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ORIGINAL PAPER

Humic substances as surfactants

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Abstract Humic substances from soils and sediments can be defined as surface active substances based on the surface tension measurements. Although there are several micellar structural models of humic substances currently available, few studies evaluating humic substances as surfactants have been conducted to date. Therefore, we evaluated the ability of humic substances and their derivatives to influence surface tension. We found that the ability of a humic substance to influence the surface tension of a solution depends on its origin. Many industrially produced humic materials exerted little or no impact on surface tension, whereas humic substances isolated from natural environments (water, soil, peat, sediments, sludge from wastewater treatment facilities) exerted a large impact on surface tension. These findings indicate that the modification of humic substances can enable their use as surfactants. In addition, these findings indicate that solutions of humic substances and their derivatives can be used to increase the solubility of organic compounds.

Keywords Humic acid · Micelles · Solubilization

Introduction

Humic substances (HS) are the most widely found naturally occurring organic substances on earth. HS form the majority of the organic portions of soil, peat and natural waters. In addition, HS influence the formation of fossil fuels and play a major role in the global carbon geochemical cycle. Furthermore, the interaction between HS and xenobiotics may modify the uptake and toxicity of these compounds, thereby affecting the fate of pollutants in the environment (Simpson et al. 2004). The structure of a humic substance is characterized by the presence of numerous aromatic, carboxylic and phenolic functionalities that are linked together with alkyl moieties, which imparts flexibility to the polymer chains (Schulten and Schnitzer 1993). These functional groups allow derivatization reactions to be performed (Almendros 1994). The derivatives of HS obtained from such reactions can then be used to evaluate their structures.

Humic substances are defined as surface active substances based on their effects on surface tension (Wershaw 1993; Engebretson and von Wandruszka 1994). It has been reported that the spontaneous aggregation of aquatic solutions of humic substances can occur at the intramolecular (involving a single polymer molecule) or intermolecular (involving multiple chains) levels (Engebretson and von Wandruszka 1996; Lippold et al. 2008). The interior of these aggregates is relatively hydrophobic, while the exterior is more hydrophilic. It has also been suggested that humic substances in solutions exist in a pseudomicellar form (Piccolo et al. 2001). However, there are several micellar structural models of humic substances currently available, few studies evaluating humic substances as surfactants have been conducted to date (Terashima et al. 2004; Lippold et al. 2008). Therefore, this study was conducted to evaluate the surfactant properties of humic acids and their derivatives.

Experimental

Humic acids (HA) were isolated from different environments (soil, peat and water) in Latvia. The HA were then

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extracted and purified using the procedures recommended by the International Humic Substances Society (IHSS) (Tan 2005). Industrially produced humic acid (Sigma-Aldrich Co) and IHSS reference humic acid isolated from Pahokee (USA) peat were used for comparison. Humic-like substances (synthetic humic acids) were obtained by oxidative polymerization of resorcin using a previously described method (Jung et al. 2005).

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

Elemental analysis (C, H, N, S, and O) was conducted using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments).

UV/Vis spectra were recorded using a Thermospectronic Helios γ UV (Thermoelectron Co.) spectrophotometer in a 1-cm quartz cuvette. The E_4/E_6 ratio (Chen et al. 1977), which is the ratio of absorbance at 465 nm to that at 665 nm, was determined for solutions comprised 5 mg of each humic or fulvic acid dissolved in 10 ml of 0.05 N $NaHCO_3$.

Analysis of functional groups was conducted using potentiometric titration. Specifically, a TitroLine easy automatic titrator (Schott-Geräte GmbH) was used to measure the carboxylic and phenolic acidity of each HA (Tan 2005).

Surface tension measurements were obtained using a Krüss K6 tensiometer (Krüss GmbH) that was fitted with a 19-mm diameter platinum ring. Samples were prepared for measurement by diluting the HA until the concentration was equal to 1,000 mg/l and then allowing them to equilibrate for 24 h. The solutions were then placed in a shallow glass dish with a diameter of 50 mm. Next, a platinum ring was inserted into the middle of the container to avoid edge effects, and the sample was then allowed to equilibrate for 90 min. The ring was then raised by manual operation of the torsion mechanism and the tension readings at the instant of surface detachment were recorded. All measurements were made in triplicate at a temperature of 22°C and the mean results, which had standard deviations that did not vary by more than ±2 mN/m were used for subsequent data analysis.

The surface excess values, Γ (mol/cm^2), represent the number of HA molecules at the air–water interface. These values were calculated based on the slope of ($d\gamma/d\ln C$), which represents the concentration dependence of the surface tension:

$$\Gamma = -\frac{1}{RT} \times \frac{d\gamma}{d \ln C}$$

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 of the function that describes the change in surface tension, $-\Delta\gamma/\Delta C$, represents the change in surface tension (mN/m) per unit change in dissolved organic carbon concentration (mg C/l) (Terashima et al. 2004) for a concentration interval of 150–250 mg/l.

The hydrophobicity of humic substances was characterized based on their distribution between the water and polyethylene glycol (PEG) phases (PEG 20000, Fluka) (Zavarzina et al. 2002) as a distribution coefficient K_{PEGW} (analogous to octanol/water distribution coefficient—K_{ow}). To accomplish this, 10% PEG–10% $(NH_4)SO_4$–HA–H_2O systems were prepared by mixing 2 ml of 30% PEG solution with 2 ml of ammonium sulfate and 2 ml of HA (2 mg/ml in 0.05 M NaOH). The mixtures were then shaken for 10 min. Following the complete phase separation, 1 ml was taken from each phase and diluted tenfold with 0.05 M $NaHCO_3$. Next, the absorbance at 465 nm was measured on a DR/2000 spectrophotometer (Hach Co). The distribution coefficients were then calculated using the following equation: K_{PEGW} = absorbance at 465 nm of the top (PEG-rich) phase/absorbance at 465 nm of the bottom phase.

Modification of humic acid with sulphopropyl groups (SP–HA, I)

A 10 g of humic acid (Sigma-Aldrich Co) was dissolved in 100 ml dimethylformamide, after which 6.40 g (0.05 mol) of 1,3-propanesultone were added and the reaction mixture was stirred at 70°C for 8 h. The reaction product was poured into 1 l of acetone, after which the precipitated modified humic acids were removed by filtration, washed with water, followed by acetone and then dried to obtain 12.82 g of modified humic acid. The properties of the obtained products are summarized in Table 1.

Modification of humic acid with trimethylammonio groups (TMA–HA, II)

A 20 g of humic acid (Sigma-Aldrich Co) was dissolved in 60 ml of 0.5 N NaOH, after which 9.25 g (0.1 mol) of 1-chloro-2,3-epoxypropane were added. The mixture was then stirred at 60°C for 2 h, after which 19.20 g (0.2 mol) of trimethylammonium chloride and 40 ml of 0.5 N NaOH were added. Next, the mixture was stirred at 60°C for 8 h, after which it was acidified by adding concentrated HCl until it had a pH of 1. Acidification resulted in precipitation of the modified HA, which were then removed by filtration, washed with H_2O and dried to give 14.85 g of modified HA. The properties of obtained products are summarized in Table 1.

Table 1 Elemental and functional composition of the humic substances used in this study and their derivatives

Humic substance	Elemental composition (%)					–COOH (mmol/g)	ArOH (mmol/g)	E_4/E_6
	C	H	N	O	S			
Commercial HA (Aldrich-HA)	60.70	3.70	1.50	34.10	0	2.15	1.17	4.51
Reference HA (Pahokee-HA)	58.84	3.60	3.74	36.62	0	8.1	1.8	3.93
Lignohumate HA (Lignohumate HA)	56.34	3.73	0.32	39.61	0	–	–	4.0
Synthetic HA (from resorcin)	61.26	3.74	0	35.00	0	0.21	2.23	3.48
TP HA (HA from typical podsol soil)	53.78	5.43	3.04	37.69	0.06	5.5	0.57	3.83
SP HA (HA from sod podsol soil)	39.13	4.27	3.41	53.12	0.07	4.4	0.84	3.71
Aquatic HA (Daugava River HA)	33.19	2.25	0.65	63.82	0.08	1.0	4.39	8.97
Olaine HA (Olaine bog peat HA)	49.12	4.68	2.84	43.36	0	4.2	3.82	5.95
Livani HA (Livani bog peat HA)	50.93	4.85	3.35	40.87	0	5.1	0.36	2.73
Kemeri HA (Kemeri bog peat HA)	52.33	4.71	1.95	41.01	0	4.8	2.41	2.48
Sludge HA (sewage sludge HA)	52.76	6.75	6.48	33.91	0.10	2.5	2.68	3.22
SP–HA (HA with sulphopropyl groups)	54.35	3.64	1.42	34.90	5.69	4.23	1.03	4.23
TMA–HA (HA with trimethylammonio groups)	46.10	4.47	5.61	43.82	0	–	0.75	4.41
SA–HA (HA with sulphoalkyl groups)	55.26	3.47	1.38	36.02	3.87	5.34	1.26	4.38
HG–HA (HA with hydroxyl groups)	58.24	3.72	1.24	36.80	0	1.87	0.45	5.05

Modification of humic acid with sulphoalkyl groups (SA–HA, III)

A 10 g of humic acid (Sigma-Aldrich Co) was dissolved in 50 ml of 16% formaldehyde (w:w), after which 11.0 g (0.1 mol) of $NaHSO_3$ were added. Next, 10% NaOH was added dropwise until the solution had a pH of 10–12. The reaction mixture was then stirred at 80°C for 6 h. Next, the mixture was filtered, after which the pH of the filtrate was reduced to 1 by the addition of 6 N HCl. The reduction in the pH resulted in precipitation of the sulphoalkylhumic acid, which was then removed by filtration, washed with water followed by acetone and then dried to give 8.6 g of humic acid. The properties of the obtained product are summarized in Table 1.

Modification of humic acid with hydroxyl groups (HG–HA, IV)

A 10 g of humic acid (Sigma-Aldrich Co) was dissolved in 50 ml of 0.5 N NaOH, after which 30.0 g (0.5 mol) of 2,3-epoxypropane were added. The reaction mixture was then stirred at 80°C for 24 h. Next, the pH of the reaction mixture was reduced to 1 by the addition of concentrated HCl. Acidification resulted in the precipitation of the modified HAs, which were then removed by filtration, washed with H_2O and dried, to give 8.99 g of modified humic acid. The properties of the obtained product are summarized in Table 1.

Results and discussion

We used well-characterized humic acids (Table 1) isolated from soils, peat and aquatic sources as well as industrially produced and reference humic matter to evaluate differences in the ability of humic substances to influence surface tension based on their origin. The composition of the HA samples evaluated in this study are presented in Table 1. The elemental composition of humic substances from soils, water and peat is generally similar to that of soil humic substances that have been previously described; however, the composition of commercially available preparations differed slightly, possibly as a result of impact of extraction process.

The concept of modifying humic substances is based on the methods used for the development of biopolymers with surfactant properties (Heinze and Liebert 2001). The sites at which modification of humic substances can occur include the first benzene ring in phenolic structures and hydroxyl groups. The suggested modification methods are designed to enable the addition of hydrophilic sulfonic, hydroxyl, or trimethylammonium functional groups, which are likely to affect the surfactant properties. Derivatives of HA were characterized based on their elemental and functional analysis as well as their IR and ^{1}H NMR spectra.

The effect of humic substances on the surface tension of their solutions is determined by their amphiphilic character and tendency to accumulate at the water–air interface. It is well known that the behavior of humic substances in aquatic solutions depends on their concentration, pH and

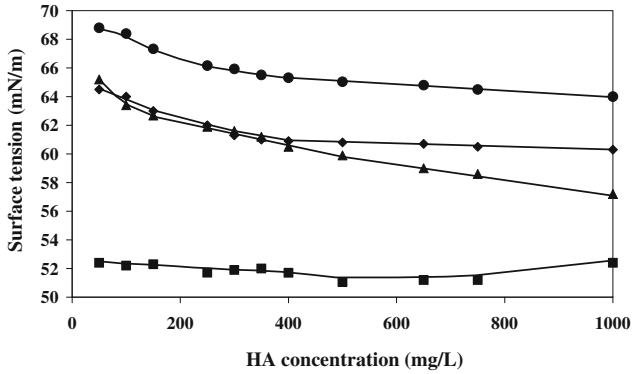

Fig. 1 Variation in the surface tension of industrially produced and synthetic humic acid solutions based on their concentrations: Lignohumate HA (*filled circle*); commercial HA (*filled triangle*); reference HA (*filled diamond*); synthetic HA (*filled square*)

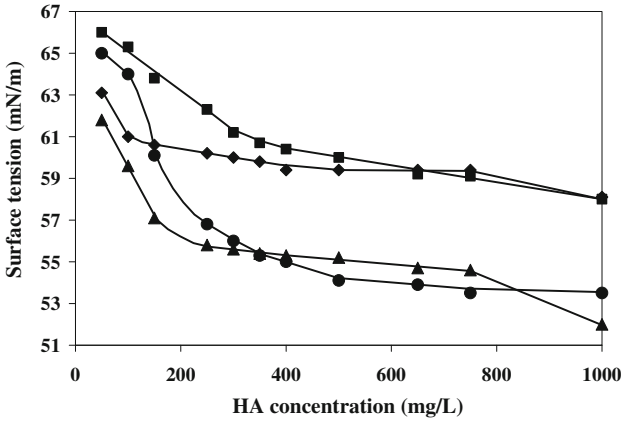

Fig. 2 Variation in the surface tension of solutions containing derivatives of humic acids depending on their concentration: TMA–HA, II (*filled square*); SP–HA, I (*filled diamond*); SA–HA, III (*filled circle*); HG–HA, IV (*filled triangle*)

the concentration of metal ions in the solutions (Engebretson and von Wandruszka 1996) and the same factors determine the influence of humic substances on surface tension and the formation of pseudomicelles. This is because both effects are manifestations of the same solution properties. In addition, it is well known that the properties of humic substances depend on their origin (Fig. 1) (Lu et al. 2000). Therefore, we evaluated differences in the ability of humic substances to influence surface tension based on their origin using well-characterized humic acids isolated from soils, peat and aquatic sources, as well as industrially produced and synthetic humic matter and their derivatives that were developed with the intention of increasing their ability to influence surface tension.

All of the humic substances evaluated in this study demonstrated the ability to influence surface tension (γ) of their solutions (Fig. 1). Specifically, as the concentration of humic substances increased from 50 to 1,000 mg/l, γ dropped from 56–70 to 43–59 mN/m. The surface tension of a solution that has been treated with a given humic substance at a fixed concentration does not vary; therefore, the surface tension can be used to describe the surfactant properties of a type of humic material. As shown in Fig. 2, the surface tension induced by humic substances obtained from different sources varied significantly. The relative ability to influence surface tension can be characterized by the slope of $\Delta\gamma/\Delta C$, which describes the change in surface tension (mN/m) per unit change in dissolved organic carbon concentration (mg C/l) for a concentration interval of 150–250 mg/l. The surface excess value, Γ, represents the amount of HA molecules at an air–water interface (Table 2). However, humic substances cannot be described as true surfactants.

The surface excess values depend on the concentration of HA in the solution; therefore, they represent the critical micelle concentration, which is the concentration at which HA develop organized structures on interfaces. We found that the surface excess values were higher for HA isolated from soil and water than for those isolated from peat. In addition, we found that the surface tension was highest for HA from soil (Table 2), but lowest for industrially produced HA (Fig. 1; Table 2). This is likely because the ability of humic substances to interact and form large clusters differs depending on their origin. In addition, these findings indicate that their properties can be altered during the derivatization process. For example, significant changes can occur during the isolation of HA from low-rank coal. However, the derivatization approaches used in this study can lead to an increase in the surfactant properties of the humic substances evaluated here (Fig. 2).

The development of micellar structures is associated with changes in macromolecules in the solution phase that lead to the exterior of the molecule (molecular aggregates) becoming more hydrophilic and the interior becoming more hydrophobic. This allows a hydrophobic microenvironment that supports the ability of the HAs to solubilize hydrophobic organic molecules. To test the effects of HA on solubility, we analyzed changes in the solubility of anthraquinone in the presence of humic substances (Figs. 3, 4). As shown in Fig. 3, the solubility of anthraquinone depends on the concentration of the modified humic acid in the solution, which determines the point at which micellar structures develop. However, we also found that all of the humic substances evaluated here had the ability to increase the solubility of anthraquinone. Taken together, these findings indicate that the ability to manipulate the formation of micellar structures can influence the behavior of hydrophobic organic contaminants in natural environments and be used to enhance the remediation of environments that have been contaminated with such compounds.

Table 2 Properties of humic substances used in this study and their ability to influence the surface tension of their solutions

Humic substance	K_{PEGW}	$\Delta\gamma/\Delta C$	Γ (mol/cm^2)	Surface tension (100 mg/l HA) (mN/m)
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
Synthetic HA	16.67	−0.012	2.13×10^{-4}	52.2
TP HA	8.21	−0.021	1.21×10^{-4}	50.0
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
Livani HA	5.25	−0.014	9.07×10^{-5}	55.1
Kemeri HA	14.61	−0.012	8.27×10^{-5}	63.5
Sludge HA	14.00	−0.039	1.20×10^{-4}	52.1
SP–HA	14.26	−0.008	4.54×10^{-5}	61.0
TMA–HA	11.21	−0.015	7.07×10^{-5}	55.3
SA–HA	5.79	−0.041	9.49×10^{-5}	54.0
HG–HA	11.13	−0.011	112×10^{-4}	49.6

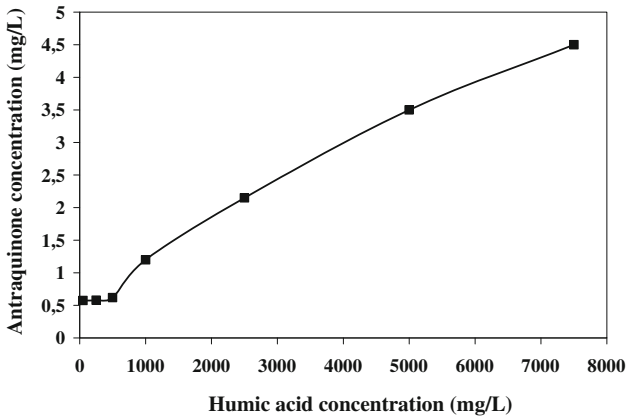

Fig. 3 Changes in the solubility of anthraquinone in the presence of humic acid derived from typical podsol soil (TP HA)

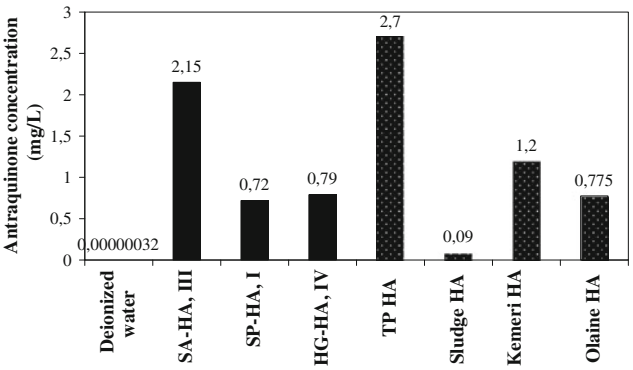

Fig. 4 Solubility of anthraquinone in the presence of different humic acids (3 g/l) and their derivatives

Conclusions

Humic substances behave like surface active substances when they are added to solutions; however, their ability to influence surface tension depends on their origin and molecular properties. For example, humic substances isolated from natural environments (water, soil, peat, and sediments) were found to have a significant impact on the surface tension the solutions they were added to, with the surface tension decreasing as the concentration of these compounds increased. However, industrially produced humic materials had little or no impact on the surface tension of their solutions. Finally, the results of this study suggest that modification of the methods used to derive HAs can allow significant increases in the surfactant properties of humic substances.

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