



## Surface tension of atmospheric humic-like substances in connection with relaxation, dilution, and solution pH

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[1] Humic-like substances (HULIS) were isolated by a solid-phase extraction procedure from PM<sub>2.5</sub> fraction urban-type atmospheric aerosol samples collected in downtown Budapest, Hungary, in the nonheating season. Their amount was derived, and the surface tension properties of their pure solutions were investigated. Carbon content of HULIS accounted for 54% of the water-soluble organic carbon and for 19% of organic carbon in the aerosol. Solution of pure HULIS in concentrations corresponding to real incipient cloud droplets decreased the surface tension of water by about 30%, and the major decrease occurred within several tens of seconds. In diluted solutions, however, the thermodynamic equilibrium in surface tension was only reached after several hours, but the equilibrium depression value was still remarkable, about 18%. Detailed analysis of the relaxation curves implied that the kinetics of the surface tension depression should be regarded as and described by a diffusion-controlled process. The surface tension curves as a function of the HULIS concentration after an elapsed time of up to about 100 s resembled the curves observed earlier, but the shape of and tendency in the equilibrium curve (the isotherm) was rather different. The deviations were linked to physicochemical properties of certain classes of compounds within the HULIS. The surface tension depended on the solution pH as well; the smallest depression was observed at about pH = 5, and it was increased by an additional 13% for strong acidic or basic conditions; hence the role of surface tension in cloud droplet formation under acid rain conditions is further amplified.

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### 1. Introduction

[2] It is increasingly recognized that both water-soluble and slightly water-soluble compounds in fine-sized aerosol particles play an important role in the atmospheric system [Shulman *et al.*, 1996; Zappoli *et al.*, 1999; Facchini *et al.*, 1999; Rodhe, 1999; Seidl, 2000; Graham *et al.*, 2002; Tuckermann and Cammenga, 2004]. They influence the properties of the gas-liquid interface of the droplets, and hence several exchange processes like condensation or evaporation, gas dissolution, and the multiphase or liquid-phase water chemistry within the system. Consequently, they alter cloud droplet nucleation, growth, critical supersaturation, and coalescence which influence substantially the indirect climate forcing of atmospheric aerosol [Haywood and Boucher, 2000], and the hydrological cycle [Ramanathan *et al.*, 2001]. The modified Köhler theory [Shulman *et al.*, 1996] describes the equilibrium relative vapor pressure over an aerosol droplet consisting of soluble and partially soluble components as function of

the droplet radius depending on many factors. The controlling variables include the chemical composition, and some physicochemical properties (solubility, osmotic and surface activity) of the components [Cruz and Pandis, 1998]. The fine-sized water-soluble and slightly water-soluble aerosol fraction is made up mainly by sulfate, nitrate and organic compounds in many environments [Saxena and Hildemann, 1996; Zappoli *et al.*, 1999]. One of the most abundant classes of the water-soluble organic compounds are humic-like substances (HULIS) [Havers *et al.*, 1998; Zappoli *et al.*, 1999; Gelencsér *et al.*, 2000; Krivácsy *et al.*, 2000; Decesari *et al.*, 2000; Fuzzi *et al.*, 2001; Kiss *et al.*, 2002; Decesari *et al.*, 2006], which are reported to be surface active [Facchini *et al.*, 1999, 2000; Mircea *et al.*, 2002; Negre *et al.*, 2002]. The most pronounced effect of their presence in fog and cloud water samples is the decrease of the surface tension of water [Facchini *et al.*, 2000; Decesari *et al.*, 2001], which in urban environments, can cause changes in the cloud droplet number that exceed the Twomey effect [Nenes *et al.*, 2002]. Nevertheless, chemical (molecular and elemental) composition and physicochemical properties of HULIS are still poorly characterized and understood [Graber and Rudich, 2006, and references therein]; and their behavior has often been approximated by that of a

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mixture prepared of model compounds [e.g., *Chan and Chan*, 2003; *Tuckermann and Cammenga*, 2004; *Svenningsson et al.*, 2006]. These compounds, however, contribute at most only a few percent by mass to the organic matter in real aerosol, and, therefore, the results obtained may not fully be representative for the real properties, and should be considered with caution. Another approach is to isolate pure HULIS from aerosol samples by class separation on the basis of their polarity or acidic properties [*Decesari et al.*, 2000; *Krivácsy et al.*, 2001; *Varga et al.*, 2001; *Dinar et al.*, 2006], and to determine their composition and properties directly and without major interference. The main advantage of the latter approach is that it yields a more realistic (multicomponent) mixture of organic compounds actually present in the aerosol. Disadvantages are the operationally defined character of the isolation (moreover, there are several isolation protocols which have not been compared yet), the limits imposed by the relatively small amounts of samples isolated, and the lack of interaction between the organic and inorganic components in the system obtained [*Li et al.*, 1998]. Furthermore, low-molecular mass water-soluble compounds (e.g., short-chain fatty acids) that could be included in the isolated fraction contribute also to the observed effects.

[3] Within the framework of a comprehensive atmospheric aerosol research project [*Salma et al.*, 2004, 2005; *Maenhaut et al.*, 2005], HULIS samples were isolated from the PM<sub>2.5</sub> fraction urban aerosol, their contribution to organic carbon (OC), and to water-soluble organic carbon (WSOC) were derived, and surface tension properties were determined in connection to their concentration, relaxation, and solution pH. The main objectives of the present paper are to report, discuss and interpret the results obtained, and to summarize their consequences.

## 2. Experimental Methods

### 2.1. Collection of Aerosol Samples

[4] The aerosol samples were obtained at a kerbside site within a street canyon at a height of about 7.5 m above the street level in downtown Budapest, Hungary (5, Rákóczi Street, latitude 47°29'37" N, longitude 19°03'38" E, altitude 111 m above the mean sea level) during an intensive field campaign from 23 April through 5 May 2002 in the nonheating season. Several aerosol samplers and in situ instruments were deployed in the campaign. For the purposes of the present study, PM<sub>2.5</sub> fraction (fine-sized) aerosol samples taken by a high-volume dichotomous (HiVol) sampler in the high air flow sampling line were used [*Solomon et al.*, 1983]. The samples were collected on quartz fiber filters (Gelman Pallflex) with an exposed area of 61.5 cm<sup>2</sup> at a mean air flow rate of 308 l/min. The filters had been preheated at 550°C for 24 h prior to sampling to remove possible organic contaminants. A total of 11 samples for daytime periods (from about 7:00 to 19:00 local daylight saving time), and 12 samples for nights (from about 19:30 to 6:30) together with 6 field blank samples were obtained. The samples were placed into aluminum foils, and were frozen at -25°C during transport and storage. The atmospheric aerosol studied was characterized by a median mass concentration of 20 µg/m<sup>3</sup> in the PM<sub>2.0</sub> size fraction, and 43% of the mass was assigned to organic matter (OM, OM = 1.4·OC), 21% to elemental carbon

(EC), 14% to crustal matter, 13% to sulfate, 6% to nitrate, and 6% to ammonium [*Maenhaut et al.*, 2005], and on average, 36% of the OC was attributed to the WSOC on a carbon basis. More information on the collections, samples, analyses, aerosol properties and their relationships can be found elsewhere [*Salma et al.*, 2004, 2005; *Maenhaut et al.*, 2005].

### 2.2. Isolation of HULIS

[5] The HULIS samples were isolated by a modified one-step version of a solid-phase extraction (SPE) protocol [*Varga et al.*, 2001; *Kiss et al.*, 2002]. Half sections of the filters were cut into pieces, and a set of two different sections was extracted jointly by high-purity reagent Milli-Q water for about 36 h. The ratio of the filter area to the water volume was about 3 cm<sup>2</sup>/ml. The extract was filtered through a syringe PVDF membrane filter with a pore size of 0.22 µm to remove the filter debris and suspended insoluble particles. The solution pH was measured (it was typically between 5 and 6), and was adjusted to 2.0 by hydrochloric acid, and the solution was subjected to a preconditioned SPE column (Oasis HLB, hydrophilic-lipophilic-balanced water-wettable copolymer, packing mass 200 mg, Waters Inc., USA). Hydrophilic organic compounds with acidic functional groups that are protonated at pH = 2 were retained by the column, while the inorganic species, and organic compounds that were very hydrophilic because of the presence of strong polar functional groups (like oxalic acid) passed into the effluent. The separation method was optimized to retain the fraction that exhibits the key spectral properties of the total WSOC fraction, i.e., more than 90% of the fluorescence activity, and 70% of the UV activity of humic and fulvic acids [*Varga et al.*, 2001]. The exposed column was rinsed with water to remove residues of inorganic constituents, and it was dried by nitrogen stream. The retained organics were eluted by 6 ml methanol yielding a markedly colored yellow liquid that contained the HULIS in pure organic form [*Varga et al.*, 2001; *Kiss et al.*, 2002]. The eluates from all samples were joined into a pool sample, which was divided into three equal volumes (for different types of measurements), and they were finally evaporated to dryness by a gentle nitrogen stream. The drying resulted in a dark yellow or brownish matter/pulp. One of the three aliquots was dissolved in 1 ml water yielding the stock solution, which was utilized for analyses, and to prepare further sets of solutions for surface tension measurements. The other two aliquots were used for determining the bulk main elemental composition of the HULIS sample, and for investigating the hygroscopic growth of HULIS aerosol (H. Wex et al., A CCN-closure-study for HULIS aerosol, unpublished manuscript, 2006). Half sections of field blank samples were treated similarly to the procedure described above.

### 2.3. Determination of OC, WSOC, and TOC

[6] Organic carbon and WSOC contents of the aerosol samples were derived from the remaining half sections of the original filters. A punch with an area of 1.5 cm<sup>2</sup> of the filter was analyzed by a thermal optical transmission (TOT) method [*Birch and Cary*, 1996] with a TOT analyzer (Sunset Lab, USA) for OC (and EC). The relative precision

of the analytical results in the (surface) concentration range measured is between 4 and 6% according to the manufacturer. Sampling validation was performed by comparing the OC data to that derived for PM<sub>2.5</sub> low-volume (LoVol) samples collected on preheated Whatman QM-A quartz fiber filters in parallel with the HiVol samples, and by TOT analysis utilizing the tandem filter subtraction method [Salma *et al.*, 2004]. The correlation coefficient and mean LoVol/HiVol concentration ratio with associated standard deviation were  $R = 0.972$  and  $1.13 \pm 0.10$ , respectively, indicating a good consistency and high quality of the data sets. The TOT analyzer was involved in an international intercomparison study, which yielded good results in comparison with other participating techniques [ten Brink *et al.*, 2004].

[7] Water-soluble organic carbon content was determined from a punch with an area of  $1.5 \text{ cm}^2$  of the original filter. The punch was extracted by 10 ml water with manual shaking for about 5 min after which it was allowed to stand for 30 min. The extract was filtered through the syringe filter, and the WSOC was measured by a total organic carbon analyzer (Shimadzu TOC-V CPH, Japan) in two steps as the difference between the total carbon and total inorganic carbon. The injection volume for both steps was  $150 \mu\text{l}$  which were repeated 3 times each, and the mean of the results was further utilized in evaluations. The detection limit for OC was about  $0.1 \text{ mg/l}$ , and the precision of the actual measurements was estimated to be less than 3%.

[8] Total organic carbon content of the HULIS stock solution was measured by the TOC analyzer similarly to the procedure described for the aerosol water extract above.

#### 2.4. Measurement of Surface Tension

[9] A series of seven HULIS solutions with decreasing OC concentration was prepared from the stock HULIS solution by sequential dilutions with overall dilution factors of 1.000, 1.250, 1.884, 2.858, 5.781, 11.75, and 23.39. Another series of HULIS solutions for measuring the effect of pH was prepared by adding the stock solution in a volume of  $50 \mu\text{l}$  to solutions of hydrochloric acid or sodium hydroxide with a volume of  $450 \mu\text{l}$  in appropriate concentrations. The actual pH value of the solutions was measured by a glass microelectrode with a precision of less than about 5% before the surface tension measurement.

[10] Surface tension ( $\sigma$ ) of the solutions was measured by a dynamic pendant drop shape method [Varga *et al.*, 2005], which is a well established technique. Advantage of the dynamic method is that it elucidates further physicochemical (kinetic) properties of the surfactant solutions in addition to the equilibrium value of the surface tension. A series of drops was formed at the tip of a Teflon capillary within a closed temperature-controlled ( $\Delta T < 0.1^\circ\text{C}$ ) chamber with wetted walls and hydrophobic windows by a syringe pump ensuring clean and fresh drop surface with a constant area. After some drops dribbled, the pump was stopped in a way that it created a well developed drop, and the drop shape started to be recorded ( $t = 0$ ) by a CCD camera. Formation of a pendant drop required a time period of 1–2 s. The volume of the drop only decreased by less than about 2% even for the longest measuring times. The measuring system was computer controlled; the digital images of the drop

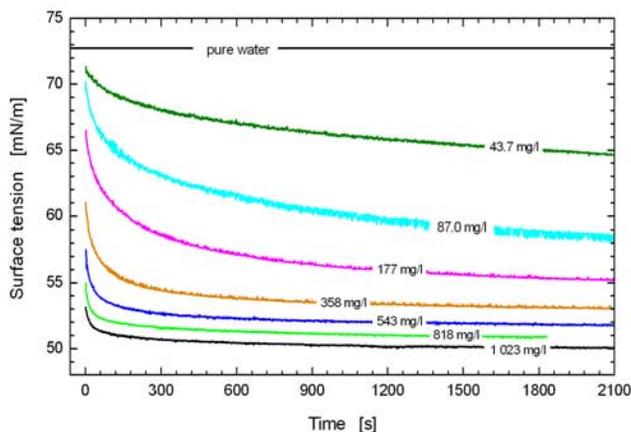
were taken approximately in every 1.5 s, and they were subjected to an edge detection and shape fitting computer program that calculated the temporal surface tension values, and finally, surface tension relaxation curves were produced on line. The measurements were carried out at a constant temperature of  $20^\circ\text{C}$ ; for which the surface tension of pure water is  $\sigma_0 = 72.7 \text{ mN/m}$  [Lide, 2004]. Precision and reproducibility of the equilibrium surface tension value were estimated to be about  $0.2 \text{ mN/m}$  [Varga *et al.*, 2005]. Measurement of several solutions was repeated after a few days, and the results were found to be within the uncertainty limit reported.

### 3. Results and Discussion

#### 3.1. Amount of HULIS and Their Contribution to OC and WSOC

[11] Concentration of OC in the HULIS stock solution was measured to be  $565 \text{ mg/l}$ . The carbon content in the HULIS was determined by thermal elemental analysis of a separate aliquot of the HULIS sample, and the mean value was found to be 55% by mass (I. Salma *et al.*, Sampling artefacts, concentration and chemical composition of fine water-soluble organic carbon and humic-like substances in a continental urban atmospheric environment, submitted to *Atmospheric Environment*, 2006). It means that the concentration above corresponds to  $1\,023 \text{ mg/l}$  of HULIS in the stock solution. Concentrations of solutes in real incipient droplets are estimated to be in the order of  $10^{-4} - 10^{-2} \text{ mol/l}$  [Ogren and Charlson, 1992], which correspond roughly to the HULIS concentration range from  $10^1$  to  $10^3 \text{ mg/l}$  assuming an average HULIS molar mass of  $200 - 500 \text{ g}$  [Kiss *et al.*, 2003], and considering the actual OM apportionment (see later in this section and Salma *et al.* [2004]), and the actual mass closure [Maenhaut *et al.*, 2005]. Hence the maximal concentration investigated corresponds to the conditions near or somewhat below the critical droplet size, where the importance of the surface tension is the largest. It has to be mentioned, however, that the study strictly regards the pure HULIS haze or cloud droplets, which are usually mixed by inorganic and other organic aerosol constituents in the natural atmosphere. These compounds can, on the one hand, limit the solubility of HULIS due to the salting effects, and on the other hand, further enhance the surface tension depression. It is noted that the solubility of pure HULIS was estimated to be about  $10 \text{ g/l}$  [Kiss *et al.*, 2005].

[12] The measured amounts of OC and WSOC for the aerosol samples were added up for all filters, and the results were compared to the OC content in the pooled HULIS sample. On average, about 54% of WSOC, and about 19% of OC were attributed to HULIS in the PM<sub>2.5</sub> fraction downtown urban aerosol over the spring period. The results fall within the range of the reported contributions for different environments or samples [Zappoli *et al.*, 1999; Facchini *et al.*, 1999; Krivácsy *et al.*, 2001; Decesari *et al.*, 2001; Mayol-Bracero *et al.*, 2002; Duarte *et al.*, 2005]. The available reported HULIS contributions to WSOC, however, vary from low level (15–36%) to high level (55–60%) implying that either the HULIS do not share completely common origin in different environments and



**Figure 1.** Relaxation curves of surface tension for solutions of atmospheric humic-like substances in different concentrations.

seasons, or that their production processes do not result in similar percentages of the OC and WSOC.

### 3.2. Surface Tension Relaxation

[13] Surface tension relaxation curves for the series of HULIS solutions with different concentration are displayed in Figure 1. It is seen that the surface tension of fresh surfaces decreases with time to an equilibrium value because of the diffusion of surfactants from the bulk solution to the surface, and to their dynamic interaction on the surface, as expected. The decrease is faster (and larger) for the more concentrated solutions for which the equilibrium value seems to be reached in several hundreds of seconds, and the major fall occurred within some seconds. For the more diluted solutions, however, substantially longer intervals were required for reaching the equilibrium. Figure 2a displays some relaxation curves with logarithmic timescale as examples. It demonstrates that several hours are actually needed to reach the equilibrium state in solutions with a HULIS concentration smaller than about 100 mg/l. The long time could have implications on the kinetics of the cloud droplet formation processes.

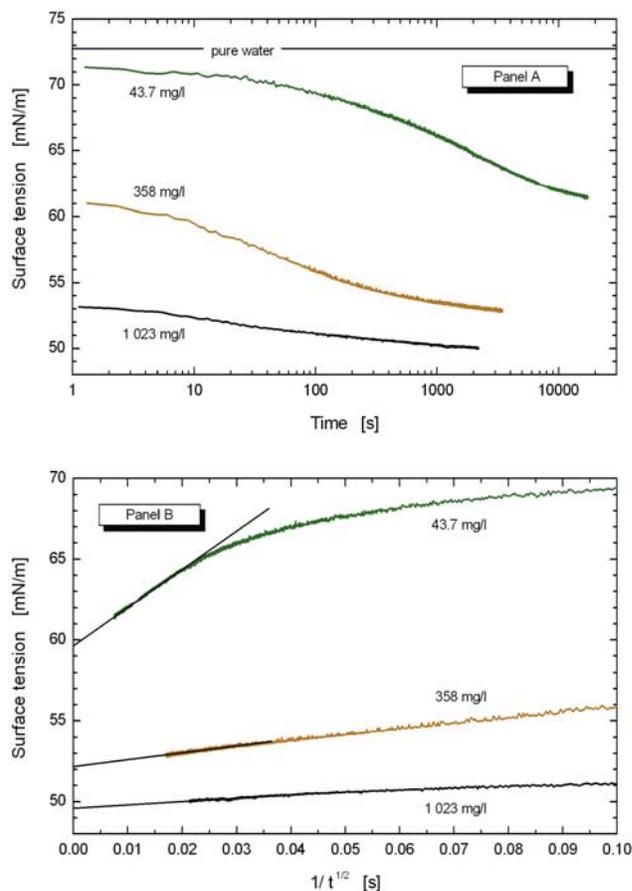
[14] The first quantitative model of the surfactant adsorption was developed by *Ward and Tordai* [1946]. The underlying model assumption is that the adsorbed layer is in instantaneous equilibrium with the adjacent layer of the bulk solution, called the subsurface layer. The concentration gradient between the subsurface layer and the bulk promotes the diffusion of the adsorbing molecules to the subsurface, and eventually their adsorption. The theory leads to an integral equation describing the surface excess as function of the adsorption time. Later, *Fainerman et al.* [1994] derived the asymptotic solution of the Ward-Tordai equation in the long time limit, as follows:

$$\sigma_{t \rightarrow \infty}(t) = \sigma_{eq} + \frac{RT\Gamma_{eq}^2}{c_0} \sqrt{\frac{\pi}{4Dt}} \sim 1/\sqrt{t}, \quad (1)$$

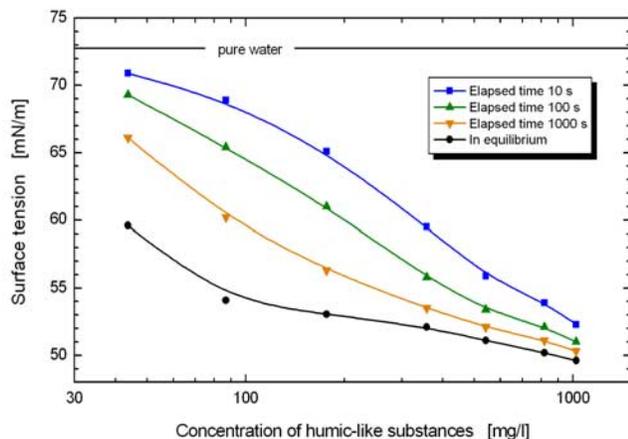
where  $\sigma_{t \rightarrow \infty}(t)$  is the dynamic surface tension in the long time limit,  $t$  is time,  $\sigma_{eq}$  is the equilibrium surface tension,  $\Gamma_{eq}$  is the equilibrium surface excess,  $c_0$  is the bulk

concentration,  $R$  is the universal gas constant,  $T$  is the thermodynamic temperature, and  $D$  is the diffusion coefficient. The equation allows estimating the equilibrium surface tension of dilute solutions from the asymptotic range of the dynamic surface tension data. The dependence obtained for our relaxation curves (see Figure 2b for examples) suggests that the kinetics of the surface tension depression should indeed be regarded as and described by a diffusion controlled process, and, therefore, the reorganization of the surface layer, or conformation of the possible surface film do not seem to be important. At the same time, extrapolation of the relationship was used to obtain the correct equilibrium surface tension values as indicated in Figure 2b. Rigorous analysis of the relaxation curves for the most concentrated solutions indicated that a remarkable additional surface tension depression was experienced with long times even in these cases.

[15] Surface tension as a function of the HULIS concentration after elapsed times of 10, 100, and 1000 s, and the estimated thermodynamic equilibrium values are shown in Figure 3. It can be seen that the surface tension for the more concentrated solutions (about 1 g/l of HULIS) decrease very considerably down to 49.6 mN/m, i.e., by 32% in comparison to pure water. None of the modeling/test



**Figure 2.** Relaxation curves of surface tension with logarithmic timescale for (a) selected solutions of atmospheric humic-like substances and (b) the corresponding extrapolation of the equilibrium values.



**Figure 3.** Dependence of surface tension on concentration of humic-like substances after different elapsed times and in thermodynamic equilibrium. The lines represent eye guides only.

organic compounds studied so far exhibited such a strong effect at this concentration level [Shulman *et al.*, 1996; Tuckermann and Cammenga, 2004]. On the other hand, our value is comparable to the depression of 25–42% derived for HULIS in continental/rural aerosol [Kiss *et al.*, 2005], to that of 30% (at the highest concentrations) for fog water [Capel *et al.*, 1990; Facchini *et al.*, 1999], or to that of about 16% for cloud water samples [Hitzenberger *et al.*, 2002]. It should be noted that the results for fog and cloud water samples were obtained for systems of inorganic and organic water-soluble aerosol components, whose interaction can further modify the effect of pure HULIS [Li *et al.*, 1998].

### 3.3. Surface Tension Isotherm

[16] Specific surface tension depression  $((\sigma_0 - \sigma)/OC)$  was introduced for comparing the surface tension modifying property of different organic fractions or groups [Facchini *et al.*, 2000]. The specific surface tension depression of 0.36 mN/m/(mg OC/l) for our HULIS sample agrees rather well with that for the polyacidic compounds (to be made of HULIS) separated according to the procedure of Decesari *et al.* [2000] of about 0.34 mN/m/(mg OC/l) for the OC concentration specified (57 mg/l) [Facchini *et al.*, 2000]. This suggests that the two separation protocols yield very similar groups of compounds (i.e., HULIS) with regard to the surface activity.

[17] The surface tension data reported previously were fitted by Szyszkowski's empirical equation [Szyszkowski, 1908]:

$$\sigma = \sigma_0 - RT \Gamma_{\max} \ln \left( 1 + \frac{C}{\beta} \right). \quad (2)$$

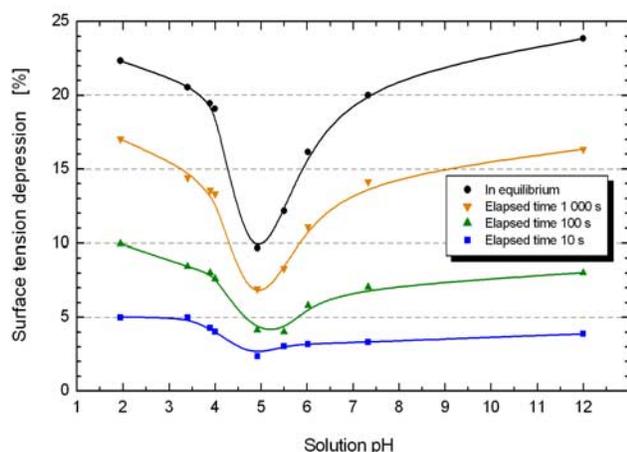
Variable  $C$  is the bulk molar concentration of the surfactant (it is replaced by a surrogate HULIS or WSOC concentration),  $\Gamma_{\max}$  is the maximum excess surface concentration (a compound-specific parameter), and  $\beta$  is the Szyszkowski constant representing the surfactant bulk (volume) con-

centration at the half of the maximum excess concentration [Li *et al.*, 1998]. The equation can also be derived in a theoretical way from the Langmuir adsorption isotherm, which is strictly valid only for nonionic noninteracting adsorption layer in a two-component (solute and solvent) system. Nevertheless, our equilibrium data were also fitted by the equation, and the fitting yielded parameters of  $\Gamma_{\max} = 1.10 \mu\text{mol}/\text{m}^2$ , and  $\beta = 0.9 \text{ mg}/\text{l}$  with a reduced  $\chi^2 = 1.4$ . The parameter  $\Gamma_{\max}$  for our urban HULIS samples is somewhat smaller than for HULIS of rural origin (which was  $2.06 \mu\text{mol}/\text{m}^2$  for a spring period [Kiss *et al.*, 2005]), or than for smog water samples ( $2.25 \mu\text{mol}/\text{m}^2$  [Facchini *et al.*, 1999]). It has also to be noted that parameter  $\beta$  depends very much on the presence of inorganic components, and it can change several orders of magnitude [Kiss *et al.*, 2005].

[18] The shape of the nonequilibrium curves (in particular for elapsed times of 10 and 100 s in Figure 3) resembles the earlier observations and plots [cf. Facchini *et al.*, 1999, Figure 1; Kiss *et al.*, 2005, Figure 1]. The equilibrium curve (the isotherm in Figure 3), however, exhibits an unexpected shape. First of all, the extent of the surface tension depression was substantial even for diluted solutions; for about 44 mg/l of HULIS, the equilibrium surface tension decreased to 60 mN/m, i.e., by about 18%. Secondly, the surface tension for the smaller concentrations in the range investigated showed an increasing tendency instead of leveling off. The behavior observed cannot be explained by changes in the chemical structure of the compounds during the dilution, namely by changes in the degree of dissociation of the weak amphiphilic electrolytes present (see later). The different trend in the surface tension can be linked to different amphiphilic properties of some functional groups or classes of constituents within the HULIS in the solutions. Humic-like substances are a very complex and multicomponent mixture of compounds that can cause complicated behavior because of the differences in the diffusion rates of the individual compounds to the surface, in their specific surface tension modifying properties, and to their dynamic interactions on the surface. In principle, two classes (subsets) of surfactant compounds can produce similar surface tension behavior if they have quite different average molar mass, and if the subset with the larger molar mass is present in a rather small concentration but exhibits larger surface activity than the class with the smaller molar mass.

### 3.4. Effect of Solution pH

[19] Dilution of the HULIS solution (that corresponds to the growth of the hydrated aerosol or droplet) can alter some controlling physicochemical properties of the system like solution pH as well. Dependence of the surface tension depression on the solution pH after different elapsed times, and in the thermodynamic equilibrium for a constant HULIS concentration of 102 mg/l (equal to an OC concentration of 57 mg/l) is displayed in Figure 4. It can be seen that the surface tension depression of HULIS increases with time as expected until it reaches the value that corresponds to the isotherm described in the previous section at the solution natural pH, which was usually between 5 and 6. The smallest depression in the equilibrium is observed at about pH = 5, and it increases significantly with both



**Figure 4.** Effect of solution pH on surface tension depression of humic-like substances with a concentration of 102 mg/l after different elapsed times and in thermodynamic equilibrium. The lines represent eye guides only.

increasing and decreasing pH by a further 13–14%, i.e., down to 55 mN/m. The additional decrease represents about 50% of the maximal depression at this concentration level. The effect can partially be caused by the increased ion strength of the solution that enhances the surface activity. Nevertheless, the curves are not completely symmetrical to the minimum, but exhibit larger depression in the more acidic range than in the basic one. The larger depression can be explained by gradual protonation of the weak organic polycarboxylic acids present in HULIS [Facchini *et al.*, 2000; Decesari *et al.*, 2000] down to a pH of about 3, which increases the surface activity. In the basic region, gradual deprotonation of amino compounds, organic nitrates or other basic functional groups cannot be excluded in principle, though these groups seem to have much less abundance in HULIS, if any. The phenomenon can have implication during acidic (rainfall) episodes in polluted real atmospheres; when the pH of the cloud droplets can reach values as low as 2. Thus the role of HULIS in cloud physics due to their surface tension can further be enhanced under such conditions.

#### 4. Conclusions

[20] The surface tension depression of HULIS was shown to be remarkable even in diluted solutions (about 18% for 44 mg/l HULIS concentration). At the same time, the diffusion for small amounts from the droplet bulk volume to the surface was also found to be very slow (several hours were needed to reach the equilibrium state). The thermodynamic description (e.g., the adsorption isotherm) provides an upper (equilibrium) limit of the effect of the investigated substance on the surface properties of the solution. The adsorption isotherms are generally measured by macroscopic (e.g., by Du Noy ring or pendant drop) methods. For dilute solutions (as it is the case of HULIS), one has to ensure in addition that the equilibrium is indeed reached. In a real process (e.g., cloud droplet formation), however, it is the kinetics that usually determines whether the thermodynamic equilibrium is reached or not, and the

kinetics does depend on the size and geometry of the system. The transport process in a real droplet can be more rapid than in the investigated system if the slightly soluble compounds occupy a distinct part of the particle surface, forming less and more hydrophilic areas. The particle hydration and droplet growth can start from the more hydrophilic area of the particle surface, and the slightly water-soluble components spread over the droplet by a surface diffusion which is thought to be much more rapid.

[21] It should be kept in mind that the impact of surface tension and solution pH on the water vapor pressure (and on critical supersaturation) must be evaluated together with the effect of the bulk hygroscopicity (solubility and dissociation) of the solutes. The Kelvin and Raoult effects cannot be considered to be independent on each other or additive. During the droplet growth, several quantities in the modified Köhler equation are related (e.g., solubility can affect surface tension through ion strength or solution pH) and change together. Therefore separating the equation into a term causing increase and into a term causing decrease of water vapor pressure is not correct, and the effects need to be studied together. This could explain partially the seemingly contradictory conclusions drawn with regard to the promoted or hindered droplet activation. Further joint studies on both surface tension and hygroscopicity are therefore needed for several chemical classes of the water-soluble aerosol constituents, including organics, and for aerosol water extracts as well, in order to fully elucidate their role in cloud physics and chemistry.

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