogen bonds among humic molecules (Piccolo *et al.*, 2001). To test the process of destruction of humic suprastructures, we studied 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 (Fig. 8).

As the ability of humic substances to influence the surface tension of their aquatic solutions significantly depends of their origin (Figs. 1, 4, Table 2), and the origin of humic

substances influences their properties and structure, we examined the relationships between basic properties of humic substances and their surfactant properties (Fig. 9). The properties of humic substances (E_4/E_6 , concentrations of functional groups, elemental composition and others) related to surfactant action were associated with their basic properties, but 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. Thus, 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 indicate that the total acidity and H/C atomic ratio are negatively correlated to surface tension value, and the E_4/E_6 ratio (illustrating the molecular mass of humic acids) and hydrophobicity indicator K_{pegw} are positively related. The E_4/E_6 ratio reflects the presence of lignin residues, and as aromaticity is low in *Sphagnum* moss, the correlation is not straightforward. 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.

In conclusion, 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 neutralisation of acidic sites, which creates amphiphilic species that migrate to the surface. The surface tension of humic

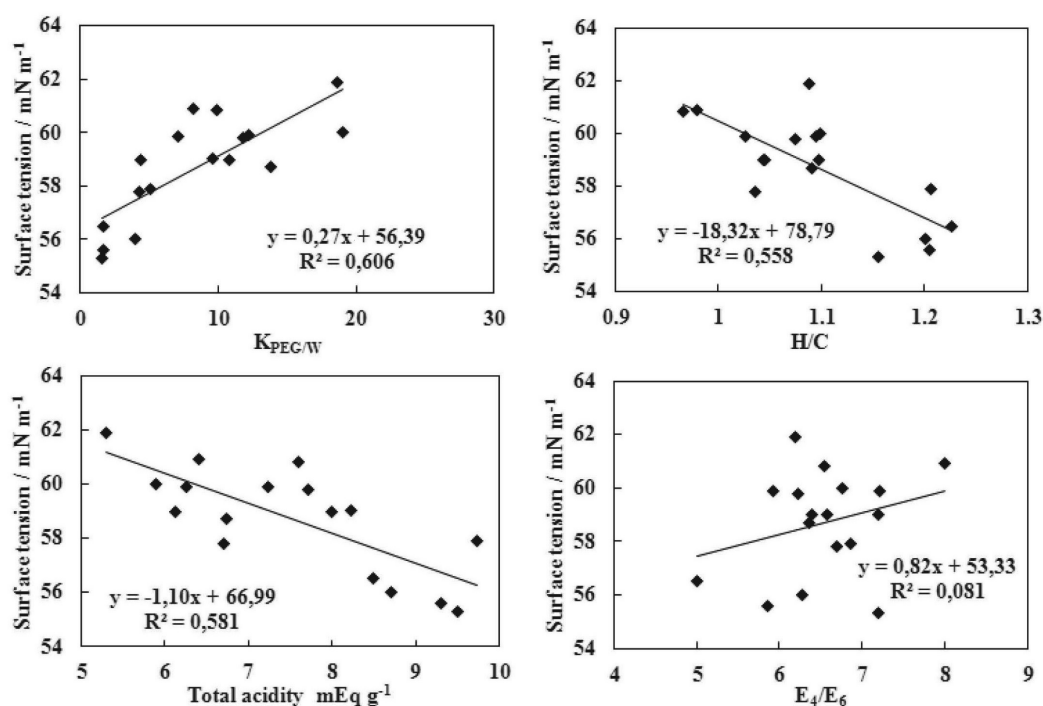


Fig. 9. Correlation between the parameters describing the properties and the ability of humic substances to influence the surface tension (surface tension for a solution with the concentration of Eipurs Bog humic acid at 100 mg l⁻¹) of their solutions.

substance solutions decreased with increasing concentration. 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 effect 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 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 can be seen by the character of relations between surface tension and precursor biological material.

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HUMUSVIELU IZCELSMES UN HUMIFIKĀCIJAS PAKĀPES IETEKME UZ TO VIRSMAS AKTIVITĀTI

Humusvielu spēja samazināt to šķīdumu virsmas spraigumu ļauj tās uzskatīt par dabīgām virsmas aktīvajām vielām, kuras var izmantot rūpniecībā. Spēja ietekmēt šķīdumu virsmas spraigumu ir atkarīga no humusvielu izcelsmes. Darba mērķis ir salīdzināt humusvielu spēju ietekmēt šķīdumu virsmas spraigumu atkarībā no to izcelsmes (augšne, ūdens, kūdra, lignīns u.c.) un noteikt īpašības, kas to ietekmē. Rūpnieciski ražotie preparāti neuzrāda vai arī parāda ļoti zemu spēju ietekmēt to šķīdumu virsmas spraigumu, taču no kūdras izdalītās humusvielas būtiski atšķiras, darbojoties kā vājas virsmas aktīvās vielas. Šķīdumu virsmas spraigums kritās, pieaugot humusvielu koncentrācijai, un ir atkarīgs no šķīduma pH. Virsmas aktivitātes izpēte humusvielām, kas izdalītas no plaši raksturota kūdras profila, parāda kūdras vecuma un humifikācijas pakāpes ietekmi. Pieaugot humifikācijas pakāpei un vecumam, humusvielu struktūras daudzveidība un spēja ietekmēt šķīdumu virsmas spraigumu samazinās. Būtiska ietekme ir organisko vielu izcelsmei (kūdras veidojošie augi un sūnas), no kā veidojušās humusvielas.