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Surfactant properties of atmospheric and model humic-like substances (HULIS)

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[1] Surface-active organics such as humic-like substances (HULIS) are abundant in aerosol particles and can lower the surface tension of cloud droplets forming on secondary organic and biomass burning aerosols. How fast is the diffusion of these species, relative to the time scale of cloud droplet growth? Here we report surface tension measurements of solutions containing HULIS extracted from smoke and pollution aerosol particles as well those of molecular weight-fractionated aquatic fulvic acids. Diffusion coefficients are estimated based on the Gibbs adsorption isotherms. The results suggest that HULIS diffusion to the surface of forming droplets is typically more rapid than the time scale of droplet growth so that cloud microphysical properties are affected. **Citation:** Taraniuk, I., E. R. Graber, A. Kostinski, and Y. Rudich (2007), Surfactant properties of atmospheric and model humic-like substances (HULIS), *Geophys. Res. Lett.*, *34*, L16807, doi:10.1029/2007GL029576.

1. Introduction

[2] High molecular weight multifunctional organic compounds may accumulate on aqueous surfaces and depress surface tension of cloud and haze droplets [Facchini *et al.*, 1999; Nenes *et al.*, 2002; Shulman *et al.*, 1996]. Depression of surface tension could affect cloud droplet formation and cloud properties such as albedo [Facchini *et al.*, 1999], because surface tension considerably affects the Kelvin term in the Köhler equation. It was previously suggested that surface-active compounds can also lead to substantial reduction of mass transfer in and out of droplets [Ervens *et al.*, 2005; Shulman *et al.*, 1996, 1997]. Recent field and laboratory studies have shown the presence of surface-active high molecular weight species (~500 AMU), termed humic-like substances (HULIS) in secondary organic aerosols, biomass burning smoke, rain drops and haze [Graber and Rudich, 2006]. As a result, it is expected that such compounds, in general, and HULIS in particular, could impact aerosol CCN properties and cloud microphysics [Kanakidou *et al.*, 2005; VanReken *et al.*, 2005].

[3] Cloud droplet activation calculations often assume that equilibrium concentrations of dissolved species are

instantaneously reached and that they are distributed uniformly throughout the droplet during the activation process [Laaksonen *et al.*, 1998; Raymond and Pandis, 2002; Shantz *et al.*, 2003]. However, compared to salts, some high molecular weight organic compounds are not very soluble in water, and diffuse more slowly in aqueous solutions. If this is the case, mass transfer of dissolving organics may not be fast enough to obtain uniform mixing at all times throughout the drop activation process, hence forming a concentration gradient in the droplet volume. This may have certain implications for cloud microphysical processes:

[4] 1. For slowly dissolving species, a concentration gradient may form inside the particle, lowering the solute concentration at the droplet surface compared with the equilibrium concentration, and increasing the droplet equilibrium vapor pressure, delaying or hindering droplet formation [Asa-Awuku and Nenes, 2006].

[5] 2. For slowly diffusing surface active material, if the surface concentration is not attained instantaneously [Asa-Awuku and Nenes, 2006], the surface tension value may change in time as more organic matter diffuses to the surface, since the value of surface tension is concentration dependent.

[6] 3. Fast diffusing surface-active species could concentrate at the droplet surface during activation, leading to lower surface tension values. If the concentration of the surface-active compound in the droplet is small enough, partitioning of the substance on the surface could deplete it from the droplet interior, decreasing the Raoult term and increasing the Kelvin effect. Thus, surface partitioning could cause an increase of the critical supersaturation (Köhler curve maximum) [Kokkola *et al.*, 2006].

[7] Thus, assuming instantaneous dissolution and equal distribution of solute throughout the droplet volume may overestimate the effect of slightly soluble and slowly-diffusing compounds on CCN activation.

[8] In this study, we measured the time and concentration-dependent behavior of aqueous solutions containing HULIS compounds isolated from collected aerosol particles. These measurements are used for estimations of diffusion coefficients and molecular dimensions of these species, with the aim of elucidating their atmospheric significance by affecting surface tension of droplets. Finally, we address the question of when accumulation at the surface may be important. Since this question depends on the rate of droplet growth or evaporation, it leads to another question: is HULIS diffusion relatively fast or slow compared to cloud droplet activation? Based on the observation that growth parameter has the same units as the diffusion

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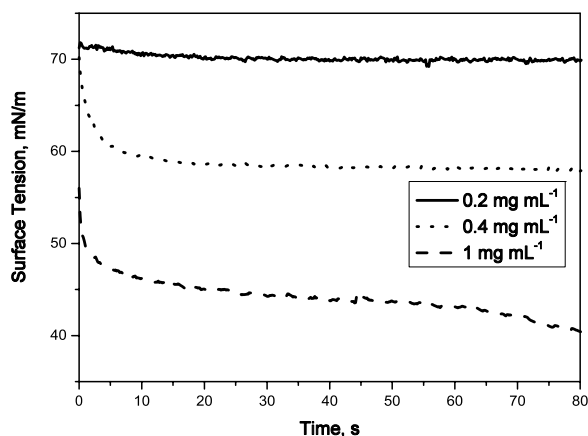


Figure 1. Surface tension of aqueous solutions containing slightly aged HULIS extracted from wood burning aerosols (LBO-Day). Changes in surface tension value as a function of time and concentration are demonstrated.

coefficient, we suggest a simple dimensionless criterion to answer these questions.

2. Experiment

2.1. Samples

2.1.1. Humic Substances Model Samples

[9] Suwannee River Fulvic Acid (SRFA, IHSS code 1R101F) was used as a model for atmospheric HULIS. It was de-ashed and separated from low molecular weight organic acids and inorganic species [Dinar *et al.*, 2006].

[10] The SRFA bulk sample contains fulvic acids with a polydisperse distribution of molecular weights. To study how surface tension and molecular diffusion vary with molecular weight, the bulk sample was coarsely divided according to the effective size of the molecules in solution using ultrafiltration. The average nominal molecular weight of the fractions was estimated using published correlations between molecular weight and UV absorbance [Schafer *et al.*, 2002]. Five fractions of water-soluble material (denoted F1 to F5), with different average nominal molecular weight, were obtained for each sample. Only the bulk and fractions F2 and F3 (estimated average number molecular weight of 570, 520 and 620 AMU, respectively) were used, as their hygroscopic properties have been shown to be more similar to ambient HULIS [Dinar *et al.*, 2006, 2007].

2.1.2. HULIS Samples

[11] Atmospheric HULIS were isolated from collected aerosol particles. The collected samples were: 1) HULIS extracted from fresh wood burning smoke particles (*LBO-night*) sampled throughout the night (26–27 May 2005, average PM10 mass concentrations of 300–400 $\mu\text{g m}^{-3}$), 2) HULIS extracted from slightly-aged wood burning smoke particles (*LBO-day*) sampled during daytime, following nighttime fires (27 May 2005, average PM10 mass concentrations of 60–180 $\mu\text{g m}^{-3}$) and, 3) HULIS extracted from ambient urban aerosol particles (*3WSFA*) collected during daytime only over a three week period (26 July to 16 August 2005), with average PM10 mass concentration of about 25 $\mu\text{g m}^{-3}$.

[12] Water soluble fulvic acids (FA) were extracted from the filters and separated from the other particle components by an isolation procedure which is detailed by Dinar *et al.* [2006]. The average molecular weight of the HULIS samples was estimated using UV absorbance assuming the same correlations as for SRFA. All HULIS and SRFA samples were in H^+ form.

2.2. Surface Tension Measurements

[13] The surface tension of aqueous solutions of SRFA (bulk, F2 and F3) and of three HULIS samples extracted from collected atmospheric particles was measured by the pendant drop method under controlled environmental conditions ($24 \pm 1 \text{ C}^\circ$, close to 100% relative humidity). Concentrations were lower than 3 g L^{-1} , below the reported critical micelle concentration (CMC) point for humic acid [van Wandruszka, 2000].

[14] In addition, surface tension of bulk SRFA solutions at concentrations up to 100 g L^{-1} was measured using a Delta-Pi microtensiometer (Kibron Inc., Helsinki, Finland) based on the Wilhelmy method and utilizing a small diameter (0.51 mm) special alloy wire. It is noted that SRFA was fully soluble in water at concentrations as high as 100 g L^{-1} . The results obtained by both methods agree well.

3. Results and Discussion

3.1. Adsorption Isotherm Analysis

[15] For all solutions, up to several hours were needed to reach equilibrium values of surface tension (γ). The final surface tension value and the rate at which equilibrium is attained depend on the concentration of the compounds in

Table 1. Parameters Derived From Equations (1)–(4)

Sample	Excess Adsorption Density, mol m^{-2}	Area per Molecule, nm^2	Molecular Diameter Hexagonal Packing, nm	$D \text{ m}^2 \text{ sec}^{-1}$	Molecular Weight
HULIS 3 WKS	6.65×10^{-6}	0.25	0.62	7.82×10^{-10}	500
HULIS LBO Night	4.36×10^{-6}	0.38	0.77	6.33×10^{-10}	610
HULIS LBO Day	7.20×10^{-6}	0.23	0.60	8.14×10^{-10}	410
SRFA F3	2.28×10^{-6}	0.73	1.06	4.58×10^{-10}	620
SRFA F2	1.69×10^{-6}	0.98	1.23	3.94×10^{-10}	520
SRFA Bulk	1.93×10^{-6}	0.86	1.15	4.21×10^{-10}	570
Salma <i>et al.</i> [2006], urban HULIS	1.10×10^{-6}	1.51	1.52	3.18×10^{-10}	
Kiss <i>et al.</i> [2005], rural HULIS spring	2.06×10^{-6}	0.81	1.11	4.35×10^{-10}	
Facchini <i>et al.</i> [1999], HULIS from haze particles	2.25×10^{-6}	0.74	1.07	4.55×10^{-10}	

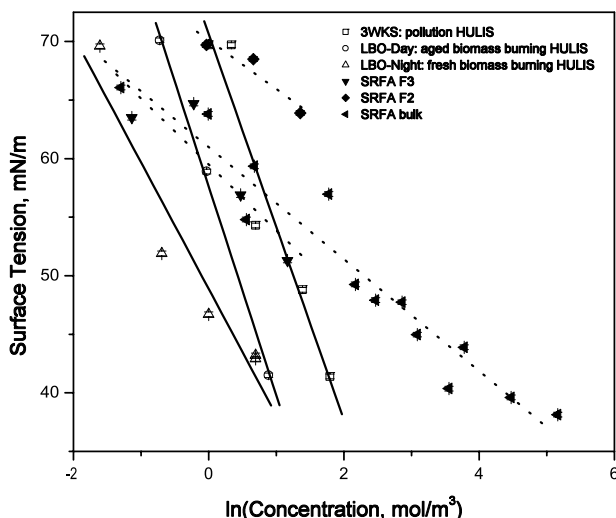


Figure 2. Surface tension isotherms of HULIS and SRFA samples (bulk, F2 and F3).

the solution (Figure 1), as was also noted previously [Salma *et al.*, 2006]. Equilibrium γ values are given in Table 1. For this study, the equilibrium value was defined as when the changes in γ were less than 0.2 mN min^{-1} within 1000 seconds. The change of γ with time was fit to a second-order exponential decay from which the final values reported here were obtained. Second-order exponential decay was found to provide the best fit for all the data sets. This may indicate that at least two time-dependent processes are involved in establishment of equilibrium: (i) diffusion of molecules to the surface, and (ii) conformational re-arrangement of molecules at the surface, or competition between disparate molecules for surface sites. In some runs, the final values of γ were obtained during the measurement according to the criterion (γ less than 0.2 mN min^{-1} within 1000 seconds) and there was no need to use a second-order exponential decay fit.

[16] Diffusion coefficients were estimated from the equilibrium surface tension values as a function of concentration. The surfactant's excess concentration on the surface compared to concentration in the bulk was calculated from surface tension isotherms using the Gibbs equation [Dukhin *et al.*, 1995].

$$\frac{d\gamma}{d(\ln a)} = -RT\Gamma \quad (1)$$

where γ is the surface tension, Γ is the excess adsorption density at equilibrium, R is the gas constant, T is the temperature, and a is the activity of surfactant in the bulk solution at equilibrium. a is assumed to equal solution concentration (C) at equilibrium (C_e), and C_e is considered to be equal to C initial on the assumption that adsorption at the surface does not significantly deplete the bulk solution.

[17] Linear adsorption isotherms of atmospheric HULIS and SRFA samples were obtained (Figure 2). The slope yields Γ_∞ , the maximal surface coverage. The Γ_∞ values are given in Table 1, together with data extracted from published studies for atmospheric HULIS from rural and

urban locations in central Europe [Kiss *et al.*, 2005; Salma *et al.*, 2006].

[18] Using the obtained Γ_∞ values, the area (S_m) occupied by a single molecule in the adsorption layer is estimated.

$$S_m = \frac{1}{N_a \Gamma_\infty} \quad (2)$$

where N_a is Avogadro's number. The S_m values are given in Table 1.

[19] Under certain simplifying assumptions, the values of S_m can be used for estimation of the molecular diameters of the studied species. This requires defining the relationship between the area at the surface occupied by a molecule and its geometry. First, it is assumed that the packing of molecules at the gas/liquid interface is determined only by interactions in this layer. In addition, we assume that the molecular projection on the layer is circular. These assumptions and the assumed close packing imply that the molecules are arranged as circles with equal diameter lying in the plane with a hexagonal arrangement. Close packing is often assumed [Kitajgorodskij, 1965] and numerous experimental evidence for hexagonal packing in organic monolayers on the air/water interface exists [Kajiyama *et al.*, 2001; Peng *et al.*, 2001; Peng and Chan, 2001]. Under these assumptions, the area occupied by each molecule is equivalent to that of a hexagon and the diameter of the molecule is equal to the distance between opposite sides of the hexagon. According to this model, the molecular diameters, d_m , can be calculated:

$$d_m = \sqrt{\frac{8S_m}{3\sqrt{3}}} \quad (3)$$

Given isoperimetric property of a circle, these d_m values (see Table 1) should be regarded as a lower bound.

[20] The calculated diameters suggest that the atmospheric HULIS and the SRFA fractions represent two groups: atmospheric HULIS (0.62 to 0.77 nm) have smaller sizes than those of the three SRFA samples (1.06–1.23 nm) by up to a factor of two. Interestingly, the HULIS collected in this study have a smaller radii compared with those calculated for the HULIS samples studied by Kiss *et al.* [2005] and Salma *et al.* [2006]. These differences may demonstrate the vast variability that HULIS can exhibit, depending on location and source.

[21] Using the calculated diameters it is possible to estimate the diffusion coefficients of the atmospheric HULIS samples and SRFA by the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta r_m} = \frac{kT}{3\pi\eta d_m} \quad (4)$$

where D is the diffusion coefficient, r_m is the molecular radius, k is the Boltzman constant, T is the temperature, and η is the dynamic viscosity of medium (water). It is assumed here that the organic molecule is spherical and that their size is at least five times that of the solvent molecules.

[22] The calculated diffusion coefficients of SRFA fractions (F2, F3 and bulk), and atmospheric HULIS extracted

in our experiments and investigated by others are also listed in Table 1. The calculated diffusion coefficients for SRFA bulk can be compared with diffusion coefficients measured by different methods (fluorescence correlation spectroscopy (FCS), pulsed-field gradient nuclear magnetic resonance spectroscopy (PFG-NMR) and flow field-flow fractionation (FIFFF) [Lead *et al.*, 2000]), which range between 1.9 and $3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, close to $4.21 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ calculated here. The calculated diffusion coefficients for the atmospheric HULIS are about a factor of two larger than the measured diffusion coefficients of the model substance. This is in good agreement with the given molecular diameter approximation. Diffusion coefficients of HULIS isolated from rural and urban locations in central Europe [Kiss *et al.*, 2005; Salma *et al.*, 2006] calculated according the same procedure give values comparable to those of SRFA.

[23] The hydrodynamic diameters of SRFA was calculated using the measured diffusion coefficients by NMR [Lead *et al.*, 2000]. The hydrodynamic diameters of SRFA bulk range between 1.5 and 2.5 nm . Naturally, these values are higher than the estimated molecular diameters obtained by assuming a closely packed layer. The difference may also be due to a hydrodynamic resistance of a solvation layer which increases the apparent hydrodynamic diameter. This suggests that molecules in the closely-packed layer are less hydrated than when they are solvated in dilute aqueous solution. An “hydration shell” (estimated to be around 0.2 nm [Zhou, 1995]) would increase the diameter of our SRFA samples to 1.5 – 1.6 nm , which is more consistent with the hydrodynamic diameter values [Lead *et al.*, 2000]. The diffusion coefficients calculated by equation (4) can be compared with those obtained for other substances having similar molecular weights. Diffusion coefficients for polyethylene glycol (PEG) oligomers of $2.6 \times 10^{-10} \text{ m}^2 \text{ sec}^{-1}$ for 400 g mol^{-1} PEG in D_2O at 25°C between 1.8 to 5.6% w/w were measured by NMR [Zhou, 1995], comparable to the results obtained here.

[24] The temperature dependence of the dynamic viscosity and of the diffusion coefficients, as well as the distribution of molecular weights in our samples could lead to some uncertainties in these estimations. However, although HULIS are highly heterogeneous material, it seems that the mean values can be used to characterize them and to predict their behavior.

3.2. Dynamic Aspects of Droplet Activation and Growth in the Presence of HULIS

[25] The presence of HULIS in a growing droplet may affect droplet activation and growth, e.g., introduction of kinetic effects as discussed by Chuang *et al.* [1997] and by Nenes *et al.* [2001]. Here we briefly examine time-dependence of surface tension from the quasi-steady growth perspective. Depending on dissolution kinetics, diffusion rate of the surfactant molecules, and the rate of droplet growth (the latter being a function of super-saturation and updraft velocity), the surface of the growing droplet may advance faster or slower than the diffusing surfactant molecules. For example, in the case of “slow” diffusion, surface tension of pure water might be relevant, while in the “fast” diffusion case, a lower, concentration-dependent surface tension value may be appropriate. Here we investi-

gate whether there is a simple way to distinguish these regimes.

[26] To that end, we use an approximate equation of droplet growth [Rogers and Yau, 1996],

$$r^2 \approx r_0^2 + 2\xi t \sim 2\xi t \quad (5)$$

where $r = r(t)$ is the radius of a droplet, and ξ is the growth parameter. Observe that ξ has the same units as a diffusion coefficient (D). Hence, a dimensionless ratio, $D/2\xi$, yields a simple “rule of thumb” for judging the relative rapidity of diffusion compared with the diffusion-like droplet growth. To illustrate, we take a typical value at $T = 0^\circ\text{C}$ and $p = 80 \text{ kPa}$. Interpolating from Figure 7.1 of Rogers and Yau [1996], $\log_{10}(\xi_1) = 1.834$ and $\xi_1 \approx 10^{1.834} \approx 70 \mu\text{m}^2/\text{sec}$. Thus, the growth parameter $\xi \equiv (S - 1)\xi_1 = s\xi_1 \approx s \times 70 \mu\text{m}^2 \text{ s}^{-1}$ ($s =$ fractional supersaturation). Since s seldom exceeds $0.5\% = 0.005$, [e.g., see Rogers and Yau, 1996, p. 107], ξ is bounded by about $70/200 \approx 0.35 \mu\text{m}^2/\text{sec} \approx 3.5 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. This value is two to three orders of magnitude lower than the measured HULIS diffusion coefficients reported here (Table 1). Assuming larger updrafts (e.g., see Rogers and Yau [1996], p. 109, Figure 7.4, curve for 2 m s^{-1}) boosts the value of s (fractional supersaturation) to 0.6% and large updrafts pushing s to 1% still yields $2\xi \approx 1.4 \mu\text{m}^2 \text{ s}^{-1}$. Furthermore, choosing extreme values of ξ (2.2 versus 1.83) may double the growth rates once more but without changing the basic conclusion that the HULIS diffusion is faster than the droplet growth rate.

[27] In summary, the HULIS estimated diffusion coefficients samples are ~ 2 orders of magnitude faster than the estimated rate of droplet growth under most tropospheric conditions. Therefore, HULIS diffusion is sufficiently rapid to conclude that these surfactants would reside on the surface and would influence droplet evolution provided that they reach high enough concentrations. The extent of that influence will still depend on the kinetics of dissolution, which was not tested in this study. Interestingly, previous studies showed that surface tension of HULIS samples did play a role in both hygroscopic growth and droplet activation [Dinar *et al.*, 2006; Wex *et al.*, 2007]. In contrast, surface tension apparently did not strongly influence droplet activation of the SRFA [Dinar *et al.*, 2007]. Since diffusion rates are apparently sufficiently large in both cases, it may be that there is a difference in dissolution kinetics between HULIS and SRFA, whereby SRFA dissolution kinetics may be hindered due to its larger molecular size [Engebretson and von Wandruszka, 1998]. Alternatively, the time required to achieve equilibrium with respect to surface tension due to adsorption limitations (rearrangement of molecules at the surface, etc.) may be greater for SRFA than in HULIS since this process depends on the rotational diffusion coefficient, which is a function of the molecular size.

[28] Our results and a very simple treatment of cloud droplet growth suggest that for most conditions in the troposphere, diffusion is fast enough to assure that throughout the droplet growth process, HULIS can reach the surface of the droplet and lower the surface tension of the forming droplet. This will be true as long as dissolution constraints do not play a role [Asa-Awuku and Nenes, 2006]. In cases where the overall concentration of these species is

sufficiently small, this surface partition may lead to the formation of a concentration gradient with reduced concentrations in the droplet interior [Kokkola *et al.*, 2006]. Formation of such gradients could potentially decrease the Raoult effect and increase the Kelvin effect in the Köhler equation. Thus, the surface partitioning could cause an increase of the critical supersaturation. It is expected that the effect increases with decreasing size of the cloud condensation nucleus [Kokkola *et al.*, 2006]. Finally, since ξ depends on super-saturation, the derived criterion immediately connects properties of surfactants with meteorological conditions (e.g., updraft velocity, super saturation, etc.)

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