Molar Mass, Surface Tension, and Droplet Growth Kinetics of Marine Organics from Measurements of CCN Activity

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The CCN-relevant properties and droplet growth kinetics are determined for marine organic matter isolated from seawater collected near the Georgia coast. The organic matter is substantially less CCN active than (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, but droplet growth kinetics were similar. Köhler Theory Analysis (KTA) is used to determine the average organic molar masses of two samples, which are 4370±24% and 4340±18% kg kmol\textsuperscript{-1}. KTA is used to infer surface tension depression, and is in excellent agreement with direct measurements. For the first time it is shown that direct measurements of surface tension are relevant for CCN activation, and this study highlights the power of KTA.

1. Introduction

Oceanic surface waters contain a substantial amount of dissolved organic matter (DOM) that is transferred to the aerosol phase during the process of sea spray generation. The ocean surface layer contains large amounts of surfactants [Cavalli et al., 2004], which can influence the ability of marine aerosol to act as cloud condensation nuclei (CCN). Measurements of primary marine aerosol composition have observed a size-dependent enrichment of organics (particularly water-insoluble species) in submicron aerosol [O’Dowd et al., 2004; Oppo et al., 1999]. Despite their potential importance, the CCN-relevant properties of marine organics are largely unknown. This is because DOM is difficult to isolate, as its concentration in bulk seawater is orders of magnitude lower than inorganic salts [Ogawa and Tanoue, 2003]. Recently, Vetter et al. [2007] developed a method to remove most of the salt in seawater samples via a combination of electrodialysis and reverse osmosis, thus enabling direct characterization of marine DOM.

Köhler Theory Analysis [KTA, Padró et al., 2007] is a technique to infer the molar volume, surfactant characteristics, and droplet growth kinetics of organic aerosol constituents, all of which are important for linking organic aerosol with cloud formation. KTA has been previously evaluated for aerosol composed of C\textsubscript{13}-C\textsubscript{29} organics mixed with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} [Padró et al., 2007], for water-soluble organics in biomass burning aerosol [Asa-Awuku et al., 2008], and for secondary organic aerosol formed from the ozonolysis of biogenic volatile organic carbon [Asa-Awuku et al., in review]. Asa-Awuku et al. [in review] first extended KTA to infer surface tension as well, which is useful when sample size prohibits direct measurement of surface tension; this aspect of KTA is further developed here.

In this study, we measure the CCN-relevant properties of marine DOM and then use KTA to infer its average molar mass and surface tension depression characteristics. The potential impact of marine surfactants on droplet growth kinetics is also explored. To evaluate KTA, inferred values of surface tension are compared against direct measurements using the pendant drop technique.

2. Experimental

2.1. Sample Collection

Seawater samples were collected near the Georgia Coast on board the Research Vessel Savannah during an October 2006 research cruise in the Atlantic Ocean. 200-l samples from the Gulfstream current (31°32.5’N, 79°13.8’W, 84 m depth) and the Ogeechee River estuary (31°56.6’N, 81°0.1’W, 2 m depth) were collected in Niskin bottles and filtered to remove suspended particulates greater than 0.45 μm with a polypropylene filter. The estuarine sample was collected under tidal conditions. Inorganic salt concentrations were similar in both samples (3.7×10\textsuperscript{4} ppm in the Gulfstream sample and 3.1×10\textsuperscript{3} ppm in the estuarine sample); however, more organics were initially present in the estuarine sample than the Gulfstream sample (4.36 ppm and 0.95 ppm, respectively).

The DOM in each sample was subsequently concentrated using the electrodialysis/reverse osmosis (ED/RO) technique of Vetter et al. [2007]. In this method, ED is first used to remove the majority of the inorganic salts and is followed by RO to remove excess water. This cycle is repeated until a desired concentration of DOM is attained, after which the sample is freeze-dried. Typical DOM recoveries range from 64-93% [Vetter et al., 2007], and water conductivities were reduced by over 99.98%. During the process, all Cl\textsuperscript{-} is depleted, and the remaining inorganic fraction is primarily Na\textsubscript{2}SO\textsubscript{4} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}.

2.2. Chemical Composition of Samples

The water-soluble organic carbon (WSOC) content of both samples was measured with a total organic carbon (TOC) analyzer (Sijvers Model 800 Turbo). Additionally, inorganic ions (SO\textsubscript{4}\textsuperscript{2-}, Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and K\textsuperscript{+}) were measured using a dual ion chromatography (IC) system (Dionex ICS-2000). TOC concentrations of the Gulfstream and estuarine dry samples are 0.111 kgC kg\textsuperscript{-1} and 0.249 kgC kg\textsuperscript{-1}, respectively. From the IC measurements, the major inorganic species present in the DOM extract are Na\textsubscript{2}SO\textsubscript{4} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}. The solution pH is neutral, suggesting that the organics do not substantially dissociate.

2.3. Surface Tension Measurements

Surface tension measurements were performed using the pendant drop method with a KSV CAM 200 goniometer.
Each droplet was allowed to equilibrate for 20-30 seconds, allowing sufficient time for organics to partition between the bulk and surface layers [Turunen et al., 2007]. The droplet shape was fit to the Young-Laplace equation to obtain the surface tension, $\sigma$, at the liquid-air interface. The temperature (approximately 297 K) was monitored throughout each set of measurements using a 50 k\Omega thermometer (Digikey ERT-D2FHL503S). Seven pendant drops were photographed at ten frames per second for each surface tension measurement.

Multiple solutions of each sample (done by preparing ~2000 ppm samples, which are successively diluted down to 100 ppm) were prepared to determine $\sigma$ as a function of dissolved carbon concentration, $C$. The data are fit to the Szyzkowski-Langmuir (SL) adsorption isotherm [Langmuir, 1917]:

$$\sigma = \sigma_w - \alpha T \ln(1 + \beta C)$$  \hspace{1cm} (1)

where $\sigma_w$ is the surface tension of water (i.e., an “infinite dilution” sample), $T$ is the absolute temperature, and $\alpha$ and $\beta$ are empirical constants obtained from least-squares fits to the data. While the SL isotherm is an adsorption model for one compound, it is able to model the complex DOM/salt system reasonably well (Figure 2). $\alpha$ and $\beta$ were determined to be 2.952 mN m$^{-1}$ and 2 x $10^{-3}$ K$^{-1}$.

2.4. CCN Activity and Droplet Growth Kinetics Measurements

The experimental setup used for CCN activity measurements is described in detail elsewhere [e.g., Asa-Awuku et al., 2008; Padro et al., 2007]. Aerosol is generated by atomizing an aqueous solution of each of the seawater samples. The particles are dried and introduced into a scanning mobility CCN analyzer [SMCA, Nenes and Medina, in review], for characterization of size-resolved CCN activity and growth kinetics. SMCA uses a differential mobility analyzer (DMA, TSI 3081), operating in voltage-scanning mode, to classify the aerosol. The monodisperse stream is then introduced simultaneously into a Droplet Measurement Technologies Continuous-Flow Streamwise Thermal Gradient CCN Counter (DMT-STGC, Roberts and Nenes, 2005) and a condensation particle counter (CPC, TSI 3022). The timeseries of the DMT-STGC and CPC counts are inverted to obtain curves of CCN/CN as a function of mobility diameter (while maintaining instrument supersaturation at a constant value). The dry diameter, $d_p$, for which 50% of particles are activated (neglecting multiply-charged particles) represents the aerosol that activates at the instrument supersaturation, $s_c$. The DMT-STGC uses an optical particle counter (OPC) to obtain the size distribution of activated droplets exiting the instrument column.

The CCN activity of aerosol containing the estuarine sample and a known amount of added (NH$_4$)$_2$SO$_4$ was also measured in order to see if a “salting out” effect could be observed. The effect occurs at relatively high electrolyte concentrations (~50 wt%, dry concentration), when the salts enhance surfactant partitioning to the droplet surface, dramatically reducing the surface tension and increasing the CCN activity [Asa-Awuku et al., in review]. Two samples were prepared to total salt concentrations of approximately 60 and 90 wt%. The 60 wt% salt sample was also used as an independent mixture to infer molar mass and surface tension depression.

For all CCN measurements, the flow rate of air through the column was maintained at 0.5 l min$^{-1}$ (10:1 sheath-to-aerosol ratio), which corresponds to a residence time of 15 seconds. The DMT-STGC instrument supersaturation was varied from 0.2% to 1.4%.

3. Results and Discussion

3.1. CCN Activity

The CCN activation curves for both samples and pure (NH$_4$)$_2$SO$_4$ are shown in Figure 1. For a CCN composed of soluble non-surfactant compounds, Köhler theory suggests that the “critical supersaturation”, $s_c$, scales with $d_p$ to the $-3/2$ power [Köhler, 1936]. However, for aerosol containing surfactants, this scaling will change, tending to be lower at smaller $d$ and approaching $-3/2$ at larger $d$. This is because at smaller particle diameters, the high concentration of WSOC depresses $\sigma$, which lowers $s_c$ more than would be expected from the solute effect alone; at larger $d$, the WSOC concentration is insufficient to induce this effect [Padro et al., 2007].

The activation curve of the Gulfstream sample aerosol (blue circles) is almost identical to (NH$_4$)$_2$SO$_4$ (yellow triangles), despite the presence of ~40 wt% surface-active DOM. It is likely that the surface tension depression from the organic fraction compensates for the decreased soluble mole fraction. The estuarine sample aerosol contains ~85 wt% organic matter and is much less CCN active than (NH$_4$)$_2$SO$_4$ (red circles in Figure 1). Additionally, the activation curve deviates from the $-3/2$ exponential power law fit (as indicated by the dotted line) at low dry particle diameters and high $s_c$, where the concentration of organic matter is high enough to significantly affect the droplet surface tension ($C > 1000$ mg l$^{-1}$, from Figure 2).

3.2. Köhler Theory Analysis (KTA)

The organic molar mass and surface tension depression were inferred from the CCN activity measurements using KTA, method b$_2$ [Padro et al., 2007; Asa-Awuku et al., 2008, in review]. For each $s_c/d_p$ measurement, the fitted CCN activity (FCA) parameter, $\omega$, is calculated from

$$\omega = s_c d_p^{3/2}$$  \hspace{1cm} (2)

KTA entails expressing FCA in terms of its constituents, assuming the aerosol is composed of N components [Padro et al., 2007]:

$$\omega = 2 \left(\frac{4M_s \sigma}{3RT \rho_w}\right)^{3/2} \sum_{i=1}^{N} \frac{\rho_w}{M_i} \left(\frac{M_i}{\rho_i}\right)^{1/2}$$\left(1 / \varepsilon_i \varepsilon_a\right)^{1/2}$$  \hspace{1cm} (3)

![Figure 1. Critical supersaturation versus dry particle diameter for all samples considered.](image-url)
where \( M_w \), \( \rho_w \) are the molar mass and density of water, respectively, \( R \) is the universal gas constant, and \( M_i, \rho_i, \xi_i, \nu_i \) are the molar mass, density, volume fraction, and effective van’t Hoff factor of component \( i \), respectively. Denoting the organic fraction as component “j” and rearranging Equation 3 to solve explicitly for \( M_j \) and \( \sigma \) yields

\[
M_j = \frac{2\sigma}{3} \left( \frac{M_w}{\rho_w} \right)^2 \left( \frac{1}{N} \right)^3 \sigma^{-2} - \sum_{i \neq j}^N \frac{\rho_i}{M_i} \xi_i \nu_i
\]  

(4)

\[
\sigma = \left[ \frac{\rho_j}{M_j} \xi_j + \sum_{i \neq j}^N \frac{\rho_i}{M_i} \xi_i \nu_i \right]^{1/3}
\]  

(5)

\[ \sigma \] corresponds to the value at activation, and the surfactant carbon concentration is given by [Padro et al., 2007],

\[
C_{act} = \frac{27}{8} x_{c,j} \rho_j \tau_j \frac{a_j^2 s_j^3}{A^3}
\]  

(6)

where \( A = \frac{4M_w - \sigma}{RT} \) and \( x_{c,j} = 0.29 \) is the mass fraction of carbon in the DOM, estimated from the Redfield ratio (C:N:P = 106:16:1) [Schulz and Zabel, 2006; Redfield et al., 1963]. In applying Equations 4-6, we assume an organic density, \( \rho_j \), of 1400 kg m\(^{-3}\) [Schulz and Zabel, 2006], an effective van’t Hoff factor of 1 for the organics [Dinar et al., 2007], and 2.5 for (NH\(_4\))\(_2\)SO\(_4\) and Na\(_2\)SO\(_4\) [Padro et al., 2007].

To compute \( M_j \) and \( \sigma \) from KTA, the following procedure is used: First, the average organic molar mass, \( M_j^* \), is estimated for each \( s/c/d_p \) pair (Equation 4) initially assuming the surface tension of pure water. Equations 5 and 6 are used to estimate \( \sigma \) for the \( s/c/d_p \) data of the sample plus 60% (NH\(_4\))\(_2\)SO\(_4\). The updated \( \sigma \) values are used to reevaluate \( M_j^* \) and this process is iterated until the \( \sigma \) and \( M_j^* \) values converge. This procedure allows the concurrent inference of \( M_j \) and \( \sigma \) as a function of WSOC concentration from the CCN activity data alone.

\( M_j \) is estimated to be 4370±26% kg kmol\(^{-1}\) and 4340±6% kg kmol\(^{-1}\) for the Gulfstream and estuarine samples, respectively, (the reported uncertainty is one standard deviation from the mean \( M_j \) over all \( s/c/d_p \) pairs). The sensitivities of \( M_j \) to each of the independent parameters is computed with the method of Padro et al. [2007] (Table 1). Using this method, the total estimated uncertainties of \( M_j \) for the estuarine and Gulfstream samples are 18% and 24%, respectively. As expected, the Gulfstream sample uncertainty exceeds the estuarine sample uncertainty, since the lower organic mass increases the \( M_j \) sensitivity to most of the independent parameters [Padro et al., 2007].

Both molar masses are consistent with each other and fall in the mid-range of the high molar-mass fraction that comprises 30-35% of the marine surface DOM [Ogawa and Tanoue, 2003]. The inferred \( M_j \) is also consistent with that of a theoretical Redfield-based molecule, (CH\(_2\)O)\(_{106}\)(NH\(_4\))\(_3\)H\(_2\)PO\(_4\) [Schulz and Zabel, 2006]. While most of the DOM is recovered, it is expected that the small amount of DOM not recovered during the ED/RO process would be low-molar-mass species that can permeate the ED membranes easiest; therefore, higher molar-mass DOM in the sample may be enriched in the process and the \( M_j \) of the sample (and hence, that inferred using KTA) may be greater than \( M_j \) of in-situ marine DOM.

The inferred \( \sigma \) is in excellent agreement with the SL fit to direct measurements (Figure 2). The agreement is still excellent if other functions for fitting the data are used; the variability in inferred \( M_j \) remains within the reported uncertainty (not shown). Since the inferred values are derived

\[
\Delta x = 1.47(2.16) \times 10^{-15} a \quad 400 \quad 0.2 \quad 0.044 b \quad 3.7 (6.9) \quad 10 (17) \quad 0.2 (0.1) \quad 15 (16)
\]

(7)

<table>
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<th>Base x Value</th>
<th>( \omega ) (m(^3)/kg)</th>
<th>( \rho_j ) (kg m(^{-3}))</th>
<th>( \nu_j ) %</th>
<th>( x_{c,j} ) %</th>
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<tr>
<td>1.47(2.16)</td>
<td>1400</td>
<td>1</td>
<td>0.29</td>
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<td>3.7(6.9)</td>
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(a) One standard deviation from the mean FCA value.
(b) Schulz and Zabel [2006].
(c) Dinar et al. [2007].
independently of the direct measurements, their agreement shows conclusively that diffusion of surface-active molecules to the droplet surface is sufficiently rapid to achieve equilibrium surface tension depression. Taranuik et al. [2007] and Asa-Awuku and Nenes [2007] showed that humic-like organic species (~500 kg kmol~1~) in growing droplets are in equilibrium; we find this to apply for marine DOM with a tenfold higher molar mass (hence, ~1/10 times lower diffusivity). The latter finding is consistent with the analysis of Asa-Awuku and Nenes [2007], as a diffusivity of 2 × 10~4~ [= 6×10~10~] with 6 × 10~10~ being the diffusivity of HULIS, Taranuik et al. [2007] implies that the organic concentration at the droplet surface is more than 90% of its equilibrium value for the supersaturation range considered here.

While the inferred and measured surface tension agree, the surfactants require tenfold higher concentrations to give the same effect as organics isolated from marine aerosol [Cavalli et al., 2004]. This difference reflects the enrichment of marine aerosol in organic surfactants from the process of bubble bursting. Hence, the samples investigated here are representative of natural marine DOM, but should be interpreted as the lower limit of CCN activity of primary marine organic aerosol.

3.3. Droplet Growth Kinetics

The mean droplet sizes for each sample measured by the DMT-STGC OPC at varying values of s are shown in Figure 3. All samples studied exhibit growth similar to that of pure (NH4)~2~SO4 for most supersaturations. For the three middle supersaturations (0.6%, 0.8%, and 1.0%) it appears that both seawater samples grow to larger droplet sizes than for pure (NH4)~2~SO4. Since it is not expected that organics would enhance droplet growth, the observed discrepancy may be caused by slight shifts in the laser scattering during the sizing measurement, resulting from the presence of a compressed film. (NH4)~2~SO4 growth could also be depressed because of water vapor depletion in the column during the calibrations; however, this is unlikely since the total CCN concentrations were relatively low (~500 cm~3~) and constant for all supersaturations. Laser shifts over long time periods are unlikely, as the results are reproducible. The data suggest that the dissolved organics, compared to pure (NH4)~2~SO4, do not significantly alter the droplet growth kinetics (i.e., the water vapor mass transfer coefficient).

4. Summary and Conclusions

In this study, measurements of CCN activity, droplet growth kinetics, and WSO4/ionic composition of marine DOM were used to infer its CCN-relevant properties. Köhler Theory Analysis (KTA) determined the molar masses of the organic matter in the Gulfstream sample and estuarine sample to be 4370 ~10~1~ and 4340 ~10~1~, with ~6~10~1~ for most supersaturations. For the three middle supersaturations (0.6%, 0.8%, and 1.0%) it appears that both seawater samples grow to larger droplet sizes than for pure (NH4)~2~SO4. Since it is not expected that organics would enhance droplet growth, the observed discrepancy may be caused by slight shifts in the laser scattering during the sizing measurement, resulting from the presence of a compressed film. (NH4)~2~SO4 growth could also be depressed because of water vapor depletion in the column during the calibrations; however, this is unlikely since the total CCN concentrations were relatively low (~500 cm~3~) and constant for all supersaturations. Laser shifts over long time periods are unlikely, as the results are reproducible. The data suggest that the dissolved organics, compared to pure (NH4)~2~SO4, do not significantly alter the droplet growth kinetics (i.e., the water vapor mass transfer coefficient).

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X - 4 MOORE ET AL.: ANALYSIS OF MARINE ORGANICS