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► **To cite this version:**

I. Salma, G. G. Láng. How many carboxyl groups does an average molecule of humic-like substances contain?. *Atmospheric Chemistry and Physics Discussions*, 2008, 8 (3), pp.10005-10020. hal-00304205

HAL Id: hal-00304205

<https://hal.science/hal-00304205>

Submitted on 18 Jun 2008

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**Carboxyl groups in
HULIS**

I. Salma and G. G. Láng

How many carboxyl groups does an average molecule of humic-like substances contain?

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Received: 17 April 2008 – Accepted: 23 April 2008 – Published: 29 May 2008

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

The carboxyl groups of atmospheric humic-like substances (HULIS) are of special interest because they influence the solubility in water, affect the water activity and surface tension of droplets in the air, and allow formation of chelates with biologically active elements. Experimentally determined abundances of the carboxyl group within HULIS by functional group analysis are consistent with our knowledge on the average molecular mass of HULIS if the number of dissociable carboxyl groups is assumed to be rather small. The best agreement between the average molecular mass derived from the existing abundance data and the average molecular mass published earlier occurs for assuming approximately one dissociable carboxyl group only. This implies that HULIS can not be regarded as polycarboxylic acid. The average molecular mass of HULIS derived from our electrochemical measurements with the assumption of one dissociable carboxyl group per molecule ranges from 248 to 305 Da. It was concluded that HULIS are a moderately strong/weak acid with a dissociation constant of about $pK = 3.4$, which fits well into the interval represented by fulvic and humic acids. The mean number of dissociable carboxyl groups in HULIS molecules was refined to be between 1.1 and 1.4.

1 Introduction and overview of the relevant experimental data

Aerosol particles containing large amounts of water-soluble organic compounds can play an important role in climate change, and they affect the environment and human health substantially (Fuzzi et al., 2006; Tsigaridis and Kanakidou, 2007). The uncertainties connected to their composition and interactions with the other aerosol components in droplets and with atmospheric gases hinder the quantification of their impacts (McFiggans et al., 2006). Valuable information on some specific compounds, classes of compounds or functional groups within the water-soluble organic fraction has become available in recent years. One of the most important groups is atmospheric HUmic-

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Like Substances (HULIS) (Graber and Rudich, 2006). HULIS are present ubiquitously in the continental troposphere, and their carbon content makes up a mass fraction up to about 60% of the fine-sized water-soluble organic carbon (Salma et al., 2007, and references therein). They are regarded to be extremely heterogeneous polymeric system with strong poly-acidic, colloidal and chromophoric properties and substantial surface activity. They could not be resolved at the molecular level but they are known to be comprised of aromatic compounds with aliphatic chains (Graber and Rudich, 2006). Hence, HULIS are defined operationally which is connected to conceptual and experimental disadvantages. Moreover, there is no evidence that HULIS isolated from aerosol samples collected in different environments of the world or seasons are actually the same supramolecular system or class of compounds. Furthermore, spontaneous change in the aggregation and conformational states of HULIS molecules can take place under even slightly changing solution conditions, and, therefore, uniform properties for such a complex mixture cannot always be expected. These features largely complicate their research.

Composition, properties and interactions of HULIS are being studied by a large variety of experimental methods and techniques. Functional group analysis by $^1\text{H-NMR}$ spectroscopy based on the approach proposed by Decesari et al. (2000) was successfully applied to identify and measure directly the abundance of several organic functional groups including carboxyl and hydroxyl groups (Tagliavini et al., 2006; Decesari et al., 2006; Samburova et al., 2007). The carboxyl group content is of special interest because it influences the solubility in water, which is one of the major media in atmospheric, climatic or environmental processes. It also affects the water activity and surface tension of droplets in the air which are two crucial properties in cloud or fog droplet formation, hygroscopic growth and water activation. Furthermore, the carboxyl groups endow these molecules with the ability to form chelates with multivalent cations (e.g. precipitate trace elements with biological role in some media and make their solutions in other media), and thus to influence the bioavailability and biogeochemical cycling. A hypothetical model compound representing the chemical composition of

polyacids (PA) chemical fraction (that is expected to consist mostly of HULIS) has been proposed, which has a molecular mass of 731 Da and contains four carboxyl and two hydroxyl groups (Decesari et al., 2006).

A chemical derivatization version of the $^1\text{H-NMR}$ spectroscopy was applied in a comprehensive way for several chemical fractions obtained from aerosol samples collected in the Amazon Basin (Tagliavini et al., 2006). The PA chemical fraction was obtained by ion-exchange chromatography from one $\text{PM}_{2.5}$ -fraction aerosol sample collected in the dry season. The mass percentage of the carboxyl group for this fraction was roughly estimated from the mol% of the carboxyl carbon (the percentage of the carboxyl carbon with respect to the total moles of carbon in the PA fraction) presented and carbon percentage of several other functional groups that were also reported for the PA fraction assuming 1 carbon atom in 9 to be present in carboxyl group (Tagliavini et al., 2006). The estimate is given in Table 1. A direct version of the $^1\text{H-NMR}$ method was utilized recently to quantify the content of some functional groups including the carboxyl group and hydroxyl group bound to the aromatic moieties in pure HULIS isolated from PM_{1-} fraction suburban-type aerosol samples (Samburova et al., 2007). The mean relative amount of carboxyl and hydroxyl groups for the summer and winter HULIS samples are also included in Table 1.

The main objectives of this paper are to present a body of indirect evidence for the number of dissociable carboxyl functional group in an average HULIS molecule of approximately one, to discuss the consistency in our knowledge, to present and interpret experimental data on the average molecular mass and acid dissociation constant of HULIS, and to formulate some conclusions for the dissociation of HULIS.

2 Experimental

Aerosol samples were collected by DHA-80 high volume aerosol sampler equipped with a $\text{PM}_{2.5}$ pre-separator (Digitel Elektronik, Switzerland) and operated at an air flow rate of 500 l min^{-1} for one week in central Budapest from 17 till 24 July 2006. Whatman

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QM-A quartz fiber filters were used as the collection substrate. The main section of the aerosol filters was utilized for isolation of pure HULIS by a modified one-step solid-phase extraction (SPE) method (Varga et al., 2001) on Oasis HLB columns (Waters, USA). A set of eight HULIS aqueous samples was prepared for electrochemical conductivity measurements. The first aqueous sample was made by adding 600 μl water to an isolated pure HULIS sample with a mass of approximately 6 mg. It was put into ultrasonic bath for 15 min, after which it was allowed to stand in an ultra-thermostat at a temperature of 20°C for one day. Finally, the pH and conductivity of the aqueous sample were measured. After the measurements, an aliquot of the HULIS aqueous sample was taken out, it was filtered through a syringe PVDF membrane filter with a pore size of 0.22 μm and with a dead volume of 10 μl (Millipore, USA), and the dissolved total organic carbon (TOC) concentration in the filtrate was measured by TOC analyzer. The remaining volume of the aqueous sample was diluted further with water, and the sample preparation and measurements were accomplished as described above. The consecutive dilution factors of the aqueous samples were 1.9, 2.1, 2.0, 2.6, 1.6, 1.9 and 10.

The TOC concentrations for HULIS solutions were determined by a Multi N/C 2100S total organic carbon analyzer (Analytik Jena, Germany). The mass concentration of dissolved HULIS was calculated from the TOC data by using an organic matter-to-organic carbon mass conversion factor of 1.81 derived especially for the same type of HULIS (Salma et al., 2007). The concentration of HULIS varied from approximately 5 g l^{-1} to 7 g l^{-1} . The relative uncertainty of the measured results was estimated to be less than 2%. The overall uncertainty of the concentration data was primarily determined by the micro-chemical operations during the sample preparation. Conductivity of the HULIS aqueous samples was derived by using electrochemical impedance spectroscopy, which is a well established technique. A cylindrical electrochemical measuring cell with an internal diameter of 4 mm and effective volume of 500 μl was made of glass and it was equipped with Pt working electrodes. The cell constant was derived by a KCl solution with a concentration of 0.02 mol l^{-1} . All measurements were per-

formed at a constant temperature of 20°C applying a sinusoidal perturbing signal with an amplitude of 5 or 10 mV over a frequency range of 1 Hz to 13 kHz. The resistance of the solution was calculated by extrapolating the real part of the complex impedance to the high frequency limit. The conductivity was derived from the average ohmic resistance and cell constant. The relative uncertainty of the measurements was estimated to be less than 2%. The pH of the aqueous sample was measured by a glass micro-electrode. More details on the samples, experimental procedures, conditions and data treatment can be found in Salma et al. (2008).

3 Results and discussion

3.1 Abundance of carboxyl group

The abundances of carboxyl group within HULIS presented in Table 1 were utilized to calculate the average molecular mass of HULIS supposing that an average molecule contains from one to four carboxyl or hydroxyl groups. The corresponding molecular masses are summarized in Table 1 as well. The values assuming one carboxyl group per molecule were 156 and 834 Da derived from the data of Tagliavini et al. (2006) and Samburova et al. (2007), respectively. The difference between the masses is rather significant. It can be caused by the fact that HULIS from different environments (in this case from an environment strongly affected by tropical biomass burning and from an urban environment) are not necessarily the same system of compounds due to the very different, mostly primary and secondary source processes, respectively. In addition, the former value should be dealt with caution since it is only based on a single sample, and since the unaccounted carbon in the fraction made up about 35 mol%. Furthermore, our HULIS sample was isolated from urban-type aerosol which is expected to be much more similar to those dealt with by Samburova et al. (2007) than to biomass burning aerosol. Therefore, we decided to rely primarily on the data reported by Samburova et al. (2007). The average molecular mass of HULIS isolated from rural

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5 fine-sized aerosol samples by the SPE method was determined by HPLC-MS, and by
vapour pressure osmometry. The values obtained were between 200 and 300 Da, and
between 215 and 345 Da, respectively (Kiss et al., 2003). Samburova et al. (2005) ap-
plied size exclusion chromatography-UV spectroscopy, and laser desorption/ionization
10 mass spectrometry to determine the molecular mass distribution of PM₁₀-fraction ur-
ban HULIS, and they derived an upper limit of approximately 700 Da. The average
molecular mass for HULIS isolated from fresh smoke particles, slightly aged wood
burning smoke particles, and local photochemical pollution particles was estimated to
be 610, 410, and 500 Da, respectively using a spectrophotometrical method based on
15 empirical correlation relationships between the molar absorptivity and molecular mass
(Dinar et al., 2006). The average molecular mass for urban-type HULIS obtained by
the same correlation relationships as above varied from 373 to 763 Da with an overall
mean value of 556 Da (Salma et al., 2008).

The estimates assuming two carboxyl groups in a molecule of the urban-type HULIS
15 seem to be already outside or at the upper end of the molecular mass range set by
the data reported earlier. The estimates corresponding to four or three carboxyl groups
are of the order of several thousands and are substantially larger than any molecular
mass data summarized above. It seems, therefore, unlikely that an average molecule
of HULIS originating from urban environments contains three or more carboxyl groups.

20 The conclusion on the very limited number of carboxyl groups per molecule is also
coherent with the findings achieved by pH titration and dissociation constant (*pK*) spec-
troscopy (Samburova et al., 2007). The authors observed a clear and large maximum
in the distribution of HULIS dissociation constant around 4.0 and a smaller maximum
around 5.5. The smaller *pK* value likely represents the carboxyl groups. There actually
25 could be several carboxyl groups present in the molecules but the majority of them
should have rather similar dissociation values.

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3.2 Average molecular mass

The electrochemical conductivity (κ) experimentally determined was utilized to calculate the average molecular mass (M) of HULIS. The acid dissociation (acidity) constant (K) assuming one dissociable carboxyl group in a HULIS molecule can be expressed by the apparent dissociation degree $\alpha = \Lambda / \Lambda_0$, with $\Lambda = \kappa / c$ being the molar conductivity and Λ_0 being the molar conductivity at infinite dilution (limiting molar conductivity) as:

$$K = \frac{\alpha^2 c}{1 - \alpha}, \quad (1)$$

where c is the initial molar concentration of HULIS in the solution. Equation (1) can be rearranged to a linear equation that relates the measured quantities:

$$\frac{m/V}{\kappa} = \frac{M}{K \Lambda_0^2} \kappa + \frac{M}{\Lambda_0}, \quad (2)$$

where m/V is the mass concentration of HULIS in the solution. The relationship between $m/V/\kappa$ and κ is displayed in Fig. 1. It is seen that for the most diluted solutions (for the five samples with the smallest concentrations) the dependence is linear with a correlation coefficient of $R=0.977$ ($p=0.004$), and the intercept and slope of the line are $A=(76 \pm 9) \text{ g S}^{-1} \text{ dm}^{-2}$ and $B=(42 \pm 5) 10^3 \text{ g S}^{-2} \text{ dm}^{-1}$, respectively. The data for the three most concentrated solutions deviate substantially from the linear line. These were saturated solutions, and the presence of some insoluble HULIS could be visually observed on the walls of the glass vial. Formation of some HULIS aggregates is expected under such conditions (Tabazadeh, 2005). Hence, the difference can be explained by the fact that activity of these three samples cannot be approximated by their concentrations. The intercept ($A=M/\Lambda_0$) of the linear line was further utilized to derive the average molecular mass of HULIS. The limiting molar conductivity of HULIS was represented by the molar ionic conductivity of the hydrogen cation to be of $\lambda_{\text{H}^+} = 325 \text{ S cm}^{-2} \text{ mol}^{-1}$ at a temperature of 20°C (Landolt-Börnstein, 1960). In this

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approach, it is assumed implicitly that the molar ionic conductivity of the anion formed by the dissociation (HULIS^-) is negligible to the conductivity of H^+ cation. This is a reasonable assumption due to the very diverse masses (and mobilities) for the hydrogen and HULIS ions. In the other limiting case, the molar ionic conductivity of the HULIS anion was approximated by the molar ionic conductivity of common small anions of approximately $\lambda_{\text{HULIS}^-} \approx 74 \text{ S cm}^{-2} \text{ mol}^{-1}$, which yielded in a limiting molar conductivity of $\Lambda_0 = \lambda_{\text{H}^+} + \lambda_{\text{HULIS}^-} \approx 400 \text{ S cm}^{-2} \text{ mol}^{-1}$. The average molecular masses corresponding to the negligible and significant molar anionic conductivities were 248 and 305 Da, respectively. The interval of the average molecular mass set by these results is in excellent agreement with the data reported earlier and summarized in Sect. 3.1. It is worth emphasizing that the range presented here was obtained by an electrochemical approach which differs in principles and realization from the previously utilized, mainly instrumental analytical and optical methods.

3.3 Acid dissociation constant and solution pH

The intercept and slope of the fitted linear line for Eq. (2) was further used to calculate the acid dissociation constant of the carboxyl group as $\text{p}K = -\log[A^2/(B M)]$ for the molecular mass interval derived in Sect. 3.2. It was assumed that an average molecule of HULIS contains one dissociable carboxyl group. The $\text{p}K$ values derived for the negligible and significant anionic conductivities were 3.3 and 3.4, respectively. These acidity constants correspond to moderately strong/weak common organic acids as formic acid ($\text{p}K=3.74$) or mandalic acid ($\text{p}K=3.41$; Lide, 2004). The values obtained are in excellent agreement with that for fulvic and humic acids of $\text{p}K=3.4$ and 3.7, respectively (Porasso et al., 2002), and with that for the SRFA standard of 3.8 (International Humics Substances Society) and of 3.6 (Gustafsson, 2001). The acidity constant is well comparable to the major maximum at $\text{p}K=4.0$ estimated by Samburova et al. (2007) for pure PM_{10} atmospheric HULIS samples.

Finally, solution pH was calculated for data validation purposes by utilizing the dis-

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sociation degree of HULIS expressed from Eq. (1) as

$$[H^+] = \alpha c = \frac{1}{2} \left(-K + \sqrt{K^2 + 4Kc} \right), \quad (3)$$

where $[H^+]$ stands for the concentration of hydrogen cation. The possible deviation of the activity coefficients from the unity was neglected. The calculated values were compared to the measured pH data. For the molecular masses of 248 and 305 Da, the correlation between the modelled and measured pH data was very strong with a coefficient of $R=0.998$ ($p<0.0001$). Nevertheless, the mean ratios of the measured to modelled pH data for both molecular masses were 1.07 ± 0.04 , which differs slightly but significantly from the unity. Scatter plot of the modelled and measured pH values and their individual ratios for an average molecular mass of 248 Da are displayed in Fig. 2 as example. It is seen that the difference mainly occurs in the most diluted five samples, and that the data for the most concentrated three solutions are somewhat separated again from the others. It means that there was somewhat more hydrogen cation present in the diluted solutions than it was calculated by the model in which a discrete number of dissociable carboxyl group of one was considered. Dissociation of the hydroxyl groups present in HULIS molecules is thought to be negligible because of the acidic pH interval.

A very simple but reasonable method of estimating the average number of dissociable carboxyl groups is to divide the limiting molar conductivity of HULIS experimentally determined by Kohlrausch's empirical equation (see Salma et al., 2008) for molecular masses of 248 and 305 Da by the molar ionic conductivity ($\lambda_{H^+} + \lambda_{HULIS^-}$) of HULIS. For the significant and negligible anionic conductivities of HULIS, the mean number of dissociable carboxyl group contained in an average HULIS molecule was expressed by an interval between 1.1 and 1.4.

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4 Conclusions

In a previous paper (Salma et al., 2008), concentration dependence of the van't Hoff factor for HULIS (which represents the average number of ions into which a molecule actually dissociates when dissolved) was experimentally determined. The relationship was presented in form of three parametric curves for the stoichiometric dissociation number (the maximum number of ions the molecule dissociates to when dissolved) of $\nu=2, 3$ or 4 (see Fig. 5 of Salma et al., 2008). The conclusions of the present paper refine the possibilities described in the paper specified above practically to one function belonging to the parameter of $\nu=2$.

The carboxyl functional group in HULIS exhibits moderately strong/weak acid character. Its dissociation depends on the interactions with other relevant chemical species as water soluble organic constituents and ions internally mixed in the droplets of real atmospheric aerosol. Nevertheless, the dissociation may be influenced in a lesser extent than generally expected because HULIS were found to be stronger acid than previously indicated and anticipated. Although pure HULIS are already considered as an extremely complex mixture of interacting substances, studies incorporating their external interactions are also desirable as the next step of research because these relationships can modify or determine the role that HULIS play in the real atmosphere.

Acknowledgements. The financial support of the Hungarian Scientific Research Fund (contracts K61193 and K67994) is appreciated. The authors thank R. Ocskay for her help in the sample preparation.

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Table 1. Estimated average molecular mass of atmospheric humic-like substances with different number of functional groups (Ar means aromatic core.)

Functional group and its mean abundance within HULIS	Number of functional group			
	1	2	3	4
COOH 5.4 m/m% ^a	834	1667	2501	3335
Ar-OH 3.1 m/m% ^a	549	1097	1646	2194
COOH 13.2 mol% ^b	156	312	468	624

^a Samburova et al. (2007).

^b Tagliavini et al. (2006).

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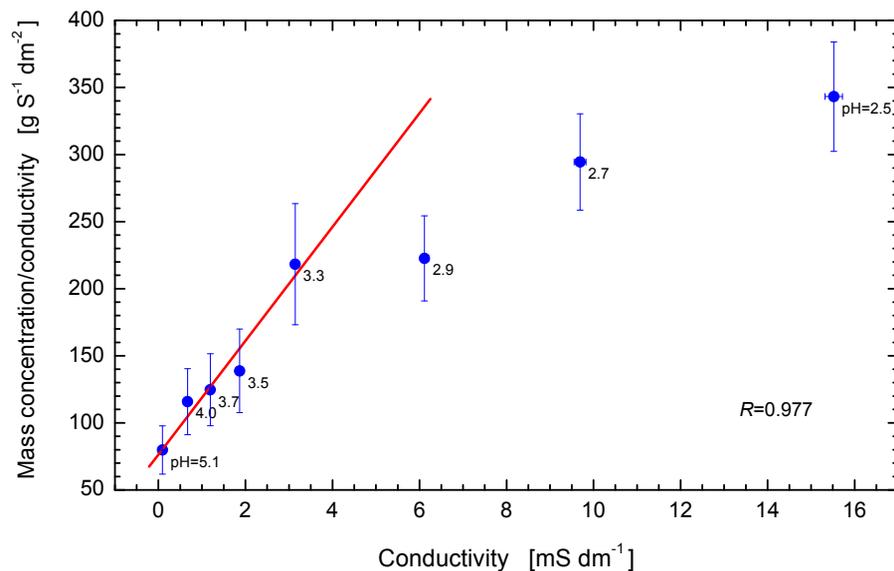


Fig. 1. The relationship for deriving the average molecular mass and acid dissociation constant of HULIS assuming one dissociable carboxyl functional group per molecule. The correlation coefficient (R) and the solution pH values are also indicated.

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I. Salma and G. G. Láng

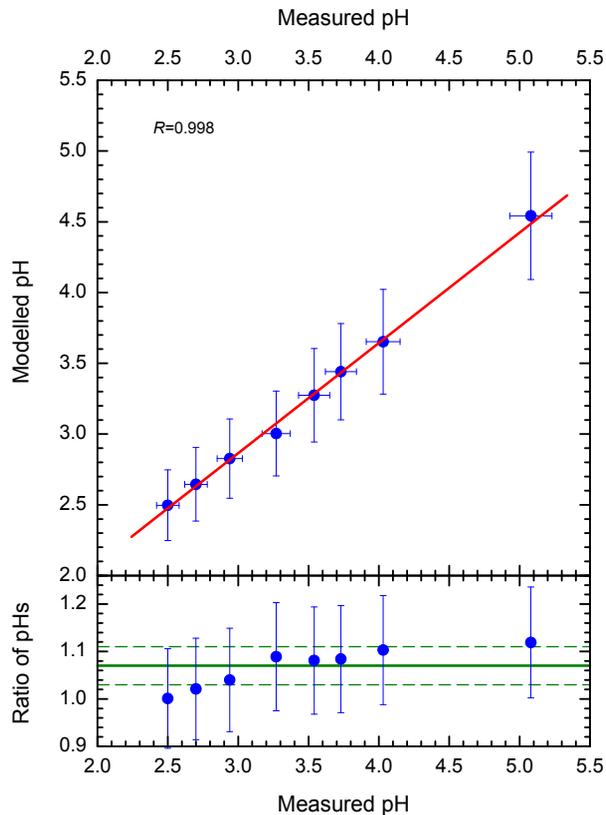


Fig. 2. Scatter plot of the modelled and measured solution pH values, and their individual ratios. The correlation coefficient (R) and the mean measured-to-modelled pH ratio and its standard deviation of 1.07 ± 0.04 are also indicated by solid and dashed lines, respectively.

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