Reversibly Physisorbed and Chemisorbed Water on Carboxylic Salt Surfaces Under Atmospheric Conditions

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1. INTRODUCTION

Particle–gas interfaces are of essential importance in aerosol systems, and they directly determine many atmospheric processes, such as surface-catalyzed chemistry, halogen chemistry, trace gas uptake, new particle formation, ozone depletion, and heterogeneous ice nucleation. Interfacial processes often start with the adsorption of gas molecules or clusters on particulate surfaces. The adsorbed molecules may then be incorporated into bulk materials, and those molecules may directly influence particle properties. Affected bulk properties, like viscosity, chemical reactivity, and crystalline structure, may in turn affect further uptake capacity, thereby acting as feedbacks. Thus, to correctly understand aerosol interfaces and to quantify atmospheric processes, one needs to precisely describe surface properties at the given environmental conditions.

Traditionally, particle–gas equilibria are well defined by classical thermodynamic theories like the Köhler theory, which describes the equilibrium water vapor pressure over soluble particles as a function of water activity and particle size. However, these simplified concepts become uncertain when considering microscopic systems like molecular adsorption on the outermost layer of particles. For example, airborne sea salt particles, which are the second most abundant aerosol particle species, deliquesce (transition from solid particles to aqueous solution droplets) by absorbing water vapor and completely dissolve at a critical relative humidity (RH), which is defined to be the deliquescence relative humidity (DRH). Likewise, they effloresce (recrystallize into salt) at an efflorescence relative humidity (ERH). The traditional conception of these transitions is captured by an understanding of bulk phase equilibrium and neglects surface effects. However, surface-sensitive studies reveal that salt surfaces begin to adsorb water at RH well below the bulk phase transition, leading to a predeliquescence solvation of the surface. Moreover, these initial surface changes can be critical for atmospheric processes due to their direct relevance for heterogeneous atmospheric chemistry.

The presence of water layers on salt surfaces is important to understand as they directly determine the surface properties and it is apparent that adsorption and even solvation begin at RHs well below the bulk DRHs. A clear understanding of when adsorption is sufficient to initiate surface solvation, and a quantification of the transition between these regimes, remains
lacking. Existing experimental methods are usually insufficient to address the question of when physisorption succumbs to solvation. For example, FTIR measurements of O−H stretching are mainly sensitive to initial water adsorption. Other techniques such as e-AFM or ETEM are sensitive to morphological changes but may not detect chemical changes. Many spectroscopic methods lack surface-specific sensitivity, which hinders the detection of surface changes prior to bulk transformations. Thus, although observations agree on the existence of adsorbed water below the DRH, it remains unclear when the water quantities are sufficient to dissolve the salts in a manner that results in stable aqueous solution layers. To date, only a few studies have attempted to discuss dissociation with a predeliquescence regime.\textsuperscript{20,27}

Carboxylic acids are prevalent in the troposphere and are involved in many important chemical reactions.\textsuperscript{28} Acetic acid is one abundant carboxylic acid that is widely emitted from biomass burning,\textsuperscript{27} motor exhaust,\textsuperscript{28} and biogenic sources\textsuperscript{29} and is an important product of oxidation of anthropogenic and biogenic volatile organic compounds (VOCs). Once released, the acid can react with inorganic salts like NaCl and form sodium acetate (and HCl), which is found in internally mixed sea salts and organic particles.\textsuperscript{30} Typically, the more volatile HCl escapes to the gas phase, resulting in chlorine-depleted sea salt aerosols.\textsuperscript{31} Thus, given the abundant source material, carboxylic salts are also widespread within the atmosphere. However, detailed studies of the phase behavior of carboxylic salts at relevant atmospheric conditions are still largely lacking. The observed temperature (T)-dependent sodium acetate DRH is between 39 and 42\% at 20 °C and slightly higher (43−44\%) at 25 °C,\textsuperscript{32,33} with ERH(T) \textasciitilde DRH(T)−7\%.\textsuperscript{33,34} In addition, after crystallization at sub-ERH (RH < 10\%) conditions, water still coexists with the salt as a mixture with a salt-to-water ratio of 2:1.\textsuperscript{33}

In this study, X-ray photoelectron spectroscopy (XPS) is employed to investigate the sodium acetate (NaAc, chemical formula CH3COONa) surface phase state and structure. In XPS, soft X-ray photons irradiate sample materials and the emitted electrons that result are collected to determine the composition and state of the sample. It is a highly surface-sensitive and chemically selective method that is used to characterize the chemical composition, oxidation state, and degree of dissociation, and with a tunable photon source it can be used to construct depth profiles of such information. The inelastic mean free path (IMFP) of emitted electrons results in an XPS surface sensitivity that, to a certain degree, overlaps with the presumed thicknesses of liquid-like layers on salt surfaces. Ambient pressure XPS (APXPS) is a technique that has been developed to directly probe surfaces under atmospheric relevant vapor pressure conditions. For example, a pioneering APXPS study investigated the premelting of ice (T > −39 °C).\textsuperscript{35} More recently, APXPS was used to investigate the existence of molecular HCl versus ionic Cl\textsuperscript{−} at gas−ice interfaces at −20 °C.\textsuperscript{31} Carboxylic acids,\textsuperscript{42−44} ketones,\textsuperscript{45} alcohols,\textsuperscript{46} and nitrates\textsuperscript{47} have also been studied for their adsorption onto, dissociation on, and diffusion into ice, including surface-disordering effects. In addition, solid-to-solution phase transitions of salt at various RHs have also been studied with APXPS, for example, KBr- and KI-water binary systems\textsuperscript{48} and the NaCl-water system.\textsuperscript{49} In the former studies, upon deliquescence, Ghosal et al. found an immediate surface enhancement of halide ions in the aqueous system.\textsuperscript{50} The implementation of APXPS applied here is innovative because of its focus on the surface-specific phase state. In particular, we investigate NaAc surfaces at subdeliquescence conditions, but over a range of increasing RH as the DRH is approached. Thus, we seek to distinguish between physisorbed water, which can reversibly desorb, and water layers, which result in the dissociation and solvation of the salt species.

2. MATERIALS AND METHODS

The APXPS experiments described here were performed at the X07DB in situ spectroscopy beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institute (PSI), using the solid−gas interface end station.\textsuperscript{36} Prior to and between measurements, the experimental cell was held under high-vacuum conditions (6 \times 10\textsuperscript{−8} mbar base pressure) to avoid contamination from the ambient environment. The NaAc sample (anhydrous, ReagentPlus, ≥99.0\%, Sigma-Aldrich) was dissolved in anhydrous methanol and deposited onto the sample holder by drop-casting. The sample holder was subsequently warmed to 60 °C to accelerate the methanol evaporation, resulting in the formation of the anhydrous salt, after which the sample was transferred into the vacuum chamber. Once mounted in the experimental chamber, a complete deliquescence−efflorescence cycle was performed by increasing the environmental cell RH to 46\% (>DRH), followed by decreasing the RH to 3\% to remove the majority of the adsorbed water. Mixtures of anhydrous and hydrated samples were observed to form after this cycle, but can be distinguished as either anhydrous-dominated or hydrated-dominated (see the hydrated sample in Figure S3), where the anhydrous-dominated samples are the focus of this study. The phase cycling also helped to ensure a more homogeneous sample distribution on the holder. Water vapor was dosed from a temperature-controlled water reservoir (T = 15 °C) via a stainless steel capillary of 800 μm inner diameter. The water source (Fluka TraceSelect Ultra; Water ACS reagent) was degassed using three freeze−pump−thaw cycles, and the resulting in-chamber vapor pressure of between 0.68 and 0.74 mbar corresponds to the saturation vapor pressure of ice at approximately −24 °C. During the experiments, the water vapor pressure was kept constant while the sample temperature was varied to change the RH. The 3\% RH value was set using a saturation vapor pressure of ice at approximately 0.2 mbar. At RH = 36.1\%, the temperature was −14 °C, while at RH = 34.6\% it was −13.5 °C. A summary of the experimental RH and temperature can be found in Table S1.

The photon source of the X07DB beamline is a bending magnet that provides photons with energies between 250 and 1500 eV. The beam size at the sample surface was approximately 0.2 × 0.2 mm\textsuperscript{2}. The XPS survey spectrum was acquired using a 1000 eV photon energy, with the carbon 1s peaks measured at 1070 eV. For depth profiling, seven kinetic energies were selected—380, 480, 580, 680, 780, 880, and 980 eV. The measured XPS spectra were fitted with Gaussian functions and a linear background. To obtain correct elemental ratios, CO gas measurements with these depth profile photon energies were conducted, and the results were used to normalize the photon flux, photoionization cross sections, and analyzer transmission for C/O ratios. Good agreements were found between literature photoionization cross sections and measured photoionization cross sections. Based on this, Na intensities were normalized by literature photoionization cross sections and measured photon flux and analyzer transmission. Partial electron yield near-edge X-ray
absorption fine structure (NEXAFS) spectroscopy is extremely sensitive to the local coordination environment of an emitter; thus, the sodium K-edge and oxygen K-edge NEXAFS experiments were performed to probe the water adsorption and changes in the local chemical environment. The NEXAFS and XPS experiments were performed, in turn, on the same samples during the beamtime.

3. RESULTS AND DISCUSSION

3.1. Sample Characterization. Figure 1a shows a wide-range XPS scan acquired with a 1000 eV photon excitation energy. An image of the sample surface inside the environmental cell during measurements, with the analyzer cone seen in the lower-right corner, is the inset. (b) High-resolution spectra of the C 1s peaks fitted with Gaussian functions representing the carboxyl and aliphatic components, respectively. The carboxyl group is identified as C1 for later reference. The excitation photon energy for the high-resolution scan is 1070 eV. In both (a) and (b), RH = 3% and T = 20 °C. A fitted C 1s spectrum at RH = 46% can be found in Figure S1. In (c) O 1s, (d) C 1s, and (e) Na 2s, photoelectron spectral peaks at three different RHs (3, 38, and 46%) are presented and are aligned by the aliphatic carbon C 1s. The photon excitation energy is 1000 eV. In (c), H2O(s) refers to the H2O in the hydrate salt or the adsorbed water remaining after dehydration. At the two higher RHs, there is an additional O 1s component at 534.9 eV, which is most likely associated with gas-phase water vapor. The reason that the gas-phase water became visible at high RHs might be the increased working distance when the salt surface turns to solution or enhanced local vapor pressure over the aqueous surface. The observed decreased intensities of the C 1s and Na 2s at RH = 38% and 46% can be attributed to increased attenuation and dilution by the condensed phase water. Conversely, the relative increase of the C 1s peak at ~285 eV with increasing RH is likely due to carbon contamination (see Figure S1).

3.2. Depth Profile. To analyze the surface composition as a function of depth, depth profiles (DPs) of the elemental ratios with increasing photon energy were derived. The depth information is based on the dependence of the electron inelastic free mean path (IMFP) on the electron kinetic energy. From the DPs, the normalized intensity ratios for C1/O, Na/O, and Na/C1 (C1 is the carboxyl peak; see Figure 1b) are calculated for four RH conditions (Figure 2). For all samples the C1/O ratio is observed to be fairly stable with increasing depth (increasing KE). Given the molar ratio of carbon to oxygen in the carboxyl group (−COOH), in a homogeneous anhydrous sample, the C1/O ratio is expected to be 0.5. The lower observed C1/O ratios (Figure 2a) may be due to the presence of additional oxygen in the adsorbed water even at low RH, which has been reported previously. At high RH, the C1/O ratios are also decreased (0.5 > C1/O ≥ 0.15) due to dilution by condensed phase water.

In a homogeneous anhydrous sample, the expected molar ratios of Na/O and Na/C1 are 0.5 and 1.0, respectively. Interestingly, a Na surface depletion is observed with respect to both O (Figure 2b) and C1 (Figure 2c). This observation is potentially related to the sample preparation after introduction in the experimental cell, which includes a full cycle of deliquescent and efflorescence. Due to the nature of basic salts when the NaAc salt completely dissolves and dissociates upon deliquescent, a portion of the acetate ions recombine with protons from water to form neutral acetic acid (Figure 3). In solution, the molecular acetic acid has a larger surface propensities than its ions; thus, these molecules are enriched at the aqueous surface and consequently force the CH3COO− anions and Na+ cations away from the surface. Such an enrichment has been previously found in liquid jet photoemission studies of acetic acid. The simplest explanation is that during subsequent efflorescence, when water molecules evaporate from the solution, the ions (CH3COO− and Na+) recombine and the salt precipitates.
but due to the spatial separation and surface properties some acetic acid (HAc) molecules are stabilized with water on the surface. The result is that the sodium is depleted from the surface relative to oxygen and carboxyl carbon (Figure 2b,c). Balancing the molar ratios of molecular components via a stoichiometry calculation suggests that at the first point along the depth profile (IMFP ≈ 1.3 nm) the surface contains a mixture of sodium acetate, acetic acid, and water, with the molar ratio of NaAc/HAc/H2O being 1:0.9:3.3 (details are found in the Supporting Information (SI)). There is no direct evidence for the precise chemical nature of the mixture but it may contain some low vapor pressure hydrates, which are also suggested by the NEXAFS features (Figure 4) detailed below. The mechanisms for forming the observed depletion and mixture are (i) the nature of the basic salt resulting in the formation of neutral acetic acid in the solution; (ii) the selective surface enhancement of these neutral molecules; and (iii) a potential kinetic barrier to re-homogenization due to spatial separation and special local conditions on the surface, resulting in varied local surface composition. In an atmospheric context, deliquescence−efflorescence cycles may occur many times, and this could lead to acidic and basic salt particles having such cation- or anion-depleted surfaces, though some factors (such as pH buffering in the atmosphere) may play critical roles in these processes.

Figure 2a,b also shows that subtle increases of RH around the DRH can substantially enhance water adsorption. The C1/O and Na/O ratios significantly decrease at RH = 36% compared to their RH = 33% values. At RH = 36%, the ratios (green pluses) are similar to those of bulk solution (red dots) when RH = 46% (DRH ≤ 38%). Thus, already at RH = 36% water adsorption must be significantly enhanced. In contrast, Figure 2c shows that the Na/C1 ratio remains unchanged at RH = 36% but changes when RH is increased to 46%. In fact,
Figure 2c illustrates that, relative to the expected unity molar ratio, Na is depleted at the surface for the full range of RH. Interestingly, the subdeliquesced states also show a local Na enrichment just below the surface. This enrichment disappears when the system is fully solvated, and the ratio further from the surface tends toward the presumed bulk value of unity. Thus, the observations are consistent with the expectations of the Figure 3 model, which describes (1) the solvation of NaAc during deliquescence; (2) the recombination of molecular acetic acid in the aqueous phase; (3) the surface enhancement of molecular acetic acid in the aqueous phase; and (4) the formation of Na-depleted surface during efflorescence.

3.3. Reversible Changes of Local Physicochemical Environment at Subdeliquescence Conditions. Complementary NEXAFS measurements are consistent with the view of continuous water absorption from low RH, but additionally demonstrate that the reversible water absorption includes the reversible solvation of the NaAc salt. In Figure 4, the sodium and oxygen K-edge NEXAFS spectra are plotted for a series of RH, with the spectra arranged vertically in their chronological, experimental order to illustrate the system history. In the sodium K-edge NEXAFS spectra, a double-peak feature can be observed at around 1080 eV photon energy (Figure 4a, peaks identified as A and B). These peaks are associated with sodium ions located in a disordered environment. As RH is increased within the experimental cell, the relative intensities of the A and B peaks change. In particular, when RH approaches 36.1%, peak A decreases and flattens. Above DRH (RH = 46%, purple curve), peak A flattens completely with respect to peak B, which indicates that peak A is related to the sodium-carboxyl bond that breaks upon dissociation and solvation. Although the adsorbed water could attenuate the signal and flatten the sodium NEXAFS spectra to some extent, it would do so for both peaks. The similarities of the spectra at 36.1 and 46% suggest that the solvation shell of sodium at 36.1% is already well developed. It is also notable that the change of peak A in the subdeliquescent regime appears to be reversible, and when the RH is decreased from 36.1 to 34.6% (green line) peak A reappears. That is, the dissociated salt ions recombine to form the salt structure. The reversibility indicates that the sample has not fully deliquesced; thus, the DRH should be slightly higher than RH = 36.1% and the ERH should be marginally higher than 26%, referring to the gap between DRH and ERH at room temperature.

In Figure 4b, the oxygen K-edge NEXAFS spectra are presented. At lower RHs (3% and 14%) peaks a and b coexist at approximately 530 eV, but at higher RH peak b vanishes. This peak is likely related to hydrate-like components on the surface, and Figure S3 shows that this peak is very strong when the existence of hydrates is confirmed visually. Peak c is indicative of free hydrogen and has previously been used as an indicator for liquid water layers on ice. Thus, here it can be used as a tracer for sorbed water on the NaAc surface. It is noted that even at RH = 3% a minor peak c is present, which is in line with previous findings that physisorbed water exists on the surface of salt at very low RHs. Similar to the sodium spectra, the oxygen spectra change dramatically at RH = 36.1%, where the broad peak f completely vanishes. Furthermore, peaks d and e emerge and can be linked to uncoordinated and tetrahedrally coordinated water molecules. In fact, at these highest RHs the spectral shape becomes very similar to that of acetate solutions.

The simultaneous disappearance of peaks f and A implies that these are both related to the sodium-carboxyl bonds. The peak f behavior with decreasing RH (36.1–34.6–33.2%) is also analogous to peak A, where the peak re-emerges in the oxygen K-edge spectra (Figure 4b). Collectively, the spectra suggest that the sorbed water does not immediately initiate sodium solvation (peak c in Figure 4b). Rather, enough water must be first present, as is the case at RH near the DRH, before Na begins to dissociate and dissolve. However, this appears to be a surface dissociation that remains reversible, likely until complete solvation occurs.

The potential differences between predeliquescence and reversibility in a nonequilibrated system must be carefully considered. In the latter case, for example, when the RH is only marginally higher than the DRH, the deliquescence process may occur slowly due to limited water flux. Given enough time to overcome such a kinetic limitation, the entire bulk will completely deliquesce. If, however, within this time frame the RH dropped below the DRH the forcing would be reversed and the dissolving solution would begin to recrystallize because the presence of the existing crystal seeds would preclude the necessity of an activated efflorescence. In these experiments, measurements were made only after such evolutionary steps were completed and the system was observed to be in a steady state.

4. CONCLUSIONS

Here we employed APXPS to investigate the surface properties and processes of an atmospheric relevant carboxylic salt, sodium acetate, at subdeliquescent conditions. The depth profiles of the elemental ratios revealed that after experiencing a deliquescence–efflorescence cycle the salt surface becomes sodium-depleted. The mechanism causing the depletion includes (i) the formation of neutral acetic acid in the solution due to the nature of the basic salt, (ii) the selective surface enhancement of neutral molecules under aqueous condition, and (iii) a kinetic barrier to re-homogenization due to spatial separation and special local conditions on the surface, resulting in varied local surface composition. A stoichiometry calculation was carried out, and it suggested that at RH = 3% the salt surface (IMFP ≈ 1.3 nm) is equivalent to a mixture of sodium acetate, acetic acid, and water with a molar ratio of 1(NaAc):0.9(HAc):3.3(H2O).

As RH gradually approached the deliquescence point, both reversible water uptake and reversible sodium solvation were confirmed by the NEXAFS spectra at the oxygen K-edge and the sodium K-edge, respectively. The solvation of sodium requires higher RH than that for water adsorption, which suggests that the water molecules were taken up onto the surface consistently but the solvation of salt surface would need sufficient water molecules to facilitate the process. In addition, as the surface was sodium-depleted, it required more adsorbed water to dissolve the surface first before reaching and dissociating the deeper sodium atoms.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c00319.

Estimation of additional acetic acid and water; additional table on experimental conditions summary; and additional figures on the XPS spectrum of sodium acetate...
solution, NEXAFS of sodium acetate and sodium acetate trihydrate mixture, and all eight depth profiles measured (PDF).

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**Notes**

The authors declare no competing financial interest.

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