Hygroscopic growth and measured and modeled critical super-saturations of an atmospheric HULIS sample

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[1]   An atmospheric HULIS (humic-like substance) sample dissolved in water was used to generate particles with different dry diameters. A HHTDMA (High Humidity Tandem Differential Mobility Analyzer) and LACIS (Leipzig Aerosol Cloud Interaction Simulator) were used to measure hygroscopic growth of the HULIS particles. LACIS also was used to measure the critical super-saturation for the activation of HULIS particles with dry diameters of 50, 75, 100, and 125 nm. Simple Köhler theory was used to simulate the measured hygroscopic growth factors. For this, a new technique was used, where the ionic density (ρ_{ion}) was defined as a combination of the HULIS physical properties for which values could not be reliably determined. By adjusting ρ_{ion} in the Köhler equation, modeled hygroscopic growth could be brought into agreement with the measurements, even without the explicit knowledge of the different HULIS properties. It was demonstrated that the values of ρ_{ion} determined with our procedure can be reproduced from combinations of physically realistic values of the physical properties represented by ρ_{ion}. Adjustments of the ionic density were done for two different surface tensions, that of water as the upper limit, and the lowest value that had been measured for this HULIS sample (published previously) as the lower limit. The two adjusted values of ρ_{ion} were used in the Köhler model to derive critical super-saturations. For more dilute droplets, measured and modeled critical super-saturations were in agreement for both values of the surface tension, whereas for the less dilute solutions, agreement only could be achieved when a lowering of the surface tension due to HULIS was taken into account. **Citation:** Wex, H., T. Hennig, I. Salma, R. Ocskay, A. Kiselev, S. Henning, A. Massling, A. Wiedensohler, and F. Stratmann (2007), Hygroscopic growth and measured and modeled critical super-saturations of an atmospheric HULIS sample, *Geophys. Res. Lett.*, *34*, L02818, doi:10.1029/2006GL028260.

1.   Introduction

[2]   Recently there has been a growing interest in a special fraction of the atmospheric aerosol called humic-like substances (HULIS) [e.g., *Graber and Rudich*, 2006]. HULIS are macro-molecular compounds that are found in the water-soluble organic fraction of the atmospheric aerosol [*Zappoli et al.*, 1999]. HULIS contributes to the hygroscopic growth of atmospheric aerosol particles, and may also influence their activation to cloud droplets by altering their surface tension.

[3]   HULIS sampled and extracted from different atmospheric aerosol samples worldwide shows a wide range of values for different physical properties. For example, the molecular weight not only ranges from 200 to 700 amu [*Kiss et al.*, 2003; *Dinar et al.*, 2006a; *Samburova et al.*, 2005], but may even have a range of values for a single sample. Densities have been reported in the range of 1.5 and 1.7 g/cm^3 [*Hoffer et al.*, 2006; *Dinar et al.*, 2006b]. Little information exists on the dissociation of HULIS in solution. [*Dinar et al.*, 2006a] found that when using the surface tension of water for HULIS in solution, van't Hoff factors ranging from 4.5 up to 9 had to be used to obtain agreement between measured and calculated values of critical super-saturations for HULIS particles. They argue that these values are extremely unlikely, because they are usually expected to be close to one.

[4]   These differences between HULIS samples can be explained by the different possible pathways for the generation of HULIS, which include biomass burning [e.g., *Zappoli et al.*, 1999], oxidation of soot [*Decesari et al.*, 2002], and oxidation of volatile species [*Kalberer et al.*, 2004]. The HULIS properties might also depend on the extraction methods used, as described by *Varga et al.* [2001]. It is also important to note that HULIS is different from terrestrial humic substances (humic and fulvic acids [*Graber and Rudich*, 2006]).

[5]   For sampling times on the order of days, usually only a relatively small amount of HULIS is available from a single atmospheric sample. Thus, it is not possible to determine all physical properties of interest for each sample. This complicates efforts to simulate hygroscopic growth and activation of HULIS particles, because sufficient data for the models may not be available for each sample. In this work we developed a modeling technique that overcomes the limitation associated with incomplete physical-property data sets.

[6]   For this work, hygroscopic growth and critical super-saturations were measured for particles with different dry sizes, generated from an atmospheric HULIS sample. Measurements were done with an HHTDMA (High Humidity Tandem Differential Mobility Analyzer [*Hennig et al.*, 2005]) and LACIS (Leipzig Aerosol Cloud Interaction Simulator [*Stratmann et al.*, 2004]). The surface tension properties of this HULIS sample had been investigated elsewhere [*Salma et al.*, 2006].

[7]   All properties of the HULIS sample for which values were either unknown or for which there was unacceptable uncertainty were combined into a single parameter called the ionic density, ρ_{ion}. Measured hygroscopic growth was

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then modeled using a simple Köhler equation by adjusting only ρ_{ion}. Adjustments were done with and without accounting for the lowering of the surface tension due to HULIS. The model was extended towards super-saturation, yielding critical super-saturations for different dry sizes of HULIS particles. The modeled critical super-saturations were compared to the measured values.

2. Measurements

[8] A HULIS sample was isolated by a modified solid-phase extraction protocol [*Varga et al.*, 2001] from PM2.5-fraction urban aerosol samples. These samples were collected on quartz filters by a high-volume dichotomous sampler in downtown Budapest, Hungary in spring (non-heating season [*Salma et al.*, 2006]).

[9] For the measurement of hygroscopic growth and activation, the HULIS sample was diluted in pure water, atomized, and dried to relative humidities (RHs) of about 10%. A DMA (Differential Mobility Analyzer) operating at an aerosol flow rate of 1 l/min and a sheath air flow rate of 10 l/min was used to select HULIS particles of different dry sizes. The RH of the HULIS sample after the DMA was below 5%.

[10] An HHTDMA [*Hennig et al.*, 2005] was used to measure the equilibrium diameters (D_{eq}) of HULIS particles with a dry size (D_{dry}) of 100 nm for RHs ranging from 80% to 98%. The RH in the HHTDMA was calibrated with ammonium sulfate particles. Growth factors g were determined as $g = D_{eq}/D_{dry}$.

[11] LACIS [*Stratmann et al.*, 2004] was used to measure the activation of HULIS particles with dry sizes of 50, 75, 100 and 125 nm, similar to the method described by *Wex et al.* [2006]. LACIS was also used to measure equilibrium diameters [*Wex et al.*, 2005] for a dry particle size of 200 nm at three RHs ranging from 98% to 100%. During the latter experiment, the RH in the flow tube was calibrated with NaCl particles before and after each measurement.

[12] The surface tensions of HULIS droplets from this sample were determined in a separate study [*Salma et al.*, 2006], for concentrations ranging from 45 to 1000 mg/l by using a dynamic pendant drop shape method. The measured surface tensions depended on the droplet concentrations and also on the age of the droplets. Measured surface tensions were in agreement with values published by *Kiss et al.* [2005]. The smallest equilibrium surface tension measured for the HULIS sample used in our study was about 50 mN/m. With increasing HULIS concentration, the measured surface tension asymptotically reached a limiting value.

[13] It was thought that the value of 50 mN/m is close to the typical surface tension in real incipient droplets [*Salma et al.*, 2006], and this value was used here as a lower boundary, although the measurements of the surface tension were done at concentrations lower than those occurring during hygroscopic growth and activation.

3. Modeling

[14] The water activity of a substance in an aqueous solution can be described as:

$$a_w = \exp(-(\phi \nu n_s)/n_w) \qquad (1)$$

with the osmotic coefficient ϕ (accounting for non-ideality of the solution), the number of ions per solute molecule ν, and the number of solute and water molecules n_s and n_w, respectively. For the solute, $n_s = (V_s \rho_s)/M_s$, where V_s is the volume of the solute (i.e., volume of the dry particles), ρ_s is the solute density, and M_s is the solute molecular weight.

[15] For the solute of this study (i.e., the HULIS sample), neither ϕ, ν, ρ_s, nor M_s were known. The combined effect of these properties was accounted for by ρ_{ion}, which represents the number of ions (or moles, if the molecules do not dissociate) that can go into solution per volume of the dry substance (unit of ρ_{ion}: mol/cm^3):

$$\rho_{ion} = (\phi \nu \rho_s)/M_s \qquad (2)$$

[16] To describe equilibrium diameters of solution droplets at different RHs, in addition to the water activity (also called the Raoult term of the Köhler equation) the curvature of the droplets must be taken into account. This is done in the so-called Kelvin term of the Köhler equation, which depends on the surface tension of the solution:

$$K = \exp\left(4M_w \sigma_s / RT \rho_w d_p\right) \qquad (3)$$

[17] M_w is the molecular weight of water, σ_s the solution surface tension. R is the ideal gas constant, T the temperature, ρ_w is the density of water, and d_p is the droplet diameter.

[18] The full Köhler equation, which describes the water vapor saturation at the surface of the droplet (S_p), can therefore be expressed as:

$$S_p = Ka_w.$$

[19] Altogether, the key parameters that determine the equilibrium diameters of solution droplets and the super-saturation at which they activate, are the surface tension and the number of ions or molecules in solution.

4. Obtaining ρ_{ion} From Measured Hygroscopic Growth

[20] In the following, it is described how the unknown number of ions or molecules in solution, combined into ρ_{ion}, was derived, based on measured equilibrium diameters.

[21] The Köhler equation was used to calculate the equilibrium diameters and growth factors of HULIS particles at RHs above 80%. In the Köhler model, ρ_{ion} was varied until the calculated hygroscopic growth factors were equal to the measured values. Values of ρ_{ion} were determined for each RH at which measurements were made.

[22] The surface tension of the droplets in our measurements was not known. To test the sensitivity of the model to the surface tension, an upper and a lower boundary for the surface tension were used. For case A the surface tension of water was used, $\sigma_{H2O} = 72.8$ mN/m, whereas for case B, $\sigma_{HULIS} = 50$ mN/m was used. Therefore, two values for ρ_{ion} were obtained for each measurement, corresponding to the upper and lower values for σ_s.

[23] Figure 1 (top) shows values of ρ_{ion} so determined. A dependence of ρ_{ion} on the relative humidity can be seen,
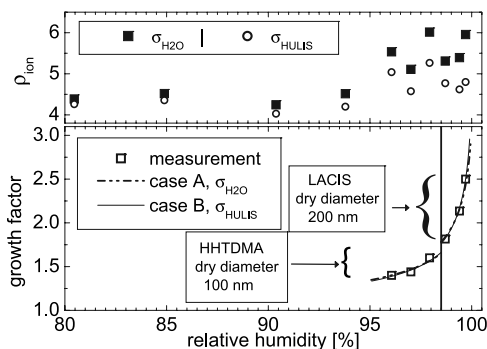
Figure 1. (top) Values of ρ_{ion}, derived separately for each RH from measured growth factors, using two different surface tensions. (bottom) Measured and modeled growth factors for HULIS particles. Surface tension and ρ_{ion} for case A and B are given in the text.

which implies a dependence of ρ_{ion} on the concentration of HULIS in the droplets. Values of ρ_{ion} increase with increasingly dilute solutions. This dependence indicates a change of the number of moles in solution, i.e. a change in the degree of dissociation (change in ϕv), with the HULIS concentration, with an increasing degree of dissociation towards the more dilute solutions.

[24] Because ρ_{ion} was determined specifically for use in calculations of the activation of HULIS particles, only values of ρ_{ion} for RHs above 95% (i.e., at the most dilute solutions) were considered in the following discussion. The average values for ρ_{ion} in this high RH range are summarized as:

case A : σ_{H2O} = 72.8 mN/m and ρ_{ion} = 5.55*10^{-3} mol/cm^3

case B : σ_{HULIS} = 50 mN/m and ρ_{ion} = 4.85*10^{-3} mol/cm^3

Figure 1 (bottom) shows the measured growth factors, and the growth factors determined from the Köhler theory using the values of ρ_{ion} given above. For both, case A and B, the calculated growth factors based on ρ_{ion} agree with the measured values within 2%. The jump in the growth curves at 98.5% RH is due to the difference in the Kelvin term for the different dry particle sizes.

[25] The single, adjustable parameter ρ_{ion} was introduced to avoid the need to determine the different HULIS physical properties with a high accuracy. This is a simplification, compared to other methods, [e.g., *Koehler et al.*, 2006], where a polynomial was used to fit measured hygroscopic growth factors. A change of the dissociation with the solution concentration can be modeled with the approach by *Koehler et al.* [2006], but not with ours. We compensate for this, however, by using information of the hygroscopic growth at very high RHs.

[26] It was tested if the values obtained for ρ_{ion} could be obtained from reasonable values for the parameters they consist of. For the relationship described by equation 2, it was found that a physically realistic set of values for ϕ, v, ρ_s, and M_s can yield the same values that were determined for ρ_{ion}. Figure 2 shows possible combinations of ϕ, v, ρ_s, and M_s that yield ρ_{ion} = 4.85 10^{-3} mol/cm^3. The grey area encloses all combinations for which values of ϕ v (i.e. the dissociation) are between 1 and 1.5, and ρ_s is between
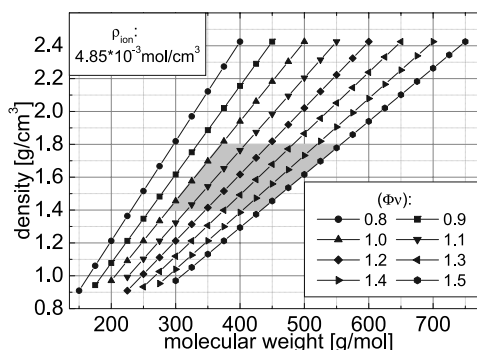

Figure 2. Single value of ρ_{ion} obtained by many different combinations of ϕ, v, ρ_s, and M_s.

1.4 and 1.8 g/cm^3. Thus, these ranges cover values which can reasonably be expected for these parameters. The corresponding values of M_s range from about 290 to 560 amu. A similar examination for ρ_{ion} = 5.55 10^{-3} mol/cm^3, with the same restrictions on ϕ v and ρ_s as above, corresponds to values of M_s between 250 and 490 amu. All these values for M_s agree with previously reported values. Thus, both values obtained for ρ_{ion} are reasonable when related to known ranges of the different HULIS properties. These values of ρ_{ion} were therefore used to determine critical super-saturations, (S_{crit}).

5. Comparison of Modeled and Measured S_{crit}

[27] The derived values of ρ_{ion} were used in the Köhler model to calculate S_{crit}. Calculations were done for dry diameters of 50, 75, 100, and 125 nm, corresponding to the measured diameters.

[28] For case A, calculated values of S_{crit} for dry sizes of 50 and 75 nm exceeded the measured values by 11% and 10% respectively, whereas the calculated values of S_{crit} for dry sizes of 100 and 125 nm are 7% and 6% lower, respectively, than the measured values. For 100 and 125 nm, measured and calculated values of S_{crit} agreed within the measurement uncertainty, whereas for 50 and 75 nm the discrepancy between measured and calculated values of S_{crit} exceeded the measurement uncertainty. For all of the calculations for case A, σ_{H2O} was used.

[29] For case B, σ_{HULIS} = 50 mN/m was used when deriving ρ_{ion}. During activation, however, further dilution of the solution occurs, causing a possible change of the surface
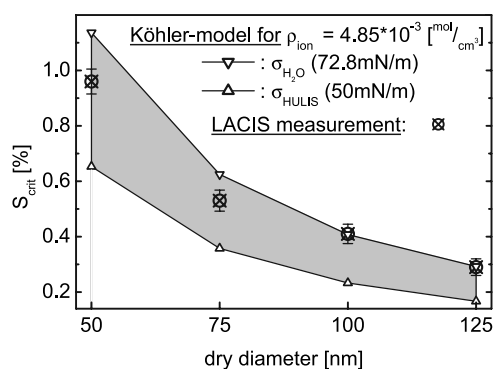

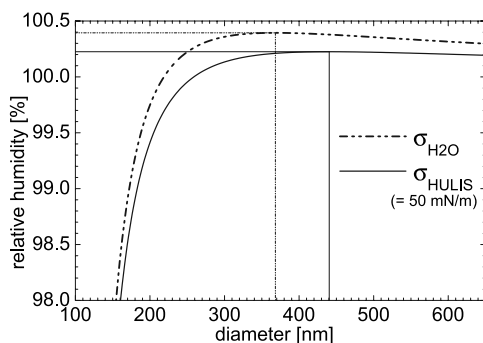**Figure 3.** LACIS measurements and modeled values of S_{crit}.

Figure 4. Calculations with the Köhler model, using the same ρ_{ion} but two different surface tensions.

tension towards that of water. *Kokkola et al.* [2006] state that for HULIS samples at droplet activation, when the droplet solution is very diluted, it is a better approximation to use the surface tension of water instead of that of HULIS, when calculating S_{crit} with Köhler theory. To test the sensitivity of our calculations to σ, for case B two values of S_{crit} were calculated for each dry size, corresponding to σ_{H2O} and σ_{HULIS}. The results are shown in Figure 3. For the larger dry diameters of 100 and 125 nm, simulation using σ_{H2O} yield S_{crit} within 1% of measured values, which also agrees with the model results by *Kokkola et al.* [2006]. There are two possible explanations for this behavior. The first explanation is that the droplets formed on these particles are already sufficiently dilute at the point of activation, so that there is no influence of HULIS on the surface tension. The second explanation is that activation happens on a time-scale too fast for surface-tension lowering to occur [*Salma et al.*, 2006]. For these particles, the Köhler equation gives sizes of the droplets at the point of activation, which are at least a factor of 3.5 above the dry size of the particles.

[30] For the dry diameters of 50 and 75 nm, using σ_{H2O} yielded S_{crit} that were about 18% larger than the measured values. Using σ_{HULIS}, for all dry sizes the calculated values of S_{crit} were 32% to 42% smaller than the measured values. The particles with the smaller dry diameters have a larger S_{crit} and a lower growth factor at the point of activation. The droplets formed on these smaller particles at the point of activation consist of a more concentrated solution than the droplets formed on the larger particles, and a surface tension lower than that of water is probable. Calculations using $\rho_{ion} = 4.85 \ 10^{-3} \ mol/cm^3$ and assuming $\sigma = 65 \ mN/m$ reproduce the measured values of S_{crit} for the 50 and 75 nm particles. However, this value for σ is only an approximation, and more data is needed to determine a more accurate value.

[31] Note that the adjusted ρ_{ion} based on growth factors that were measured for RHs < 100% does not contain information about σ at activation. The reason for this is illustrated in Figure 4. The Köhler model was used to calculate two different hygroscopic growth curves. For both curves, the same value for ρ_{ion} was used, but σ_{H2O} was used in one calculation and σ_{HULIS} in the other. For RHs < 95%, the difference in equilibrium diameters at a fixed RH was less than 2% between the two calculations, and even at 98% RH the difference was only 4%. However, for these two different values of σ, S_{crit} differed by more than a factor of

1.5 ($S_{crit} = 0.23\%$ for σ_{H2O} and 0.39% for σ_{HULIS}), resulting in more than a 20% difference in the diameter at the point of activation. This indicates that σ only weakly affects hygroscopic growth for RH < 100%, whereas it strongly affects S_{crit} and the activation process. If measured hygroscopic growth factors are to be used to model critical super-saturations, and if a change in σ occurs, hygroscopic growth factors must be measured at RHs as high as possible.

6. Conclusion

[32] Critical super-saturations of HULIS particles were modeled, based on measurements of their hygroscopic growth. Modeled super-saturations agreed with measured values when an influence of HULIS on the surface tension of the droplets, σ, was considered.

[33] Some physical properties of the HULIS sample needed for the Köhler model are difficult to determine. These properties were combined into a single new parameter, called the ionic density, ρ_{ion}. This ρ_{ion} was adjusted based on measured hygroscopic growth factors at RHs ranging from 95% to 99.7%.

[34] When deriving ρ_{ion}, σ_{H2O} was used as an upper and $\sigma = 50 \ mN/m$ [*Salma et al.*, 2006] as a lower limit for σ. For both limits, the values derived for ρ_{ion} suggest a molecular weight of the HULIS sample of some hundred amu, as in earlier studies.

[35] Critical super-saturation of the HULIS particles, S_{crit}, was calculated by using the calculated values for ρ_{ion}. Agreement between measured and calculated values of S_{crit} was achieved when ρ_{ion} was based on the lower limit for σ, and when also σ was assumed to have a value between 50 mN/m and that of water during activation of droplets with dry diameters between 50 and 75 nm. For the dry diameters of 100 and 125 nm, agreement was achieved when the value of σ was that of water. These findings are in agreement with the fact that the particles with larger dry diameters have a lower critical super-saturation, but a larger growth factor at the point of activation, so that they are more dilute.

[36] When deriving the values for ρ_{ion} based on measurements made for RH < 100%, information about σ is not contained, because in this humidity range σ only has a minor influence on the value of ρ_{ion}, whereas it strongly affects the value of S_{crit}. This implies that σ plays a major role when determining the activation of particles to cloud droplets. It is important to include measured surface tensions when deriving S_{crit} based on measured hygroscopic growth data.

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