Hygroscopic Growth and Deliquescence of NaCl Nanoparticles Mixed with Surfactant SDS

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Received: October 8, 2009; Revised Manuscript Received: January 5, 2010

Several complementary experimental and theoretical methodologies were used to explore water uptake on sodium chloride (NaCl) particles containing varying amounts of sodium dodecyl sulfate (SDS) to elucidate the interaction of water with well-defined, environmentally relevant surfaces. Experiments probed the hygroscopic growth of mixed SDS/NaCl nanoparticles that were generated by electrospraying aqueous 2 g/L solutions containing SDS and NaCl with relative NaCl/SDS weight fractions of 0, 5, 11, 23, or 50 wt/wt %. Particles with mobility-equivalent diameters of 14.0(±0.2) nm were size selected and their hygroscopic growth was monitored by a tandem nano-differential mobility analyzer as a function of relative humidity (RH). Nanoparticles generated from 0 and 5 wt/wt % solutions deliquesced abruptly at 79.1(±1.0)% RH. Both of these nanoparticle compositions had 3.1(±0.5) monolayers of adsorbed surface water prior to deliquescing and showed good agreement with the Brunauer−Emmett−Teller and the Frenkel−Halsey−Hill isotherms. Above the deliquescence point, the growth curves could be qualitatively described by Köhler theory after appropriately accounting for the effect of the particle shape on mobility. The SDS/NaCl nanoparticles with larger SDS fractions displayed gradual deliquescence at a RH that was significantly lower than 79.1%. All compositions of SDS/NaCl nanoparticles had monotonically suppressed mobility growth factors (GFm) with increasing fractions of SDS in the electrosprayed solutions. The Zdanovskii−Stokes−Robinson model was used to estimate the actual fractions of SDS and NaCl in the nanoparticles; it suggested the nanoparticles were enhanced in SDS relative to their electrospray solution concentrations. X-ray photoelectron spectroscopy (XPS), FTIR, and AFM were consistent with SDS forming first a monolayer and then a crystalline phase around the NaCl core. Molecular dynamics simulations of water vapor interacting with SDS/NaCl slabs showed that SDS kinetically hinders the initial water uptake. Large binding energies of sodium methyl sulfate (SMS)−(NaCl)₄, H₂O−(NaCl)₄, and SMS−H₂O−(NaCl)₄ calculated at the MP2/cc-pVDZ level suggested that placing H₂O in between NaCl and surfactant headgroup is energetically favorable. These results provide a comprehensive description of SDS/NaCl nanoparticles and their properties.

Introduction

Thin water films are ubiquitous on many common environmental surfaces including atmospheric particles. In many instances, these thin films are responsible for macroscopic observations, even though they may only constitute a very small fraction of the system’s total mass or volume. Thin water films on atmospheric particles participate in a variety of chemical reactions and physical interactions including the nucleation of cloud droplets. Thus, it is critical to understand the fundamental interactions of water with atmospheric aerosol including the relative humidity at which solid particles deliquesce, as well as the effects of particle size and chemical composition on hygroscopic properties.

NaCl has routinely been used as a model system for sea-salt aerosols. Previous measurements on bulk crystalline NaCl showed that above 70% relative humidity (RH), 3.5−4 monolayers (ML) of water are adsorbed onto the surface. As the RH above the NaCl surface increases, enough water adsors to the surface to initiate a deliquescence transition from the crystalline to aqueous phase at the deliquescence relative humidity (DRH). Measurements in several laboratories including this one showed that DRH values for NaCl particles less than 100 nm in size are higher than the DRH of 75% measured for larger NaCl particles (>100 nm) and bulk NaCl. This size dependence originates from the surface tension contribution of the thin water film to the system’s free energy, which for small enough particles is comparable in magnitude to that from the NaCl bulk. This changes the Gibbs free energy of deliquescence such that more water vapor above the surface is required to initiate the deliquescence. Consequently, as the size of the dry nanoparticle decreases, its DRH increases.

Numerous studies have addressed the effects of organic material on the hygroscopic properties of inorganic particles. Researchers often assume that organic/inorganic particles will phase segregate into a “core-shell” morphology with an organic “shell” coating an inorganic crystalline “core” as shown in the...
mixed with glutaric and pyruvic acid. Woods et al. found that deliquescence point to lower RH for 100 nm NaCl particles inorganic core. For example, Chen and Lee noted a shift in the affect both the degree of the water uptake and DRH for the situation is somewhat more complicated for particles containing sodium dodecyl sulfate (SDS). In this laboratory, experiments 100 nm NaCl particles with roughly one coverage layer of NaCl nanoparticles (9 and 14 nm in mobility equivalent diameter) on mixed sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/NaCl coating does not always inhibit growth of the soluble inorganic core, even for cases in which the organic material comprised the majority of the particle mass. In many cases, water uptake can be accurately predicted by the Zdanovskii—Stokes—Robinson (ZSR) model, which assumes the individual particle constituents adsorb water independently in proportion to their volume fraction. As poorly soluble organics are not expected to take up any measurable amount of water at humidities between 5 and 95%, the soluble inorganic core is therefore expected to contribute solely to hygroscopic growth of mixed particles. The situation is somewhat more complicated for particles containing sparingly soluble organics, where the presence of organics can affect both the degree of the water uptake and DRH for the inorganic core. For example, Chen and Lee noted a shift in the deliquescence point to lower RH for 100 nm NaCl particles mixed with glutaric and pyruvic acid. Woods et al. found that deliquescence was shifted to lower humidity by ~1% RH for 100 nm NaCl particles with roughly one coverage layer of sodium dodecyl sulfate (SDS). In this laboratory, experiments on mixed sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/NaCl nanoparticles (9 and 14 nm in mobility equivalent diameter) measured the onset of deliquescence at significantly lower RH (up to 10% lower) than for pure NaCl particles of the same size. Results were attributed to interactions between NaCl−H2O−Na+ and −O3SO−R at the surface that were comparable to the magnitude of the Na−Cl binding energy. These results suggest the surfactants affect the deliquescence of NaCl in a size-dependent way and motivate the present investigation of hygroscopicity of mixed SDS/NaCl nanoparticles.

Typical minimum cloud condensation nuclei (CCN) activation diameters at 100.5% RH are 20–30 nm for soluble inorganics, such as NaCl, and 100–200 nm for weakly soluble organics, such as SDS. Furthermore, field measurements show marine-based aerosols are typically in the micrometer size regime. The size of particles studied in this work is therefore not representative of the real atmosphere. However, we elect to study nanoparticles because of their unique surface properties. There is also an experimental advantage to studying nanoparticles: the surfactant and water coating on predeliquesced aerosol is a larger and more easily quantifiable fraction of the total diameter than for larger particles.

Herein, we present a combined experimental and computational investigation designed to gain a comprehensive picture of the hygroscopic growth of hybrid surfactant−NaCl nanoparticles. SDS is chosen as a model single-chain surfactant. Computational investigations include molecular dynamics (MD) simulations to visualize how adsorbed water interacts with SDS/NaCl slabs as well as high-level ab initio calculations to characterize the structural and energetic aspects of interactions between NaCl, H2O, and SDS. Experimental investigations include tandem nano-differential mobility analysis (DMA) to characterize the water uptake by the size-selected SDS/NaCl nanoparticles generated by electrospraying a solution containing SDS and NaCl. Activity measurements (see discussion below) over bulk mixtures of NaCl and SDS are conducted to compare to nanoparticle hygroscopic growth. X-ray photoelectron spectroscopy (XPS), FTIR, and atomic force microscopy (AFM) are used to characterize the dry nanoparticle composition and morphology. Table 1 serves as a guide for the techniques employed in this work, their application, and the range of the SDS content these techniques probe.

Experimentally, water uptake and deliquescence can be characterized using the mobility growth factor GFm, defined in eq 1 as a ratio of the wet mobility diameter $d_m(RH)$ to that of the dry mobility diameter $d_m(0)$. Mobility diameters are typically quantified using tandem DMA techniques.

$$GF_m = \frac{d_m(RH)}{d_m(0)}$$

This macroscopic metric of water uptake may not seem appropriate for nanoparticles given that their size can be on the order of molecular dimensions. However, GFm and DRH can still be accurately predicted for single component soluble inorganic nanoparticles using bulk thermodynamic treatments.

### Table 1: Techniques Employed in this Work and their Applications

<table>
<thead>
<tr>
<th>Technique</th>
<th>Provides Information About</th>
<th>wt/wt % SDS/NaCl or SDS Coverage Probed</th>
</tr>
</thead>
<tbody>
<tr>
<td>tandem hygroscopic growth</td>
<td>equilibrium water uptake by nanoparticles</td>
<td>0–90%</td>
</tr>
<tr>
<td>water vapor activity</td>
<td>equilibrium water uptake by bulk mixtures</td>
<td>0–100%</td>
</tr>
<tr>
<td>MD simulations</td>
<td>qualitative visualization of dynamics of the initial water uptake by the NaCl/SDS surfaces</td>
<td>&lt;1.0 monolayer</td>
</tr>
<tr>
<td>ab initio calculations</td>
<td>binding energies and interactions between NaCl clusters, H2O, and SDS</td>
<td>individual molecules and small clusters</td>
</tr>
<tr>
<td>AFM imaging</td>
<td>morphology and size of NaCl/SDS nanoparticles</td>
<td>23%</td>
</tr>
<tr>
<td>FTIR spectroscopy</td>
<td>phase state of SDS in the nanoparticles</td>
<td>23%</td>
</tr>
<tr>
<td>XPS spectroscopy</td>
<td>relative amounts of SDS/NaCl in the nanoparticles</td>
<td>0–50%</td>
</tr>
</tbody>
</table>
When properly accounting for particle shape, Koehler theory has previously been used to predict GF_m for NaCl nanoparticles and will be used to interpret GF_m data for NaCl and SDS/NaCl nanoparticles in this work.

Upon deliquescence, NaCl particles become saturated aqueous solutions and subsequently dilute as they take up more water. Due to the nonideality associated with concentrated electrolyte solutions, vapor pressure, solubility, free energy of mixing, freezing-point depression, boiling-point elevation, and osmotic pressure must be determined experimentally. Water activity a_w is often used in association with equilibrium vapor pressure p_{vap,aq} over nonideal aqueous solutions. Equation 2 shows water activity for bulk liquids and eq 3 for particles with small diameters, which includes a Kelvin effect correction term C_K(a_{aq},d_m).

\[ a_w = \frac{\rho_{vap,aq}}{\rho_{vap,H_2O}} = \frac{\text{RH}}{100} \]  
\[ a_w C_K(a_{aq},d_m) = \frac{\text{RH}}{100} = a_w \exp\left(\frac{4M_w a_{aq}(w_i)}{RT a_{aq}(w_i) d_m(RH)}\right) \]  

M_w is the molecular weight of water and d_m(RH) is the particle diameter (which changes with RH in our experiments). Activity a_w(w_i), density \rho_{aq}(w_i), and surface tension \sigma_{aq}(w_i) of the electrolyte solution have been determined experimentally as a function of NaCl_{aq} weight percent w_i for 0 < w_i < 45%. Surface tensions over NaCl and NaCl solution have been shown to decrease with size, and corrections to account for this are available in the literature. However, these corrections are significant only for particles below ~10 nm in size. Therefore, they were not included in eq 3 in order to simplify the calculations for the 14 nm particles studied in this work.

As NaCl particles are not spherical, appropriate shape corrections are required in order to relate their mobility equivalent diameter and their actual size. Equation 4 corresponds to "Model 4" from Biskos et al., which is a version of Koehler theory from Cinkotai et al. with an inclusion of shape effects on particle mobility.

\[ GF_m = \left(\frac{100\rho_w}{w_i(a_w\rho_{aq}(w_i))}\right)^{1/3} A(Kn,\chi_s) \]  

The term A(Kn,\chi_s) has a unique solution in each flow regime which satisfies the relationship in eq 5, where d_m(0) is the envelop equivalent, often referred to as volume equivalent diameter under dry conditions.

\[ d_m(0) = A(Kn,\chi_s) d_m(0) \]  

It was found that the experimentally measured GF_m could be predicted reasonably well by use of Koehler theory for NaCl particles between 6 and 60 nm, provided the correct flow regime was used for a particle of a given Knudsen number. The critical parameter in the Koehler theory analysis is the surface tension–diameter relationship provided by the Kelvin effect. By purposely adding molecules that affect this surface tension (i.e., surfactants), RH and hygroscopic growth are expected to be altered significantly. The goal of this research is to understand at a fundamental level the effect of surfactants on hygroscopic growth of NaCl nanoparticles both below and above the deliquescence transition in NaCl.

**Experimental Methods**

**Generation of NaCl and SDS/NaCl Nanoparticles.** NaCl and SDS/NaCl nanoparticles were generated with an electrospray particle generator, designed in-house and described in detail elsewhere. Variable amounts of NaCl (Sigma-Aldrich, 99.999%) and SDS (Fluka, ≥99.0%) were dissolved in HPLC grade water (OmniSolv, <8 µΩ·cm) and a small amount (<5%) of methanol (HPLC grade, Sigma-Aldrich) to achieve a combined NaCl + SDS weight concentration of ~2 g L⁻¹. Solutions were pushed through a 100 µm capillary from a syringe pump operating at a typical flow rate of ~1 µL min⁻¹ with a ~3 kV positive potential applied to the stainless steel tip of the syringe. The electrospray was operated in a stable cone-jet mode and generated a dry polydisperse population of particles with number density of the order of 10^7 cm⁻³. The size characteristics of the initial particle distribution from the electrospray source were sensitive functions of applied voltage, syringe pump flow rate, and distance (l) from the capillary tip to the electrically grounded neutralizer entrance. Table 2 summarizes the electrospray conditions and typical particle size characteristics that resulted from the varying solution compositions. These conditions represent optimized electrospray protocols for sustaining the cone-jet mode over long periods of time (~6 h). The final relative SDS/NaCl concentration in the nanoparticles is a function of the electrospray dynamics and is unknown a priori. Consequently, the various compositions of SDS/NaCl nanoparticles will be referred to by the solution composition from which they were generated and all values refer to the relative weight percents of SDS relative to NaCl (wt/wt %).

**TABLE 2: Electrospray Conditions and Particle Size Characteristics for Various SDS/NaCl Solutions Used in This Work**

<table>
<thead>
<tr>
<th>wt/wt % SDS/NaCl</th>
<th>Z_{NaCl}</th>
<th>total solution concn (g L⁻¹)</th>
<th>applied potential (kV)</th>
<th>flow rate (µL h⁻¹)</th>
<th>l (mm)</th>
<th>d_m (nm)</th>
<th>particle concn (×10^3 cm⁻³)</th>
<th>GSD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.00</td>
<td>1.52</td>
<td>3.4</td>
<td>109</td>
<td>4.0</td>
<td>15.2</td>
<td>0.67</td>
<td>1.29</td>
</tr>
<tr>
<td>5.0</td>
<td>0.99</td>
<td>1.98</td>
<td>3.2</td>
<td>83</td>
<td>4.0</td>
<td>15.2</td>
<td>0.57</td>
<td>1.27</td>
</tr>
<tr>
<td>11</td>
<td>0.98</td>
<td>2.05</td>
<td>3.1</td>
<td>81</td>
<td>5.0</td>
<td>15.5</td>
<td>0.67</td>
<td>1.26</td>
</tr>
<tr>
<td>23</td>
<td>0.94</td>
<td>1.93</td>
<td>3.2</td>
<td>81</td>
<td>4.0</td>
<td>17.9</td>
<td>1.04</td>
<td>1.36</td>
</tr>
<tr>
<td>50</td>
<td>0.83</td>
<td>2.03</td>
<td>3.1</td>
<td>81</td>
<td>6.0</td>
<td>24.5</td>
<td>1.43</td>
<td>1.33</td>
</tr>
</tbody>
</table>

* Dry weight percent of SDS in solution containing 2 g/L total of SDS and NaCl. "Dry mol fraction of NaCl in solution. " Electrospay distance from capillary tip to neutralizer entrance. " Geometric mean mobility diameter of electrospayed nanoparticles prior to the size selection. " Geometric standard deviation (GSD) prior to the size selection.
Hygroscopic Growth Measurements of NaCl and SDS/NaCl Nanoparticles. Nanoparticles were size selected and their hygroscopic growth was monitored by use of tandem-nano differential mobility analysis techniques, described previously. A fixed voltage was applied to the first differential mobility analyzer (DMA1) under dry conditions (RH < 1.0% at 295 K) located downstream from the neutralizer, which selected a narrow distribution (geometric standard deviation, GSD ~ 1.05) from the initial populations shown in Table 2. The electrospray was operated continuously, RH was increased gradually, and the \( d_{50}(\text{RH}) \) distribution was monitored throughout the course of experimentation by a humidified, scanning DMA (DMA2) connected to an optical particle counter.

A custom LabView program was used to monitor the signal from Vaisala HMP237 RH probes. \( GF_{n,\text{a}} \) are reported in this paper as a function of the final RH encountered by particles in the DMA2 sheath flow. All RH probes were calibrated against the vapor pressure over saturated salt solutions. In some experiments DMA2 was maintained roughly 3% RH above the environment between DMAs 1 and 2. Particles therefore were only exposed to the final RH value for the time they spend inside the DMA2 column (\( \sim 1 \) s). In other experiments particles were exposed to 7 and 67 s of RH. This was achieved by using a uniform RH throughout the entire particle flow, including DMA2, and increasing the length and volume of the humidified environment between DMAs 1 and 2.

Bulk Measurements of \( \text{H}_2\text{O} \) Activity over NaCl/Na2SO4 and NaCl/SDS. Equilibrium vapor pressures over bulk saturated solutions containing NaCl and SDS were also measured. Similar measurements were conducted for the mixture of NaCl and Na2SO4 for validation purposes. Solutions were prepared in a 280 cm\(^3\) Vaisala HMK15 humidity calibrator chamber and allowed to equilibrate for 24 h before measurement with Vaisala HMP237 humidity probes. RH probes were calibrated as previously described for nanoparticles experiments. In these studies, 3.00 g of total material (NaCl and SDS or NaCl and Na2SO4) mixed in varying proportions and ground to a fine powder was immersed in 5.00 mL of HPLC grade water (OmniSolv, < 8 µΩ·cm) followed by sonication. After an initial equilibration for 24 h, RH probes were inserted in the O-ring sealed chamber ports and humidities were reported after 1 h probe exposure when the humidity was less than 90% RH and after 12 h when the humidity was greater than 90% RH.

Characterization of Dry SDS/NaCl Nanoparticles. In a separate set of experiments, dry nanoparticles prepared from each NaCl/Na2SO4 solution were collected from the electrospray source using a home-built nanoparticle jet impactor based on the design of De La Mora et al. The nanoparticle beam was expanded into an evacuated region at \( \sim 25 \) Torr through a 200 \( \mu \)m pinhole where a suitable substrate for impaction was located \( \sim 5 \) mm downstream. The flow through the pinhole was 330 sccm (standard cubic centimeters per minute); all the excess flow from the electrospray particle generator was vented. This impactor collected nanoparticles for physical imaging using AFM and chemical analysis using X-ray photoelectron spectroscopy (XPS) and FTIR.

XPS (VG Scientific Ltd.) analysis was carried out on the full particle distribution (Table 2) emerging directly from the electrospray particle source for each composition to maximize the measured XPS signal. Nanoparticles were impacted on highly ordered pyrolytic graphite (HOPG, Union Carbide) for roughly 6 h, after which time a deposition ring approximately 0.5 mm in diameter was visible on the substrate surface. The XPS experiments were carried out under ultrahigh vacuum conditions with base pressures below 1 nanoTorr. Incident photons were generated from an Al K\( \alpha \) source operating at 14 kV and 34 mA. The HOPG substrate was positioned such that the nanoparticle ring was centered directly under the optimized position for sampling by the electron energy analyzer, which was set to 20 eV for all experiments. Sulfur S(2p) and chlorine Cl(2p) photoelectrons were analyzed as proxies for SDS and NaCl, respectively, with identical step sizes and dwell times for comparison.

Samples of SDS/NaCl nanoparticle material were impacted on ZnSe windows (Edmund Optics) and were monitored using transmission FTIR spectroscopy. Infrared spectra were collected over the spectral range of interest, 4000–650 cm\(^{-1}\), as single-beam spectra at 4 cm\(^{-1}\) resolution using 2560 scans for both the background and sample spectra, respectively, with a Nicolet AVATAR FTIR instrument (now Thermo Electron Corp., Madison, WI). Infrared absorption spectra were obtained by ratioing the single-beam spectra of the deposited nanoparticle material to the background spectrum of a clean zirconium selenide window (CVD ZnSe, Cradel Crystals Corp.). Particle impaction time for FTIR analysis was also 6 h, after which time a visible particle deposition ring was present on the ZnSe window. Prior to analysis, impacted nanoparticle material remained in the FTIR chamber for several days under dry conditions (< 1% RH at 295 K) until gas-phase water bands were no longer visible and degassing of water from the collected particles had thus ceased. FTIR spectra were only collected for the dried SDS/NaCl nanoparticles; interference from gas-phase water prevented us from getting reliable spectra of wet particles.

Samples of SDS/NaCl nanoparticle material impacted on HOPG or mica were imaged at ambient pressure and humidity using a Park Scientific Instruments AutoProbe CP Research (now Veeco Metrology Inc., Santa Barbara, CA) scanning probe microscope in intermittent contact mode. As AFM analysis required significantly fewer particles, collection times of 30–45 min were typically employed and particles were size selected by DMA prior to the impaction. AFM images were acquired using highly doped silicon tips (BudgetSensors) with a force constant of 3 N/m in intermittent contact mode. The 5 \( \mu \)m piezoelectric scanner was calibrated in the \( xy \) directions using a grating and in the \( z \) direction using several conventional height standards. Topographs were obtained as 256 \times 256 pixels, flattened line-by-line and analyzed using the AutoProbe image processing software. AFM images of nanoparticles were taken under ambient conditions at 295 K and ~40% RH. It is therefore expected that all imaged nanoparticles have a thin surface layer of water, which may contribute to the imaged morphology.

Molecular Dynamics. SDS/NaCl slabs were generated consisting of either a crystalline NaCl core or an aqueous NaCl solution core that were decorated by SDS molecules. Individual slabs were generated in an \( x-y-z \) periodic simulation box of dimensions \( x = 39.40 \) Å, \( y = 39.40 \) Å, \( z = 200.00 \) Å. Varying the number of SDS molecules in individual slabs simulated the effect of a varying coverage layer (\( \Theta_{\text{SDS}} \)) of SDS on NaCl nanoparticles in the limit of 0.0 ML < \( \Theta_{\text{SDS}} \) ≤ 1.0 ML.

The NaCl crystalline core was generated manually using a standard NaCl crystal structure with a lattice constant of 5.63 Å, which gave a nearest-neighbor spacing of 2.81 Å. A full coverage monolayer of dodecyl sulfate anions (DS\(^-\)) was arranged in a rectangular lattice 5.00 Å apart on the NaCl slab with an appropriate number of sodium cation counterions. This defined the slab with \( \Theta_{\text{SDS}} = 1.00 \) ML while five additional slabs were generated by increasing the monolayer spacing constant to achieve \( \Theta_{\text{SDS}} = 0.00, 0.25, 0.40, 0.60, \) and 0.80.
Hygroscopicity of Mixed SDS/NaCl Nanoparticles

ML. SDS molecules were positioned such that the sulfur was placed 6.61 Å above the surface of the NaCl slab with sodium cation counterions placed between the surfactant headgroup and NaCl surface.

Prior to the interaction with water, the hybrid SDS/NaCl slabs were relaxed following an initial energy minimization with a 1 ns trajectory using the NAMD program. NAMD was developed by the Theoretical and Computational Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana–Champaign. The SDS molecules and Na\(^+\) and Cl\(^-\) ions were described using the CHARMM27 lipid force field, and the SHAKE algorithm constrained the lengths of covalent bonds to hydrogen. Long-range electrostatic interactions were computed using the smooth particle mesh Ewald (PME) method, and van der Waals interactions were truncated at a 12 Å cutoff distance. All simulations were run with a 1 fs time step and snapshots were saved at 1 ps intervals for detailed analysis. Langevin dynamics maintained a simulation temperature of 300 K.

Following the 1 ns relaxation of the SDS/NaCl slabs, 6 water molecules were added above each of the slabs and the simulations were run for an additional 1 ns. This amount of water is equivalent to the adsorption of \(\sim 0.04\) ML of water, assuming a molecular packing density of \(1 \times 10^{15}\) molecules \(\text{cm}^{-2}\). The condition for water molecules sticking in the simulations is the water molecule coming within a specified distance from the NaCl surface and remaining there for the rest of the simulation. The TIP3P force field is used to model water as it is optimized for interactions of molecules with the CHARMM27 force field. Density profiles of water, NaCl, and SDS were generated after these 1 ns trajectories.

In addition to the slab simulations, several runs with relaxation times between 0.1 and 1 ns were done with isolated NaCl/SDS particles built as shown in Figure 1. The goal of these simulations was to probe the behavior of SDS on corners and edges of the underlying NaCl crystal. MD simulations of water uptake by such isolated particles will be reported elsewhere.

The MD simulations reported here were performed to provide qualitative microscopic insight into the structure of the SDS–NaCl interface and the dynamics of water uptake on these surfaces as a function of SDS coverage. A number of previous studies have emphasized the importance of explicitly treating electronic polarization for an accurate description of the interfaces of aqueous ionic solutions. Nonpolarizable potentials were employed, in part because the SDS model chosen was refined for use with nonpolarizable water and counterions. While we can expect slight changes in the interfacial composition in the SDS/NaCl(aq) systems, the effects of neglecting polarizability in simulations of NaCl(s) are not well established. In any case, although certain atomic-scale structural features and the kinetics of water uptake might be slightly different if polarizable force fields were employed, we are confident that the simulations presented herein are sufficiently accurate to provide the qualitative insight for which they were intended.

**Ab Initio Calculations.** Binding energies of \(\text{H}_2\text{O}\)–(NaCl)\(_4\), sodium methyl sulfate (SMS)–(NaCl)\(_4\), \(\text{H}_2\text{O}\)–SMS, and SMS–\(\text{H}_2\text{O}\)–(NaCl)\(_4\) were calculated to explore the interactions occurring on the SDS/NaCl nanoparticle surface. SMS was chosen as a proxy for SDS and the (NaCl)\(_4\) cluster was used to represent the NaCl particle in order to minimize computation time. The minimum energy structures were located using second-order Møller–Plesset (MP2) perturbation theory with the cc-pVDZ basis set\(^{47,48}\) (MP2/cc-pVDZ). Geometry optimizations\(^{49–51}\) were carried out with the largest component of the analytic gradient\(^{44,52}\) being smaller than 10\(^{-4}\) hartree/bohr. Minima were confirmed by an all-positive Hessian that was good agreement with the observed DRH of 79.1% RH. Humidity agreement. This indicates that any kinetic effect of water uptake and deliquescence occurs on time scales faster than the 1 s minimum duration of the RH exposure.

As the weight percent of SDS increases in the nanoparticles, GF\(_m\) are suppressed and the apparent location of DRH shifts to

![Figure 2. Hygroscopic growth curves of mobility equivalent diameter selected 14.0(±0.2) nm SDS/NaCl particles. The legend details wt/wt % of SDS/NaCl in solutions that were electrospayed. The DRH of 14 nm NaCl particles from ref 10 is indicated by the thick solid line. The thin curve is a plot of the Köhler theory for 14 nm NaCl particles (eq 4). Labels 1 and 67 s refer to the time the nanoparticles were exposed to RH before being sized.](Image)
lower values of humidity in comparison to pure NaCl nanoparticles. Although growth factors are suppressed by the presence of SDS, the growth curves still have the same qualitative shape when compared to NaCl nanoparticles. Nanoparticles originating from the 5.0 wt/wt % SDS/NaCl solution display discontinuous deliquescence at the same RH value where pure NaCl nanoparticles deliquesce, 79.1(±1.0)% RH. Discontinuous deliquescence is not observed for nanoparticles generated from solutions containing more than 5.0 wt/wt % SDS. Nanoparticles from the 11 wt/wt % SDS/NaCl system deliquece gradually between 73–77% RH and display a post-deliquescence growth curve that is qualitatively similar to pure NaCl nanoparticles, albeit at lower absolute GF_m. The nanoparticles from the 23 wt/wt % SDS/NaCl solution continue this trend but their growth curve has several unique features. For these nanoparticles, a fairly sharp growth region is observed between 68–71% RH, followed by a slower growth region until roughly 73% RH. Interestingly, there are indications of another growth factor increase between 73 and 75% RH but only for the nanoparticles exposed to RH for 67 s. After that the particles appear to grow steadily with RH with the rate characteristic of SDS/NaCl nanoparticles. Although growth factors are suppressed by the presence of SDS or Na2SO4, there are indications of another growth factor increase between 73 and 75% RH but only for the nanoparticles exposed to RH for 67 s. After that the particles appear to grow steadily with RH with the rate characteristic of SDS/NaCl nanoparticles.5

**Water Vapor Activity over Bulk Mixtures.** Figure 3 shows measured water vapor activity, a_w, as a function of dry NaCl mole fraction, χ_{NaCl}, in the NaCl/SDS (filled circles) and NaCl/Na2SO4 (open circles) mixtures submerged in H2O. Since these are bulk measurements, the activity was calculated from eq 2.

![Figure 3](image-url)
for this measurement; the full nanoparticle size distribution of each composition is impacted for analysis. Spectral features of S(2p), Cl(2p), O(1s), and Na(1s) did not change significantly after several exposures totaling 30 min and thus are not affected by beam damage. Differences in the absolute peak areas of the S(2p) and Cl(2p) are attributed to difficulties in positioning the nanoparticle deposition ring directly under the optimum sampling position for the electron energy analyzer. To avoid these problems, only relative intensities are used in the analysis. It should be noted the S(2p)/Cl(2p) ratio is not an absolute measure of the relative SDS content in nanoparticles because the effective XPS probe depth depends on the particle morphology, which is unknown a priori.

Figure 4b shows the S(2p)/Cl(2p) ratio of integrated peak areas as a function of solution composition from which nanoparticles are generated. Nanoparticles from different solutions display markedly different S(2p)/Cl(2p) ratios, which increase with the amount of SDS. The largest increase is observed in going from the 5.0 to 11 wt/wt % SDS. As the fraction of SDS increases further (23 and 50 wt/wt % SDS), the S(2p)/Cl(2p) ratio shows signs of saturation. Table 2 shows that the size of the nanoparticles from the 5.0 and 11 wt/wt % SDS solutions is similar, while the impacted sizes for the nanoparticles from the 23 and 50 wt/wt % SDS/NaCl systems are larger. This size difference may affect both the average composition of nanoparticles generated by the electrospray source and the relative XPS response. It is assumed the effect of the impacted particle size on the relative S(2p)/Cl(2p) XPS response is minimal, and the S(2p)/Cl(2p) measurement is positively correlated with the relative amount of SDS and NaCl on the surface of the particles.

Figure 5 shows an FTIR spectrum of nanoparticles from the 23 wt/wt % SDS system impacted on a ZnSe window without size selection. The CH-stretching region (2700–3100 cm$^{-1}$) is plotted to show characteristic vibrations of the aliphatic moiety of SDS. The peaks at 2848, 2918, and 2956 cm$^{-1}$ are attributed to the symmetric $\text{CH}_2$– stretch ($v_{\text{sym}}$), the asymmetric $\text{CH}_2$– stretch ($v_{\text{as}}$), and the symmetric $\text{CH}_3$ stretch, respectively. Bands associated with the $\text{O} = \text{SO}_3^-$ / Na$^+$ moiety were detectible at lower frequencies; however, the signal-to-noise ratio was poor due to the small amount of material analyzed.

Figure 6 shows representative AFM images of 23 wt/wt % SDS/NaCl nanoparticles impacted on HOPG. For these measurements, the particles were size selected (21 nm, GSD = 1.05) prior to impaction. These AFM images reveal that particles preferentially align along the HOPG step edges. The measured particle heights are in good agreement with the mobility equivalent diameter.
patches of solution exposed to the MD simulation vapor phase, which is similar to the $\Theta_{SDS} = 0.60$ ML simulation on a crystalline core. In contrast to the crystalline core trajectory, all 6 water molecules quickly entered the solution core and remained in the condensed phase for the remainder of the simulation time. This difference is attributed to the greater degree of disorder in the SDS shell on the aqueous core.

**Ab Initio Structures and Binding Energies.** The located minimum energy structures and corresponding binding energies of selected complexes are shown in Figure 8, where oxygen is colored red, hydrogen is white, sodium cation is black, chloride anion is green, and carbon is also black. The optimized structures of $\text{H}_2\text{O}$, SMS, and ($\text{NaCl})_4$ are given in Figure 8, a, b, and c, respectively. A number of possible structures of SMS bound to ($\text{NaCl})_4$ were found and three representative structures are shown in Figure 8d–f. Binding energies were calculated as a difference in energies of the bound with respect to free species. The weakest binding of $-12.1$ kcal mol$^{-1}$ was found for cases when the methyl group in SMS is interacting with ($\text{NaCl})_4$ as seen in Figure 8d. As expected, the strongest binding energies were found when the polar headgroup in SMS is interacting with ($\text{NaCl})_4$. Binding energies were in range of $-31.9$ to $-34.7$ kcal mol$^{-1}$ for these complexes. Shown are two representative structures with binding energies of $-34.7$ kcal mol$^{-1}$ in Figure 8e and $-32.5$ kcal mol$^{-1}$ in Figure 8f. A large distortion of the ($\text{NaCl})_4$ lattice due to SMS binding is observed in some of the complexes. Such lattice distortions are expected to be much less pronounced in the extended lattice of the NaCl nanoparticle. The binding energy of adsorption to an extended NaCl surface may therefore be different from the binding energies calculated for the model systems presented in Figure 8. However, it is clear that SDS should form a very strong ionic bond to NaCl and these bonds are expected to be stable at ambient temperatures.

Three representative complexes between $\text{H}_2\text{O}$ and ($\text{NaCl})_4$, SMS, and SMS−($\text{NaCl})_4$ are shown in Figure 8, g, h, and i, respectively. Only one preferred configuration was found for $\text{H}_2\text{O}$ binding to ($\text{NaCl})_4$. In this complex, the oxygen atom in $\text{H}_2\text{O}$ interacts with a sodium cation in ($\text{NaCl})_4$. In addition, a hydrogen atom in $\text{H}_2\text{O}$ is hydrogen bonded to the adjacent chloride ion. The binding energy of this complex (Figure 8g) is $-20.2$ kcal mol$^{-1}$ at the MP2/cc-pVDZ level of theory and $-14.8$ kcal mol$^{-1}$ at the CCSD(T)/cc-pVTZ level of theory. SMS binds $\text{H}_2\text{O}$ in several possible configurations involving different oxygen atoms of SMS’s polar headgroup and one of the hydrogen atoms of $\text{H}_2\text{O}$. Aside from the hydrogen bond being present in all of the located minimum energy structures, another common motif is binding of the oxygen atom from $\text{H}_2\text{O}$ to the sodium cation in SMS. The calculated binding energy of $\text{H}_2\text{O}$ to SMS ranges from $-23.2$ to $-25.6$ kcal mol$^{-1}$ (MP2/cc-pVDZ). Shown in Figure 8h is the complex with the strongest binding energy of $-25.6$ kcal mol$^{-1}$ at the MP2/cc-pVDZ level of theory and $-18.4$ kcal mol$^{-1}$ at the CCSD(T)/cc-pVTZ level of theory.

Most relevant to this work is the structure that involves binding of both $\text{H}_2\text{O}$ and SMS to ($\text{NaCl})_4$, Figure 8i. In this structure, the oxygen from $\text{H}_2\text{O}$ interacts with the sodium cation from SMS, while both hydrogen atoms from $\text{H}_2\text{O}$ are hydrogen bonded, one to the S−O−C oxygen from SMS and the other to a chloride ion in ($\text{NaCl})_4$. The overall binding energy for this structure ($-61.5$ kcal mol$^{-1}$) exceeds the sum of binding energies of $\text{H}_2\text{O}$ and SMS, suggesting strong cooperation of their interactions.

Calculated vibrational frequencies of $\text{H}_2\text{O}$ in selected structures are reported in Table 3. The frequencies of the symmetric and asymmetric stretches decrease relative to gas-phase $\text{H}_2\text{O}$ (Figure 8a) when $\text{H}_2\text{O}$ is bound to ($\text{NaCl})_4$ (Figure 8g), SMS (Figure 8h), or both (Figure 8i). This is consistent with ordered thin films of water on NaCl surfaces under ambient conditions. For water interacting with structures that

**Figure 7.** MD simulation snapshots of varying SDS coverage ($\Theta_{SDS}$) on SDS/NaCl slabs on (a) crystalline NaCl core and (b) aqueous NaCl solution core. As the SDS coverage decreases the $\text{H}_2\text{O}$ sticking probability increases. Coloring scheme: O, red; S and Na$^+$, yellow; C and Cl$^-$, cyan; H, white.
include SMS (Figure 8h,i) the H2O bending mode increases relative to the gas phase, likely due to ring structures resulting from hydrogen bonds.

**Discussion**

**Predeliquescent Wetting of NaCl and SDS/NaCl Nanoparticles.** Crystalline NaCl is known to adsorb 3.5–4.0 ML of water at humidities just below 75.4% RH at room temperature and pressure.1,3,4 For a 100 nm particle this would translate in a GFm of ∼1.01. Quantification of ML coverage on large (>100 nm) NaCl particles is therefore difficult in a tandem DMA experiment. On the other hand, the GFm of a 10 nm particle with 3.5–4.0 ML is ∼1.10, which is well above the minimum detectable growth under experimental conditions employed in this work (GFm = 1.00 ± 0.02). Here we take advantage of the tandem DMA approach to learn about predeliquescent water uptake on SDS/NaCl particles.

TABLE 3: Calculated Shifts in the Frequencies of H2O Vibrations in Selected Complexes Relative to Free H2O

<table>
<thead>
<tr>
<th>structure</th>
<th>$\nu_{as}$ (cm$^{-1}$)</th>
<th>$\nu_{sym}$ (cm$^{-1}$)</th>
<th>$\nu_{bend}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O (a)</td>
<td>3772</td>
<td>3659</td>
<td>1594</td>
</tr>
<tr>
<td>H2O–(NaCl)$_4$ (g)</td>
<td>-57</td>
<td>-111</td>
<td>-6</td>
</tr>
<tr>
<td>H2O–SMS (h)</td>
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<td>-281</td>
<td>+32</td>
</tr>
<tr>
<td>SMS–H2O–(NaCl)$_4$ (i)</td>
<td>-172</td>
<td>-160</td>
<td>+33</td>
</tr>
</tbody>
</table>

a Selected structures from Figure 8. b The top row contains calculated frequencies for free H2O; the remaining rows are frequency shifts with respect to free H2O.

include SMS (Figure 8h,i) the H2O bending mode increases relative to the gas phase, likely due to ring structures resulting from hydrogen bonds.

Figure 9 shows the same measured GFm vs RH data presented in Figure 2 with special attention given to the predeliquescence region. Error bars have been omitted to reduce congestion. The 10 Å scale bar demonstrates the sensitivity to molecular scale growth when examining 14 nm particles in a tandem-nano DMA experiment. The solid line represents the Frenkel–Halsey–Hill (FHH) water adsorption isotherm, and the dashed line represents the Brunauer–Emmett–Teller (BET) isotherm. The DRH of 14 nm NaCl particles is also indicated by the thick solid line. For convenience, the isotherms are converted...
into growth space (GFm vs RH) and include a correction for the Kelvin effect Cw(σwρwmolec d)= as well as a shape correction A(Kννν).

Isotherms are converted into growth space by use of the definition of a water coverage layer (Θw = Sd/σwρwmolec)3 and plugging the appropriate isotherm equation Θw(S) into eq 6. Sw is the surface density (molecules cm⁻²) of water calculated from measured GFm and SNaCl is the surface density of ion pairs for the (001) face (6.4 × 10⁻¹⁴ cm⁻²).60 A derivation of Sw is available in a previous publication.3 In eq 6, the envelope equivalent diameter is d(0) = 12.6 nm and the shape correction parameter is A(Kνννν) = 0.898. Appropriate FHH (Λ = 0.96, B = 1) and BET (c = 1.5) constants are used for water adsorption on the NaCl(001) surface.13,58,59 The bulk density of water (997.1 kg m⁻³) is converted to the molecular units (33 molecules nm⁻³) for ρwmolec.

\[ GFm(RH) = \left( \frac{6S_{NaCl}A(Kνννν)}{\rho_{wmolec}d(0)} \right)\Thetaw(S) + 1 \right)^{1/3} \tag{6} \]

As can be seen in Figure 9, there is fair agreement between the measured GFm of NaCl and 5 wt/wt % SDS/NaCl 14 nm particles and eq 6 in the region corresponding to 1.5 ML < Θw < 3.0 ML (1.02 < GFm < 1.06) occurring at roughly 70% RH. At the lower values of RH, the experimental growth factors are reproducibly lower than the ones predicted from the isotherms. In fact, the measured GFm of NaCl are actually smaller than 1.00 near ~40% RH. This is attributed to dynamic reshaping of NaCl nanoparticles upon interaction with initially adsorbed surface water at Θw < 1.0 ML.61,62 This restructuring of the NaCl nanocrystal changes its shape toward sphericity thus reducing its mobility equivalent diameter. The data points above Θw > 3.0 ML (GFm > 1.06) for both NaCl and 5 wt/wt % SDS/NaCl nanoparticles are from mobility histograms that contained two mode diameters (see discussion below). Consequently, the error in the Θw calculation is large in this region due to fluctuations of particles coexisting in a wetted crystalline state and dissolved droplet state.

Inversion of eq 6 at the DRH of 14 nm NaCl (79.1% RH)10 results in a predicted coverage of 2.4 ML of adsorbed surface water according to the FHH isotherm and 2.3 ML according to the BET isotherm. Similar inversion that starts with the measured GFm value (at 1 and 67 s RH exposure) reveals an estimated surface coverage of Θw = 3.1(±0.5) ML (propagation of 2σ error in measured GFm) of adsorbed surface water on 14 nm NaCl particles. Note that 79.1% RH above a 14 nm particle surface is equivalent, after accounting for the Kelvin effect (eq 4), to 67.3% RH (20.0 mbar at 297K) above a bulk NaCl crystalline surface, which has roughly 3 ML of adsorbed surface water.1 It can be concluded that the thickness of the water film on predeliquescent NaCl particle is quantitatively consistent with measurements done on bulk NaCl after properly accounting for the Kelvin effect.

A similar analysis for 5.0 wt/wt % SDS/NaCl nanoparticles reveals an estimated water surface coverage of Θw = 3.1(±0.5) ML, which is identical to the coverage on pure NaCl nanoparticles within experimental uncertainties. This suggests that a submonolayer to a full monolayer coverage of SDS (estimation of the SDS coverage is detailed below) does not greatly interfere with predeliquescent water uptake. This adsorbed water is likely to sit on the surface of the NaCl crystal, with SDS floating on the surface in the form of a soapy film. Similar conclusions about the morphology of wetted but not fully deliquescent NaCl/SDS particles were reached in a recent experimental study that relied on a probe molecule spectroscopy technique.18

**Molecular Dynamics Simulations of SDS/NaCl Slabs and Particles.** According to the MD simulations results presented in Figure 7a, bare patches of NaCl facilitate adsorption of water molecules to the NaCl surface. Figure 10 shows density profiles of the full coverage slab (ΘSDS = 1.0 ML) and half coverage (ΘSDS = 0.50 ML) slab after 1 ns of interaction with 6 water vapor molecules. As can be seen in Figure 10a, water molecules are unable to penetrate the full SDS layer and remain in the “gas phase,” which in the simulation is a vacuum. In Figure 10b, 3 water molecules are adsorbed to the SDS/NaCl interface, one is interacting with a terminal methyl group and the remaining waters are still in the “gas phase.” The initial adsorption of water molecules on nanoparticles with a moderate SDS coverage should therefore occur on bare NaCl patches. Water molecules are likely to end up in the vicinity of a polar SDS headgroup because of their ability to form a hydrogen bond to both Cl⁻ and the SDS headgroup as depicted in the *ab initio* structure presented in Figure 8i.

In addition to modeling slabs of NaCl coated with SDS, we also conducted several MD simulations on isolated SDS/NaCl particles with the goal of visualizing the behavior of SDS on the edges of the NaCl nanocrystal. Figure 1 provides an example of such a simulation after 100 ps relaxation time. These simulations predict a significant degree of distortion of the NaCl structure by SDS near the edges and corners of the NaCl crystal. These sites are the least protected from water by the alkyl tails of SDS, and therefore represent the most likely sites for the initial H₂O adsorption. From there, H₂O can percolate in between NaCl and SDS, and eventually deliquesce the NaCl crystal.

The direct comparison between the MD simulations and the experiment is not straightforward. The experiment gauges the
size of the SDS/NaCl particle in equilibrium with water vapor; it provides only a crude upper limit of 1 s for the time scales involved in the initial water uptake and deliquescence. The MD simulation demonstrates that SDS introduces a sizable kinetic barrier to the initial water uptake; a significant reduction in the amount of adsorbed water is observed on the 1 ns time scale of the simulation. Despite these limitations, the MD simulations presented here make it possible to visualize the processes involved in the initial adsorption of water to SDS/NaCl surfaces on a molecular level. Future MD simulations will explicitly probe interactions of “gas-phase” water molecules with a structure similar to that presented in Figure 1 or that in Figure 8i.

Structure of SDS/NaCl Nanoparticles Inferred from Their Hygroscopic Growth. Hygroscopic growth of SDS/NaCl nanoparticles can teach us about the composition and morphology of SDS/NaCl nanoparticles produced in the electrospray process. SDS and NaCl are likely to phase-segregate during the primary and progeny droplet evaporation in the electrospray source. Once the evaporation stage is complete, nanoparticles should have a NaCl crystalline core decorated by a film of SDS molecules and possibly some residual water remaining in between SDS and NaCl (the evidence for the residual water comes from very long drying times for the SDS/NaCl nanoparticles in the FTIR spectrometer). Zelenyuk et al.21 reported residual solvent in SDS/NaCl nanoparticles (>100 nm) after diffusion drying and its presence in SDS/NaCl nanoparticles could lead to a variety of different SDS meso-phases (i.e., liquid crystals, micelles, etc.) which will contribute to markedly different SDS densities.21 Assuming core—shell morphology, the submonolayer film on NaCl is likely to have the –O–SO3 Na+ headgroup of SDS pointing to the NaCl surface in an inverted micelle like orientation. This is consistent with the morphology of 70–100 nm SDS/NaCl particles deduced by Woods et al.18 from probe molecule spectroscopy. The MD simulations and the ab initio structures presented in Figure 8d–f also indicate there is a strong energetic benefit for SDS to exist in this morphology on the NaCl nanoparticle surface.

When the amount of SDS exceeds the amount needed for one monolayer, the excess SDS can either accumulate in a “blob” attached to the particle or coat the surface more uniformly with a multilayer film of SDS. The effective thickness of the SDS coating should increase with the SDS weight fraction in the solutions that were electrosprayed. This appears to be a good initial assumption as GFm are monotonically suppressed in the solutions that were electrosprayed. This appears to be a good one monolayer, the excess SDS can either accumulate in a benefit for SDS to exist in this morphology on the NaCl model,5 which assumes core thickness of the SDS film can be estimated using a simple forward for a number of reasons (see below). The actual S(2p)/Cl(2p) ratio into the absolute SDS wt % is not straight-forward for the best agreement between the ZSR predictions and experimental observations. Figure 11 shows the results for 14 nm (17 nm for pure SDS) particles composed of (b) 5.0 wt/wt % SDS/NaCl; (c) 11 wt/wt % SDS/NaCl; (d) 23 wt/wt % SDS/NaCl; (e) 50 wt/wt % SDS/NaCl; (f) pure SDS. The ZSR model clearly fails with the assumption that the nanoparticle composition is identical to that of the electrosprayed solutions. The agreement improves significantly if one allows for an enhancement of SDS relative to NaCl in the electrosprayed droplets. The dotted lines in Figure 11 represent optimized dry NaCl volume fractions based on GFm measurements of SDS/NaCl nanoparticles. There is excellent agreement in the shape of predicted GFm in the parametrized ZSR model with measured GFm. Table 4 summarizes the results of this analysis, where the SDS weight percent calculated from the ZSR model is compared to the composition of the initial solution.

The ZSR model predicts significant SDS enhancement in nanoparticles relative to the solutions from which they were electrosprayed. In our previous experiments with the AOT/NaCl particles,5 an AOT enhancement was also observed, however, not to the extent as for the SDS/NaCl particles. These differences likely reflect stronger surfactant properties of SDS relative to AOT. The observation of surfactant enhancement in nanoparticles in this work and previously7 is consistent with other studies involving electrospraying surface active materials. Tang and Smith61 observed smaller satellite and progeny droplets generated by the spray formation and asymmetric fission processes to be enhanced in surfactants SDS and Fluorad carbon (FC-171, C12F25SO2N(C2H4O)7CH3), a nonionic liquid surfactant. It is uncertain which generation of droplet fission in the electrospray process the SDS/NaCl nanoparticles originated from. It was empirically found that the nanoparticle size characteristics changed dramatically when the electrospray protocols presented in Table 2 were altered. Specifically, variance of the electrospray distance l had the largest effect on the size distribution as well as measured hygroscopic properties of the resulting SDS/NaCl particles. This suggests different generations of droplets could likely have a different SDS content, which is consistent with Tang and Smith’s observations of surfactant enhancement in the progeny droplets. It should be noted the electrospray
apparatus used in this work is custom built and without detailed knowledge of the electric field characteristics, it is difficult to compare our apparatus to commercial electrospray particle generators. Nevertheless, we can expect that other electrospray particle generators should similarly produce particles that are enhanced in the relative amount of surface active species.65 The effective SDS coverage for Θ_{SDS} ≤ 1.0 ML can be calculated from the assumed values of Θ_{NaCl} (either from the solution composition or from the ZSR fits).5 This analysis reveals for the 5.0 wt/wt % SDS/NaCl nanoparticles Θ_{SDS} = 0.4 ML assuming the composition is that of the electrosprayed solution. The parametrized ZSR model composition of these nanoparticles predicts that the actual SDS fraction in these particles is roughly 14 wt/wt %, translating to Θ_{SDS} = 1.0 ML. The true SDS coverage is likely to be in between these two values. The adsorption isotherm analysis presented above shows that water forms a film of the same thickness on pure NaCl and on the 5.0 wt/wt % SDS/NaCl particles. This suggests that SDS does not greatly interfere with NaCl–H2O interactions at Θ_{SDS} ≤ 1.0 ML. The thickness of the SDS layer for the remaining SDS/NaCl compositions is expected to exceed 1.0 ML based on the parametrized ZSR model results.

**Deliquescence in SDS/NaCl Nanoparticles.** In this paper, “discontinuous deliquescence” refers to the coexistence of two distinct phases, wetted crystalline and aqueous droplet, over a very narrow range of RH (±1% RH). This coexistence manifests itself in a bimodal mobility equivalent diameter distribution in the vicinity of the DRH values, with the lower diameter corresponding to particles that have not yet deliquesced and the larger diameter corresponding to the aqueous droplets.10 Once RH increases slightly the dry phase disappears in a discontinuous manner, and only the aqueous particles remain. In contrast, “gradual deliquescence” refers to a smooth evolution in the particle size distribution over the range of RH corresponding to the particle deliquescence.

Whereas pure NaCl nanoparticles undergo discontinuous deliquescence, presence of sufficient amounts of SDS or AOT (sodium bis(2-ethylhexyl) sulfosuccinate) makes the deliquescence more gradual. Discontinuous deliquescence is still observed with 5.0 wt/wt % SDS/NaCl nanoparticles at the same RH as pure NaCl nanoparticles. Per the above discussion these particles are coated with a submonolayer of SDS. Discontinuous deliquescence is no longer observed in particles with higher SDS weight fractions, which correspond to SDS coverage in excess of a monolayer.

The end point of a gradual deliquescence transition can be clearly recognized when viewing the data plotted with the parametrized ZSR models. The ZSR model describes an aqueous phase and, therefore, a phase transition from crystalline to aqueous phase can be viewed as complete when the growth curve converges onto the respective ZSR model predictions. The 11 and 23 wt/wt % SDS/NaCl data sets converge to their respective ZSR models over several %RH units, with particles achieving fully deliquesced states at 76.8% RH and 70.7% RH, respectively. Only one mode diameter is observed in mobility histograms across the entire RH range studied for both of these compositions. It is therefore concluded that the 11 and 23 wt/ wt % SDS/NaCl nanoparticle growth curves. ZSR analysis reveals the NaCl volume fraction of these nanoparticles to be 0.05; therefore, it is not surprising the nanoparticles barely grow, even at high RH values.

**SDS/NaCl Nanoparticle Activity vs NaCl/SDS Bulk Mixtures.** Soluble multicomponent particles display mutual deliquescence at the eutonic point (\(\chi_{\text{solute}}/\chi_{\text{NaCl}}\)) of the corresponding bulk mixture.13 In Figure 3, the eutonic composition of NaCl/SDS occurs at \(\chi_{\text{NaCl}} = 0.92\). At NaCl mole fractions exceeding this composition, the activity is nearly the same (±1% RH) as that of a pure NaCl solution. SDS/NaCl nanoparticles studied in this work should therefore display mutual deliquescence in the same vicinity (±1% RH) as pure NaCl nanoparticles at compositions of 0.92 ≤ \(\chi_{\text{NaCl}} < 1.00\). Table 4 indicates that, if the composition of the nanoparticles were the same as the electrospayed solutions, then the 5.0, 11, and 23 wt/wt % SDS/NaCl nanoparticles would have displayed mutual deliquescence at roughly the deliquescence point of pure NaCl nanoparticles. This is not the case as only the 5.0 wt/wt % SDS/NaCl nanoparticles displayed mutual deliquescence at the NaCl nanoparticle deliquescence point. This observation is more consistent with compositions from the ZSR model, which predicts that 5.0 wt/wt % SDS/NaCl nanoparticle is the only composition satisfying the condition 0.92 ≤ \(\chi_{\text{NaCl}} < 1.00\).

The observations for the mutual deliquescence of the bulk NaCl/SDS mixtures and the corresponding nanoparticles are in disagreement with each other at higher SDS volume fractions (Table 4). SDS/NaCl nanoparticles that are at \(\chi_{\text{NaCl}} < 0.92\) (assuming ZSR-derived composition) display mutual deliques-
ence at lower values of activity in comparison to pure NaCl nanoparticles. On the contrary, NaCl/SDS bulk mixtures at $\gamma_{NaCl}/\gamma_{NaCl(solid)} < 0.92$ result in greater water vapor activity relative to a pure saturated NaCl solution. Because activity is a colligative property,\textsuperscript{26} this would imply SDS is more miscible with NaCl in the nanometer regime as opposed to the bulk regime. An alternative and more likely interpretation is that the presence of SDS greatly affects the values of surface tensions at the NaCl(solid)–H$_2$O(adsorbed) and H$_2$O(adsorbed)–H$_2$O(gas) interfaces, which are theoretically predicted to have a large effect on the deliquescence phase transition in NaCl nanoparticles.\textsuperscript{12} Regardless of the explanation, this dramatic change in the deliquescence behavior from the bulk to the nanoparticles is a clear manifestation of the importance of interfacial molecules in thermodynamic phase transitions experienced by nanoparticles.

**XPS Characterization of SDS/NaCl Nanoparticles.** Our hypothesis that SDS/NaCl nanoparticles are enhanced in SDS prompted us to investigate their composition using XPS methods. Absolute determination of the SDS coverage is not experimentally attainable from the information presented in Figure 4. However, a qualitative assessment of the nanoparticle surface can be made as XPS is a surface sensitive technique. The entire depth of sample is irradiated by X-rays; however, photoelectrons are collected from a relatively small depth in the sample due to inelastic scattering of photoelectrons. The inelastic mean free path (IMFP) of an electron through NaCl is roughly 4.0 nm.\textsuperscript{5} The Al source produced 1456 eV photons and the binding energy of Cl(2p) is 170 eV, thus the majority of electrons collected for NaCl would originate roughly 3.5 nm deep into the sample if no SDS existed on the surface. IMFP through aliphatic chains of the SDS, which are theoretically predicted to have a large effect on the deliquescence phase transition in NaCl nanoparticles,\textsuperscript{12} would originate roughly 3.5 nm deep into the sample if no SDS existed on the surface. IMFP through aliphatic chains of the SDS is roughly 4.0 nm for an electron which has existed on the surface. IMFP through aliphatic chains of the SDS is roughly 3.5 nm deep into the sample if no SDS existed. Table 4 shows that the particles examined by XPS have an SDS thickness ranging from 0 to 3.9 nm or 0 to 5.5 nm depending on whether one assumes the solution composition or ZSR composition for the nanoparticles. The S(2p)/Cl(2p) ratio should increase greatly over this range of SDS coat thicknesses. Figure 4 demonstrates that the measured S(2p)/Cl(2p) signal increases less than linearly with increasing SDS weight fraction. These observations suggest the core–shell morphology is not the best picture at high SDS weight fractions.

The XPS results are more consistent with a “zone-inclusion” model, whereby NaCl and SDS still segregate in separate phases but the NaCl zone is no longer in the very center of the nanoparticle as the core–shell model assumes. With the NaCl zone positioned near the edge of the particle, the Cl(2p) photoelectrons originating from NaCl could be fairly close to the surface and detectible by XPS. Note that the zone-inclusion model is just as consistent with the hygroscopic growth results as the core–shell model.

**FTIR and AFM Characterization of SDS/NaCl Nanoparticles.** The phase state of SDS in the nanoparticles dominated by SDS (23 and 50 wt/wt %) is uncertain. Some of the possibilities include (1) a glassy state with the alkyl chains being fairly disordered and (2) a crystalline state with a higher degree of order. All known crystalline forms of SDS pack head-to-head and tail-to-tail; however, because of chain tilting stronger bonding occurs between tails and hence the growth rate for the monohydrate and hemihydrate forms are much faster than the 1/8 hydrate and anhydrous forms.\textsuperscript{67} If SDS is in a crystalline state, the 23 and 50 wt/wt % SDS/NaCl nanoparticles are likely to be of the monohydrate variety as the habit of this crystal domain is rectangular and ideally could pack well with the cubic NaCl crystal habit.

The 23 wt/wt % SDS/NaCl nanoparticles were examined by FTIR because this composition should have well in excess of one monolayer of SDS. FTIR spectra were difficult to obtain due the small amount of material impacted on the ZnSe window. However, the resulting spectra in the CH-stretching range (Figure 5) were quite informative. Most significantly, the symmetric and asymmetric $-\text{CH}_2-$ stretches, occurring at 2848 and 2918 cm$^{-1}$, respectively, are quite narrow, indicating minimal heterogeneous broadening of the peaks.

FTIR spectra of various SDS phases (crystalline and disordered) have been reported previously.\textsuperscript{68} The position of the symmetric $-\text{CH}_2-$ stretch is consistently below 2852 cm$^{-1}$ for crystalline phases of SDS, while that for micellar solutions of SDS and water is consistently above 2852 cm$^{-1}$.\textsuperscript{69} The position of the asymmetric $-\text{CH}_2-$ stretch is just at or below 2920 cm$^{-1}$ for crystalline phases of SDS, while for micellar solutions and liquid crystal phases of SDS is above 2920 cm$^{-1}$.\textsuperscript{69} The position of the peak relative to 2920 cm$^{-1}$ is not necessarily a function of order, but can also be related to packing density.\textsuperscript{69} In disordered SDS phases, (i.e., micelles and liquid crystals) broadening of symmetric and asymmetric $-\text{CH}_2-$ peaks was observed relative to ordered, crystalline SDS phases (i.e., SDS anhydrous, SDS$\cdot\frac{1}{2}$H$_2$O, SDS$\cdot\frac{1}{2}$H$_2$O, and SDS$\cdot$H$_2$O) as well as a decreased molar absorptivity of the asymmetric $-\text{CH}_2-$ stretch relative to the symmetric $-\text{CH}_2-$ stretch.\textsuperscript{69} The FTIR spectra presented in Figure 5 in this work appears to be more representative of an ordered, crystalline phase of SDS with high packing density.

AFM images of the sort shown in Figure 6 suggest that 23 wt/wt % SDS/NaCl nanoparticles are uniform and spherical. Higher resolution (0.5 × 0.5 µm) images were acquired (data...
Conclusions

It is peculiar that AFM images suggest 23 wt/wt % SDS/NaCl nanoparticles are spherical yet the FTIR spectrum presented in Figure 5 suggests that SDS is in a crystalline state. These differences may reflect the large effect of the residual water on the morphology of SDS (see Zelenyuk et al. 21). The conditions used to characterize the nanoparticles were quite different. For example, the AFM measurements were done under ambient RH, whereas FTIR and XPS spectra were taken under very dry conditions. In the hygroscopicity experiments, the SDS/NaCl nanoparticles were diffusion dried for a very short time (∼1 s), whereas in the FTIR analysis nanoparticles were exposed to dry air for several days. The phase state of SDS in the particle increases. XPS analysis suggests that the surface tension. The FTIR analysis reveals alkyl tails are fairly spaced to accommodate all of SDS on the surface and this leads to a strong energetic benefit for the SDS headgroups to interact with the NaCl surface, whereas FTIR analysis nanoparticles were exposed to dry air for several days. The phase state of SDS in nanoparticles could potentially be different in all of our experiments. This should be kept in mind when interpreting data presented in this work.

Acknowledgment. This study was supported by the National Science Foundation (grants CHE-0431312 and CHE-0909227). M.S.G. was supported by a grant from the Air Force Office of Scientific Research.

References and Notes