The effect of low solubility organic acids on the hygroscopicity of sodium halide aerosols

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ABSTRACT

In order to accurately assess the influence of fatty acids on the hygroscopic and other physicochemical properties of sea salt aerosols, hexanoic, octanoic or lauric acid together with sodium halide salts (NaCl, NaBr and NaI) have been chosen to be investigated in this study. The hygroscopic properties of sodium halide submicrometer particles covered with organic acids have been examined by Fourier-transform infrared spectroscopy in an aerosol flow cell. Covered particles were generated by flowing atomized sodium halide particles (either dry or aqueous) through a heated oven containing the gaseous acid. The obtained results indicate that gaseous organic acids easily nucleate onto dry and aqueous sodium halide particles. On the other hand, Scanning Electron Microscopy (SEM) images indicate that lauric acid coating on NaCl particles makes them to aggregate in small clusters. The hygroscopic behaviour of covered sodium halide particles in deliquescence mode shows different features with the exchange of the halide ion: whereas the organic covering has little effect in NaBr particles, NaCl and NaI covered particles change their deliquescence relative humidities, with different trends observed for each of the acids studied. In efflorescence mode, the overall effect of the organic covering is to retard the loss of water in the particles. It has been observed that the presence of gaseous water in heterogeneously nucleated particles tends to displace the cover of hexanoic acid to energetically stabilize the system.

Keywords: marine aerosol, fatty acids, heterogeneous nucleation, hygroscopicity.
1. INTRODUCTION

Marine aerosol is one of the most abundant types of natural particulate matter in the Earth's troposphere. Sea salt particles play an active role in the Earth's radiative balance, influence mass transfer from gaseous substances and cloud-precipitation mechanisms, contribute to the formation of cloud condensation nuclei and have highly reactive surfaces that take part in heterogeneous and multiphase chemical reactions (Andreae and Rosenfeld 2008; Carslaw et al 2010; D O'Dowd and De Leeuw 2007; Finlayson-Pitts 2003; Lewis and Schwartz 2004; Quinn and Bates 2011; Rossi 2003). They also can uptake significant amounts of water, exhibiting deliquescence and efflorescence properties under atmospheric conditions (Freney et al 2009; Martin 2000; Metzger and Lelieveld 2007; Mikhailov et al 2013; Wise et al 2012), that can change the particles' phase and size, together with other interrelated physico-chemical properties: for example, water uptake increases particle size, thus favouring their sedimentation. In parallel, bigger particles increase the scattering of solar visible light, thus influencing atmospheric radiative transfer and visibility. The presence of water in atmospheric particles can also change the adsorption of trace gases and their chemical reactivity (e.g., sulfate chemistry proceeds by adsorption of gaseous SO$_2$ on aqueous particles, followed by oxidation to sulfate; this pathway is absent in crystalline particles).

Marine aerosol is generated either by the mechanical action of the ocean surface (primary sea-salt aerosol), or by gas-to-particle conversion processes (secondary aerosol) mainly in the form of nonsea-salt sulphate and organic species (O'Dowd et al 1997). Sodium chloride is the principal component of sea salt: typical sea water composition has $1.05 \times 10^4$ mg/L of Na$^+$ and $1.9 \times 10^4$ mg/L of Cl$^-$ (Lide 1994). Bromide ions are a minor component of seawater, and hence of sea salt particles, with a molar ratio of bromide to chloride of 1:650 (Lide 1994). Despite such a small contribution to the composition of sea salt particles, bromine plays a comparatively large role in tropospheric sea salt chemistry. The most important is the drop of surface-level ozone concentrations in the Arctic at polar sunrise. This is due to the tendency of Br$^-$ to segregate to the salt surface in the presence of water, substantially increasing Br/Cl surface molar ratios, and to the fact that bromide ions exhibit a higher surface reactivity than chloride (Baker 2005; Ghosal et al 2008; Zangmeister et al 2001). Sea salt particles have been shown to be the source of BrO, which is involved in catalytic cycles that destroy ozone (Finlayson-Pitts 2009; Frinak and Abbatt 2006; Hunt et al 2004; Read et al 2008; Von Glasow 2008). Although the concentrations of I present in seawater are much smaller than those of bromine and chlorine (the molar ratio of I$^-$ to Cl$^-$ in seawater is $\sim 1:10^6$), there is evidence that iodine in the marine boundary layer has an influence on ozone destruction, the oxidizing
capacity of the troposphere, denoxification, and particle formation (Carpenter 2003; Saiz-Lopez et al 2008). A similar role to BrO is played by IO, although its source is believed to come from marine algae (Read et al 2008). Recently advances have been made in quantifying the link between seawater chemical processes, and the production, size, and chemical composition of sea spray aerosol particles by simultaneous measurements of seawater, particle size distributions, and size-resolved single particle chemical composition in a laboratory setting reproducing the chemical complexity of sea spray aerosol, including natural seawater, breaking waves and controlled phytoplankton and heterotrophic bacteria concentrations (Ault et al 2013; Prather et al 2013). It has been shown that the mixing state of sea aerosol is sensitive to the presence of heterotrophic bacteria, that transform dissolved organic matter.

Organic compounds are present in marine salt aerosol in variable proportions, that may represent a large fraction of the aerosol dry mass (Cavalli et al 2004; Gantt and Meskhidze 2013; Middlebrook et al 1998). The presence of significant concentrations of organic matter in marine aerosol was detected in earlier studies (Kleefeld et al 2002; Middlebrook et al 1998; Putaud et al 2000). Measures over the North Atlantic Ocean have revealed that the organic fraction contributes up to 63% to the submicrometre aerosol mass, of which about 45% is water-insoluble and 18% water-soluble (O'Dowd et al 2004). 37% hydrocarbon and 63% oxygenated hydrocarbon speciation was observed for the organic mass, indicating that at least 37% of the organic mass is produced via primary sea-spray (Ovadnevaite et al 2011a). It was found that predominantly organic particles contribute between 25 and 30% to general background marine number concentration, 35% for open ocean nucleation cases, and 60% for anthropogenically influenced cases (Bialek et al 2012). The organic fraction of marine aerosol can be highly enriched due to oceanic biological activity (Ault et al 2013; Gantt and Meskhidze 2013; O'Dowd et al 2002; Ovadnevaite et al 2011a; Rinaldi et al 2010). Much of the organic fraction corresponds to water insoluble fatty acids present as surface films on particles (Donaldson and Vaida 2006; Mochida et al 2002; Tervahattu et al 2002), but also as organic carbon more homogeneously mixed with cations and anions (Ault et al 2013). Moreover, fine mode marine organic aerosol can have a size distribution independent from that of sea-salt, while coarse mode aerosols are more likely to be internally mixed with sea-salt (Gantt and Meskhidze 2013). Primary marine aerosols mixed with a surfactant can be generated by wind action on the sea surface, which is covered by a low solubility organic layer (Donaldson and Vaida 2006). Alternatively, heterogeneously nucleated particles can form when low vapor pressure organic vapors condense on pre-existing aerosol particles, forming a surface coating, that can be evenly or unevenly distributed. It has been proposed that the organic compounds arrange in a hydrophobic organic monolayer that encapsulates an aqueous particle, forming an “inverted micelle” structure.
This model shows agreement with recent molecular dynamic simulation results (Chakraborty and Zachariah 2008). Other models predict that certain fatty acids form pockets of micelles within the aerosol, modifying the surface tension of the particle and therefore changing the water uptake properties of atmospheric aerosols (Tabazadeh 2005), and that core-shell structures are not always the most stable (Kwamena et al 2010), again affecting the particle water uptake properties and optical properties.

The presence of an organic film at the surface of a particle may affect its physical and chemical properties in a number of ways. The film may act as a barrier to transport across the interface, inhibiting uptake of atmospheric gases or reactions between gas phase reactants and particle surface, such as the heterogeneous reaction NaCl(s) + 2NO2(g) → ClNO(g) + NaNO3(s) (Donaldson and Vaida 2006; Finlayson-Pitts 2003). In particular, the surface film can affect the process of cloud condensation nuclei formation and growth (Andrews and Larson 1993; Chuang 2003). Organic compounds can also change the amount of light scattered by inorganic particles (Dall'Osto et al 2010; Fierz-Schmidhauser et al 2010; Vaishya et al 2013). Marine primary organic aerosol (POA) can cause large local increases in the cloud condensation nuclei concentration by 15% to more than 100% (O'Dowd et al 2004; Ovadnevaite et al 2011b), and the ambient mass concentration and organic mass fraction of sea-spray aerosol are related to surface ocean biological activity. Despite considerable work has been carried out in the last years, there is still much uncertainty about fundamental issues of marine, such as chemical composition, mixing state, hygroscopicity, cloud droplet activation, formation, aging and removal mechanisms (Gantt and Meskhidze 2013; ICCP 2013). Several laboratory studies about the effect of organic surfactants, such as palmitic and oleic acids, on NaCl, ammonium sulfate or mineral dust aerosol particles as a function of relative humidity have been reported employing a variety of experimental techniques, such as electrodynamic balance, infrared spectroscopy, electrical mobility, optical tweezers, cavity ring-down spectroscopy or nonlinear spectroscopy (Cwiertny et al 2008; Davies et al 2013; Dennis-Smith et al 2012; Ebben et al 2013; Garland et al 2005; Hansson et al 1998; Najera and Horn 2009; Robinson et al 2013; Rossi 2003; Rubasinghege et al 2013). The general conclusions are that hygroscopic growth, deliquescence relative humidity (DRH) and efflorescence of the particles may be affected by several factors, such as coating thickness or structural arrangement of the organic film. Special effort has been carried out to study the morphology and phase partitioning of aerosol particles consisting of hydrophobic and hydrophilic phases (Ciobanu et al 2009; Kwamena et al 2010; Reid et al 2011; Veghte et al 2013). On the other hand, molecular dynamics calculations are becoming a commonplace theoretical approach in atmospheric aerosol modeling, that includes sea
salt particles mixed with organic molecules (Ma et al 2011; Sun et al 2012; Sun et al 2013; Takahama and Russell 2011).

As a whole, laboratory studies on inorganic particles coated with surfactant organics have mainly focused on a few organic molecules, and most of them have been carried out with ammonium sulfate or sodium chloride. Very few studies of hygroscopic behavior have been carried out on particles containing bromide or iodide. Furthermore, sodium chloride, bromide and iodide particles exhibit very different hygroscopic properties and interact differently with water soluble dicarboxylic acids such as succinic acid (Minambres et al 2011). It has been reported that rates of gaseous iodine emissions during the heterogeneous reaction of O$_3$ with interfacial iodide are enhanced several-fold by the presence of alkanoic acids on water, such as octanoic and hexanoic acid (Hayase et al 2011). In the present work we study the hygroscopic properties of NaX (X=Cl, Br, I) sodium halide salts coated with either one of three different surfactant carboxylic acid molecules by Fourier-transform infrared extinction spectroscopy in an aerosol flow tube, aided by particle sizing methods. The examined acids, all contain one carboxylic group at the end of the molecule, are hexanoic (CH$_3$(CH$_2$)$_4$COOH), octanoic (CH$_3$(CH$_2$)$_6$COOH) and dodecanoic or lauric acid (CH$_3$(CH$_2$)$_10$COOH), hereafter shortened as HA, OA and LA, respectively. These acids belong to the family of alkanoic acids, that make a significant proportion of the organic compounds emitted from several sources to the atmosphere, such as seed oil and meat cooking procedures or emission by plants. HA, OA and LA have been observed in the atmosphere of remote marine and continental locations (Duce et al 1983; Gill et al 1983; Limbeck and Puxbaum 1999; Samy et al 2010; Schauer et al 1999; Schauer et al 2002; Yassaa et al 2001). OA and LA exist as liquid and solid, respectively, at typical tropospheric temperatures and pressures. HA has higher vapor pressure than the atmospherically more abundant long chain acids, that may contribute more substantially to vapor phase processes. HA, OA and LA have water solubilities of 9.9, 0.68 and 0.058 g/L at 20ºC, respectively (see Table 1), and have been selected as they are expected to influence the hygroscopic behaviour of sea-salt particles differently in view of their water solubilities: HA has intermediate solubility between highly soluble and highly insoluble organic acids, whereas LA, on the other end, can represent highly insoluble fatty acids, OA lying in-between. Due to their overall low water solubility, pure fatty acids are not expected to present significant intrinsic hygroscopic properties.

Infrared spectroscopy is a well-known sensitive technique and has been applied to the study of organic/inorganic aerosol systems (Garland et al 2005; Najera and Horn 2009). It can yield aerosol composition, water content, and particle phase. Variations in the wavenumbers and widths of spectral bands (precisely their FWHM: full width at half maximum) can also reveal information about molecular interactions in mixed systems and the formation of new species. Infrared spectra
have been combined with electron scanning microscopy (SEM) of particles, a technique that has
been demonstrated to be useful to study the chemistry of isolated, individual particles of
atmospheric relevance (Krueger et al 2003; Veghte et al 2013). A few studies have been presented
describing the effects of octanoic and lauric acids on the hygroscopicity of NaCl (Hämeri et al
surfactant layers tend to slow NaCl deliquesce rate and to slightly lower its DRH. This may
affect particle size and phase, changing the amount of scattered solar radiation and also the
adsorption behavior of trace gases onto particles. Molecular dynamics simulations of water vapor
molecules impinging on a slab of water coated by octanoic acid film showed that the mass
accommodation coefficient decreased with the degree of surface coverage of the hydrocarbon
backbones (Takahama and Russell 2011).

2. MATERIALS AND METHODS

The configuration of the experimental setup used in this work is based on a system described
previously (Minambres et al 2010), that has been modified for the present study. The main elements
are depicted in Figure 1. Submicrometric particles are formed by injecting a 0.01 kg/L aqueous
solution of sodium halide salts (NaCl, NaBr and NaI, ≥98%) in a commercial atomizer (TSI 3076).
Their relative humidity (RH) can be controlled (from 0 to around 95%) by combining two serially
connected diffusion driers and a flow of N₂ with a controlled amount of water vapor. The inorganic
particles are coated by passing the aerosol flow (1.8 L/min) through a heated cell that contains a
sample of either hexanoic (99%), octanoic (≥98%), or lauric acid (≥98%). Table 1 summarises the
most relevant physical properties of these acids.

The heating cell consists of an horizontally-set cylindrical borosilicate glass tube 30 cm long
having 3 cm internal diameter, that has two smaller glass tubes (30 and 20 cm long, 1 cm int. diam.)
coaxially attached at its ends. Acid sample (either liquid or solid) is placed uniformly along the
central tube. The whole cell is thermally isolated by wrapping it with alumino-silicate refractory
ceramic fiber. To allow for sufficient vaporization of the acid, the central tube and exit arm of the
cell are heated up to 100°C by means of flexible resistors coiled around them. The temperatures at
both cell locations (T₁ refers to the central part, T₂ to the exit arm, see Figure 1) are controlled by
placing two K-type thermocouples at the cell outer walls. To form heterogeneously nucleated
particles, $T_1$ varied from 75 to 100°C and $T_2$ from 60 to 90°C. Higher temperatures resulted in stronger absorption bands, indicating a higher efficiency of heterogeneous nucleation, that forms a thicker coating of NaCl particles. The temperature measurement errors are estimated to be in the 4-7°C range (the higher value corresponds to the highest temperature). A prominent baseline shift was observed in all cases, in agreement with particle formation. This shift increases with $T_1$ and $T_2$, indicating bigger particles. Purely homogeneously nucleated particles were formed by passing a flow of gaseous nitrogen through the heated oven at $T_1=80-100ºC$ and $T_2=60-90ºC$ containing the carboxylic acid. This coating method can get a reproducible amount of fatty acid on particles in a fast and convenient way, and has been used by other authors in laboratory experiments (Abbatt et al 2005; Garland et al 2008; Garland et al 2005; Rouviere and Ammann 2010; Stemmler et al 2008).

Although in the troposphere the whole process of heterogeneous nucleation of organic vapors takes place at overall lower temperatures, in our experiment the heated organic vapor gets in contact with the nitrogen gas flow at ambient temperature, that effectively cools the vapor by rapid heat exchange (the number density of nitrogen molecules in the gas flow is much higher than the number density of organic vapor molecules in the tube). Eventually, cooled gas-phase organic molecules heterogeneously nucleate on salt particles in the nitrogen gas flow. In that way, the way to generate heterogeneously nucleated particles can be assumed to follow the same physical process than in the atmosphere, although the temperatures can vary over a broad range.

The final aerosol flux was directed simultaneously to a condensation particle counter (CPC, either TSI 3781 or MSP 1040XP models, inlet flow 0.6 L/min), an aerodynamic particle spectrometer (APS, TSI 3321, inlet flow 1.0 L/min) and a Fourier-transform infrared spectrometer (Nicolet Magna 860), to obtain particle number, size distribution and their infrared extinction spectra, respectively. Infrared extinction spectra are recorded in the 650-4000 cm$^{-1}$ range and 4 cm$^{-1}$ resolution. Infrared radiation from a colimated source (ORIEL 6580) travels lengthways a 1 m long, 50 mm diameter pyrex absorption cell at ambient temperature with ZnSe windows. The outgoing radiation is directed to the infrared spectrometer (Figure 1), where the infrared beam is divided into two. Both beams take slightly different path lengths, and recombine to construct an interferogram. The recombined intensity is recorded as the path length difference is changed. By applying the Fourier transform technique, the variation of the intensity with wavenumber is retrieved. The optical path is sealed and flushed by a current of dry air to reduce interference from ambient water and carbon dioxide. Background spectra are recorded after pumping out the aerosol cell. Sample spectra are averaged by collecting typically 32 scans. To complete analytical on-line methodology, particle shape and size of both pure and mixed particles were determined off-line using a JEOL JSM-7000F scanning electron microscope (SEM), equipped with a Schottky field emission gun.
(FEG) and an Oxford Inca Pentafet X3 energy dispersive X-ray analyser (EDX). The EDX microanalysis was performed using an accelerating voltage of 20 kV and a current intensity of $10^{-10}$ A, with a working distance of 10 mm. The aerosol of interest was collected at the exit of the extinction flow cell onto a glass slide, and particles were coated with an Au layer (20 nm) deposited by evaporation using a Quorum Q150T Sputter Coater to provide electrical conductivity.

Particle size distribution in the 0.5-20 µm is retrieved by an aerodynamic particle spectrometer (TSI 3321), that give a tail in the 0.5-3.5 µm range. Information about the size distribution of pure salt particles in the 0-0.5 µm range was obtained by processing the SEM images with the help of the ImageJ software [rsbweb.nih.gov/ij/]. The obtained distribution fitted satisfactorily to a lognormal distribution with a count median diameter of 46 nm and sigma = 2.0. Particles appear mostly isolated, without a tendency to aggregate. Representative examples of number size distributions of pure NaCl particles and also covered with hexanoic acid are presented in Figure 2.

### 3. RESULTS AND DISCUSSION

#### 3.1. Infrared spectra of pure carboxylic acids

The infrared absorption spectra of bulk HA, OA and LA recorded at ambient temperature are presented in Figure 3. The spectra of HA and OA were recorded in an infrared cell for liquids, whereas for LA one drop of the sample dissolved in ethanol was deposited on a BaF$_2$ window until solvent evaporation, after which the absorption spectrum of the film was recorded. The main absorption bands are common to all three acids, with small differences in band position and intensity.

The sharp carbonyl stretching band can be seen near 1710 cm$^{-1}$, the broad band in the 2500-3500 cm$^{-1}$ range has been assigned to associated COO–H stretchings (broadened by intermolecular association by hydrogen bonding), whereas the group of three peaks in the 2800-3000 cm$^{-1}$ range, exhibiting a different resolvable structure for the different acids, has been assigned to –C–H stretchings. A more complex band system appears in the 800-1500 cm$^{-1}$, specific of each acid. On
the other hand, the gas phase infrared spectra of the three acids (NIST Chemistry Webbook: [http://webbook.nist.gov/chemistry](http://webbook.nist.gov/chemistry), not shown in Figure 1) show several differences with the bulk phase spectrum: the intense C=O band locates in the 1780-1790 cm\(^{-1}\), whereas a narrow band appears near 3580 cm\(^{-1}\) (COO–H free stretch), absent in the condensed phase. Overlapped bands appearing in the 2800-3000 cm\(^{-1}\) range are coincident with peak positions in bulk phase spectra. Finally, a number of bands is present in the 800-1600 cm\(^{-1}\) region, several of which can be distinguished from condensed phase spectra.

Figure 3 also shows the extinction spectra of homogeneously nucleated particles. Bands belonging to each acid were detected in all cases, their absorption intensity growing with increasing \(T_1\) and \(T_2\). CPC measurements confirmed the presence of particles, that were assumed to belong to the carboxylic acids. For HA, the obtained spectra are mostly coincident with the gas phase spectrum. A weak band located at near 1730 cm\(^{-1}\) has been assigned to the C=O stretch originating from small particles of liquid HA due to homogeneous nucleation. This band is 21 cm\(^{-1}\) displaced to higher wavenumbers with respect to bulk liquid HA, possibly due to surface effects in small particles: due to the interactions between surface molecules and the surrounding medium, the surface region has different structural properties (and thus spectroscopic features) than the core of the particles (Firanescu et al 2006). This hypothesis is supported by the spectrum of liquid HA adsorbed at the air/water interface by vibrational sum-frequency spectroscopy (Soule et al 2007), that locates the C=O band in the 1726-1730 cm\(^{-1}\) range, depending on the polarization conditions. For OA, the C=O band was peaked at near 1700 cm\(^{-1}\), but broader than the one corresponding to condensed phase. Also an overlapping band system in the 1540-1650 cm\(^{-1}\) range was observed. No lines of gaseous OA were detected. For LA, no gas band features were present, in accordance with its low vapor pressure. Further evidence of the presence of particles is given by the baseline increase to higher wavenumbers (Figure 2), which is indicative of particle scattering (Hinds 1998). This effect is more pronounced as \(T_2\) is increased. A broad band in the 3100-3500 cm\(^{-1}\) range is observed for homogeneously nucleated hexanoic and octanoic acid, that is absent in the bulk spectrum. This feature has been attributed to the presence of small amounts of liquid water outgassed from the acid that become trapped into the particles.

The most notable differences in band wavenumber and bandwidth for the three acids are observed for the C=O stretching band, and are summarised in Table 2. These differences can be significant, as can be related with surface effects that can give information about the particles. Carbonyl bandwidth in the bulk acids is in the 20-29 cm\(^{-1}\) range, and increases with molecular mass. These values change in homogeneously nucleated organic particles, either increasing (HA and OA) or decreasing (LA). Relative variations in its magnitude are in the 25-75% range.
3.2. Infrared extinction spectra of heterogeneously nucleated NaX particles with carboxylic acids

Representative infrared extinction spectra of heterogeneously nucleated sodium halide particles are shown in Figure 2. The band intensities of heterogeneous nucleation spectra are much bigger than those of homogeneous nucleation (e.g., 4:1 for NaCl/OA at $T_1=90^\circ$C, $T_2=80^\circ$C). For NaX/HA particles, bands of gaseous and condensed phase HA were observed. The latter increase in intensity with $T_1$ and $T_2$, whereas the former remain constant. For NaX covered with OA or LA, practically all infrared bands originate from condensed phase, gas phase OA bands being very weak or absent. Their observed carbonyl absorption band wavenumber and bandwidth for the various acids are collected in Table 2. The changes in these magnitudes with respect to their bulk phase values are indicative of organic molecule/inorganic ion interactions, and can be used to address the effect of the ionic salt environment near the organic acid molecules. For all acids, the C=O stretch wavenumber of the acid coating on NaX varies with the salt and is between the wavenumber of the corresponding bulk acid and that of homogeneously nucleated acid particles (Table 2). In all cases, bulk wavenumber of C=O locates around 70 cm$^{-1}$ lower than in the gas phase, bulk LA showing the lowest wavenumber (1700 cm$^{-1}$). On the other hand, the bandwidths of the C=O stretch coming from heterogeneously nucleated particles depend on the nature of the salt, the organic acid and the degree of covering: for HA-covered particles, the full width half-maximum (FWHM) can reach 40 cm$^{-1}$, doubling the bulk HA value, whereas for LA-coated particles it is smaller than the bulk acid bandwidth. The relationship of these results with the hygroscopic properties of particles will be discussed later.

3.3. Morphology of pure and mixed particles

SEM images of pure NaCl and LA particles, and of NaCl particles after covering them with LA, were recorded and are presented in Figure 4. This technique was not well suited to study
particles that included OA or HA, due to their high vapor pressure at room temperature that
difficulted their manipulation in the SEM vacuum chamber. Images of pure NaCl particles show
particles of cubic form as expected but with their edges somewhat rounded, as a result of a short
exposure of deposited particles to ambient air before being coated with the gold layer; as NaCl is
very hygroscopic, they have uptaken a small amount of gaseous water enough to change their
original morphology (see Figure 4a).

Images of LA particles (Figure 4b) show a much smaller amount of particles that tend to
form big aggregates, typically of 1-2 µm length, in accordance with previous studies (Gadermann et
al 2008). The particles are amorphous and mostly elongated. Images of NaCl particles deposited
jointly with LA (after heterogeneous nucleation, see Figure 3c) show a small number of particles,
much fewer than in the case of pure NaCl, although the initial amount of NaCl aerosol was identical
in both cases (this may be due to the low affinity of the mixture with the supporting material or to
higher tube losses). Most particles present cubic form, and tend to appear as aggregates. Although
pure LA particles can be observed, they are very scarce. A thin layer covering the NaCl particles
can be observed, smaller NaCl particles appearing with a thicker covering. Thus it can be said that a
thin layer of lauric acid is deposited on NaCl particles, acting as a glue that tends to link individual
NaCl particles.

3.4. Deliquescence and efflorescence of heterogeneously nucleated NaX particles with HA, OA
and LA

3.4.1. Infrared spectra of particles at various RHs

To examine the deliquescence behavior, dry NaX particles coated with each of the
carboxylic acids were mixed with a flow of gaseous water at different RHs. As a representative
elementary example, Figure 5 shows three spectra of NaBr particles covered with OA at various RHs. The
presence of liquid water can be detected and quantified by the broad band centered at near 3400 cm⁻¹
1. For all cases, no infrared absorption bands arising from aqueous dissolved acids were detected, so
in all the subsequent discussion all the organic acids are assumed to be undissolved in liquid water.
In all cases, we paid special attention to the C=O stretching band of the acids near 1700 cm\(^{-1}\), and we analyzed it as a function of RH, organic acid and halide anion measured. In OA/NaX and LA/NaX particles, the carbonyl band absorption intensity of condensed phase acid keeps constant with RH; on the contrary, for NaX/HA particles the band intensities of liquid HA decrease as RH increases, although the intensities of gaseous HA remain unchanged. As an example, Figure 6 plots the intensity variation of the carbonyl band versus RH for liquid and gaseous HA in NaBr particles. It can be seen that, while the C=O band intensity of gaseous HA keeps roughly constant with RH, the band intensity for condensed HA lowers at higher RH. The largest decrease was observed in NaBr, and the smallest in NaI. In all salts, the particles retained liquid HA at RHs higher than their DRH. On the other hand, the spectrum baseline also decreases at high wavenumber as RH increases (due to decrease of particle scattering), indicating a thinner coating of the particles.

The efflorescence behavior of coated aqueous NaX particles was investigated by passing NaX aqueous particles along the heated oven containing the carboxylic acid vapor. For all the systems, at RH near saturation the spectra show bands of condensed phase organic acid. The intensity of these bands keeps roughly constant with RH in OA and LA, but liquid HA band intensities decrease notably as RH is reduced (a factor in the range 3-7 from RH≈100% to 27%, depending on the salt). Figure 5 shows the case for NaBr/HA. Also the scattering signal is decreased with RH, indicating that particles get smaller.

3.4.2. Deliquescence and efflorescence curves

Deliquescence and efflorescence curves were recorded by measuring the integrated absorbance of liquid water in the particles in the 3400-3600 cm\(^{-1}\) range and plotting the values versus RH. This interval was selected as it is mostly free of interference with nearby absorption spectral features. The scattering component of the liquid water extinction spectrum was removed by subtracting the sloping baseline present at high wavenumbers to obtain integrated absorbances. The results for all the systems are presented in Figure 6. The curves for the pure inorganic salts have also been measured and are included in the figure. Hereafter, we describe the effect of the various acids in each of the inorganic salts.

1) NaCl particles
The deliquescence curve of NaCl/HA is very similar to that of pure NaCl particles, that deliquesce at DRH (298 K) = 75.3% (Tang and Munkelwitz 1993). No water uptake is detected until near 73% RH, where particles abruptly become liquid. However, SEM results show that particles uptake small amounts of water before sudden deliquescence, that are not enough to change their size, but modify their size slightly (becoming more "roundish" with increasing RH). The quantity of liquid water uptaken by NaCl particles is unaffected by the presence of the HA covering. However, for NaCl/OA and NaCl/LA, particle deliquescence occurs near to 56% RH, substantially lower than in pure NaCl. These results are in agreement with previous reports in which a slight lowering of the DRH of NaCl was observed when the particles were covered with OA and LA acids (Hansson et al 1998). In NaCl/OA, the particles uptake larger amounts of water vapour than in pure NaCl, whereas the opposite is observed for NaCl/LA. The efflorescence curves for all the three acids locate the ERH close to 40%, very similar to pure NaCl particles. The curves are coincident in the RH=20-60% range, but diverge towards higher RHs. For all acids, particles retain larger amounts of water than pure NaCl in the RH=60-95%, the quantities being in the order LA>OA>HA. Also the amount of HA and OA in the particles decreases as liquid water is removed from them until the ERH is reached, whereas no change in the amount of LA is observed with RH.

2) NaBr particles

According to Figure 7 data, NaBr/HA particles deliquesce at somewhat higher RH than pure NaBr particles: liquid water in NaBr/HA particles is not detected until 49.6% RH. This value does not change with the degree of coating, and contrasts with the value of DRH=37% for pure NaBr particles (Minambres et al 2008). On the other hand, OA and LA coverings do not have any effect on the deliquescence behavior of NaBr: the deliquescence curves are practically coincident with those of pure NaBr. Also, the amount of uptaken water is similar to pure NaBr, except for OA-covered particles, that grow faster for RH>70%. Efflorescence curves for all acid covering are very similar to pure NaBr (ERH=23%) in the 20-60% RH (although OA retains slightly more water at all RHs), but at RH>60% acid-covered particles retain higher amounts of liquid water than pure NaBr (up to double for NaBr/LA at 90% RH). Thus the presence of the organic covering causes water loss to happen more gradually than in the pure salt at high RHs.

3) NaI particles
The deliquescence curves of acid-covered NaI particles exhibit substantial differences with respect to the pure salt. Whereas pure NaI particles take up water at all RHs (Minambres et al 2011), NaI/HA and NaI/LA particles do not uptake water until RH=16% and 21%, respectively. Liquid water is not detected in NaI/OA particles until RH=75%. It can be concluded that organic acid covering substantially retards the uptake of water in NaI particles, specially OA. The amount of liquid water in HA and LA-covered particles in the RH=20-80% is higher than in pure NaI. The efflorescence curve of NaI/LA is practically coincident with the pure NaI curve in the RH range measured. However, HA-covered particles lose water more gradually, retaining higher amounts of water than pure NaI in the RH=30-80% range. Finally, OA-covered particles follow closely the pure salt curve for RH>80%, but retain more water at lower RHs. The general tendency is that the presence of acid covering retains more water in the particles, except for LA, which shows little effect.

3.4.3. Discussion of deliquescence and efflorescence processes

The obtained results on the hygroscopicity of sodium halide particles covered with organic acids having low water solubility show an overall complex behavior. The deliquescence curves of Fig. 7 indicate that the water uptake process is dependent on both the inorganic salt and the organic acid. Whereas HA, OA and LA have a smaller effect on water uptake of NaBr (only HA slightly retards the DRH), they produce a lowering of the DRH in NaCl respect to the pure salt. On the contrary, in NaI these acids prevent particles to uptake liquid water at low RHs, unlike in pure NaI, which admits water at any RH. This retarding effect is especially attributed to OA. In efflorescence, a similar behavior is observed for all systems: the presence of the organic acid makes the particle to retain more water at a given RH, all curves converging at the ERH.

The observed hygroscopic behavior can be due to several factors. Although the morphology of particles can sometimes influence their hygroscopic behavior, all NaX salt dry particles are expected to be cubic, as all of them have an octahedral crystal structure. Another possibility is that each organic acid interacts differently with each inorganic salt. Organic acids in the surface of inorganic salts will tend to orientate with their polar groups facing the salt surface, so that ion-dipole interactions will arise that will diminish the system Gibbs free energy. The polarizability of the halogen atoms increases in the order Cl (14.7) < Br (21.8) < I (35.1, all in atomic units) (P. Schwerdtfeger, Table of experimental and calculated static dipole polarizabilities for the electronic ground states of the neutral elements, http://ctcp.massey.ac.nz/dipole-polarizabilities), so differences in the interaction magnitude are expected. In addition, the surface of particles will
become more populated by anions as halide polarizability increases (Jungwirth and Tobias 2001). Also elongated carbonated chains are known to be easily polarizable. Additionally, it has been proposed that the structure of the monolayers formed with insoluble surfactants determines their resistance towards gas uptake (Stemmler et al 2008). Fatty acids form a highly ordered film in the so-called liquid condensed state, whereas in the liquid expanded state they form a less ordered film and do not hinder the uptake. In that way, the differences in retardation in water uptake can arise from the different degrees of compression of such films (Donaldson and Vaida 2006; Takahama and Russell 2011). Another possibility is that gaseous water transport occurs through open sections of the surface, that can be due to incomplete packing by the organic film or to random fluctuations (Donaldson and Vaida 2006). The observed salt-specific behavior is in accordance with the observed deliquescent behavior of internally mixed particles formed of sodium halide and water soluble organic acids (Minambres et al 2011).

The hygroscopic behavior can be correlated with the spectral features of the organic acids shown in Table 2, where the wavenumber and the bandwidth of the C=O band in different environments are shown. The band center wavenumbers shift in the -6 / +10 cm\(^{-1}\) range in the presence of NaX salts, but the bandwidth (FWHM) variation (respect to the C=O vibration for the bulk acid) is in the -16 / +20 cm\(^{-1}\) range, representing a change in the FWHM of more than 100% in some cases. The wavenumber shift and broadening of a spectral band may arise from a change in the internal force constant of the C=O bond due to the formation of intermolecular bonds with other molecules, for example hydrogen bonds with water (Kalsi 2007). These results are indicative of the effect of the ionic salt environment near organic acid molecules. Although it is not easy to establish clear correlations with the changes in deliquescence behavior, some remarks can be outlined. For systems with NaBr, the changes in FWHM of the C=O band are the smallest (except for HA/NaBr), which correlate with a quite small change of DRH (except for HA/NaBr). For NaI mixed with an organic acid, although the changes in FWHM are considerable (indicating strong ion-polar head group interaction), the explanation for the water uptake behavior can be attributed to the hydrophobic effect exerted by the organic acids, forming a barrier that prevents the entrance of gaseous water molecules inside the particles. This effect is very pronounced for NaI/OA, and we have not found a satisfactory explanation for it. Finally, in NaCl/organic acid systems, the opposite effect is observed, in which the presence of acids slightly enhance the entrance of gaseous water. This can be attributed to the ion-polar group interaction that slightly lowers the Gibbs free energy of the system, favoring the acceptance of gaseous water molecules. The efflorescence process in NaX aqueous particles is not substantially affected by the presence of the acid. As there is not an energy barrier to the efflorescence process (in contrast to deliquescence), water loss takes place gradually.
as RH is lowered. Additionally, the salting out effect of NaCl will make dissolved organic acid molecules (specially the most water soluble HA) gradually move to the surface as the concentration of the salt solution increases (Demou and Donaldson 2002), and will be eventually removed from the surface together with water. However, the magnitude of the salting out effect for HA is rather small (Demou and Donaldson 2002).

The results on water uptake and release in the special case of HA covered particles give information on how the dynamics of water exchange in inorganic particles is affected by the presence of a surface layer having small water solubility. In all deliquescence curves, there is a competition for surface positions between adsorbed HA and gaseous water, as indicated by the evolution of the amounts of liquid HA and water with RH (or, equivalently, the relative amount of gaseous water) in Figure 6. This can be reasoned as follows: in the deliquescence spectrum of Figure 6, the amount of liquid HA decreases as RH (and consequently the amount of gaseous water) increases, indicating that, if we start from a dry crystalline NaX particle covered with HA, gaseous water tends to displace HA molecules away from the particle surface, to try to accommodate themselves on the NaX solid surface. This effect must be a consequence of the change in the Gibbs free energy of the system in the deliquescence process: as the energetically most stable system is obtained when gaseous water molecules remain near the solid NaX surface (producing deliquescence when the number of gaseous water molecules reaches a given value), HA molecules will tend to be displaced from their surface locations. In efflorescence, however, the observed behavior is different: removal of liquid water from aqueous particles having an organic HA coating due to the decrease of RH is accompanied by removal of HA from the particle surface. This effect can be explained assuming that liquid HA uniformly covers the NaX aqueous particle. For water molecules to exit the particles, a "hole" in the HA layer must be made, and water molecules exiting the particle will sweep away HA molecules from their surface locations. NaX-gaseous water interactions must be stronger in NaCl than in NaBr and NaI or, alternatively, NaX-HA interactions will be weaker for NaCl than for NaBr and NaI. For that reason, in NaX/HA particles, HA is displaced more effectively from the surface at the DRH of pure NaCl. In NaBr and NaI, however, the number density of gaseous water molecules nearby the particles at the DRH of the pure inorganic particle is not enough to remove the HA cover, and a higher number of gaseous water molecules (higher RH) is needed to produce particle deliquescence.

3.5. Estimation of the relative amounts of organic acid and water in the particles
The relative amounts of liquid water and a given organic acid in the aqueous NaX particles can be calculated on average from measured absorbances in their infrared spectra. The number of molecules $N_i$ of a given species $i$ per unit volume of aerosol sample is related with the integrated band absorbance of that species via the Beer-Lambert law (Weis and Ewing 1996):

$$A_i = \bar{A}_i N_i z / 2.303 \times 10^2,$$

where $A_i$ is the integrated absorbance of a given band (cm$^{-1}$), $\bar{A}_i$ the integrated absorption cross section per molecule (m molecule$^{-1}$) of that band, and $z$ is the optical path length of the aerosol flow cell (m). Applying the previous equation, we can obtain the organic acid/liquid water mole ratio for samples measured in the same aerosol cell, if $A_i$ and $\bar{A}_i$ are known:

$$N_{\text{org}} / N_{\text{H}_2\text{O}} = \bar{A}_{\text{org}} / \bar{A}_{\text{H}_2\text{O}} \bar{A}_i / \bar{A}_i.$$

The absorption cross section of liquid water has been obtained from pure water data in the 2800-3600 cm$^{-1}$ range (Downing and Williams 1975), $\bar{A}_{\text{H}_2\text{O}} = 1.3 \times 10^{-18}$ m molecule$^{-1}$. The absorption cross sections for liquid HA and OA have been obtained by measuring the integrated absorbance of a solution of the acid in methanol of known composition in a 150 µm long cell for liquid samples. The C=O band in the 1668-1774 cm$^{-1}$ range was chosen to compute the integrated absorbance. The obtained values are $\bar{A}_{\text{HA}} = 9.87 \times 10^{-19}$ m molecule$^{-1}$ and $\bar{A}_{\text{OA}} = 1.71 \times 10^{-19}$ m molecule$^{-1}$. From these data, the average $N_{\text{HA}}/N_{\text{H}_2\text{O}}$ and $N_{\text{OA}}/N_{\text{H}_2\text{O}}$ ratios have been calculated for the various salts at several RHs. The results appear in Figure 8. The obtained results indicate that $N_{\text{HA}}/N_{\text{H}_2\text{O}}$ values are comprised in the 0.1-0.6 range for RH in the 30-98% interval, the lowest values corresponding to the highest RHs. In contrast, the $N_{\text{OA}}/N_{\text{H}_2\text{O}}$ quotient spans from 0.2 to 1.9 (for RHs in the 40-96% range), when again the highest values correspond to the lowest RH conditions. The highest $N_{\text{OA}}/N_{\text{H}_2\text{O}}$ ratio (1.9) is obtained for NaI efflorescing particles. The results in Fig. 8 indicate that, in general, OA-covered particles tend to displace liquid water more efficiently than HA-covered particles.

The spectroscopic results indicate that gaseous HA, OA and LA easily nucleate onto dry and aqueous NaX particles. The amount of acid uptaken increases with the temperature of the oven. Additionally, SEM images of NaCl particles with LA show NaCl particle aggregates, indicating that they are "glued" by lauric acid. However, SEM images provide no visual evidence of the presence of an organic cover, so we can conclude that the cover must be much thinner than the size of the salt particles. A rough higher limit for the cover thickness can be set at 20 nm, which is the resolution of the SEM images. This estimate can be compared with HA and OA cover thickness on aqueous particles, calculated assuming that liquid HA or OA arrange in a hydrophobic organic layer in the surface of an aqueous particle, according to one proposed model (Ellison et al 1999), and taking...
into account the spectrally measured relative proportions of water and organic acid. The volume of a spherical aqueous particle of radius $R$ will be $V_{\text{H}_2\text{O}} = \frac{4}{3}\pi R^3$, whereas the volume of liquid organic coating of thickness $r$, assuming uniform coverage, can be written as $V_{\text{org}} = \frac{4}{3}\pi[(R+r)^3 - R^3]$. On the other hand, $V_{\text{org}}/V_{\text{H}_2\text{O}} = N_{\text{org}}\rho_{\text{H}_2\text{O}}/(N_{\text{H}_2\text{O}}\rho_{\text{org}})$, where $\rho$ stands for density. As the $N_{\text{org}}/N_{\text{H}_2\text{O}}$ ratios have been determined previously, from the previous equations we can obtain $r$ in terms of the aqueous particle radius $R$: 

$$r/R = [1 + N_{\text{org}}\rho_{\text{H}_2\text{O}}/(N_{\text{H}_2\text{O}}\rho_{\text{org}})]^{1/3} - 1$$

For typical values of $N_{\text{HA}}/N_{\text{H}_2\text{O}} = 0.1$, 0.3 and 0.6, $r/R = 0.035$, 0.098 and 0.181, respectively, indicating that the thickness of the organic layer increases roughly linearly with the number of molecules of liquid HA. For example, if $N_{\text{HA}}/N_{\text{H}_2\text{O}} = 0.3$ and $R = 0.3\ \mu\text{m}$ (roughly corresponding to NaCl particles appearing in Figure 4c), the HA coating thickness yields an estimation of $r = 29\ \text{nm}$ for a particle coated with HA. This value can be compared with the upper limit of 20 nm estimated for the cover thickness in the LA/NaCl system. The former HA-coating thickness is much bigger than the estimated thickness of a monolayer, although we cannot affirm whether the particles are uniformly covered. Previous investigations indicate that the degree of insoluble acid coverage do not substantially alter DRH. Complete coverage of inorganic particles by fatty acids had no dramatic effect on NaCl particle DRH (Andrews and Larson 1993). On the other hand, DRH of ammonium sulfate was only slightly lowered for oleic acid thickness up to 109 nm (Najera and Horn 2009), much bigger than our estimated thickness of around 30 nm. No variations in DRH with acid covering thickness were observed in this work.

4. CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

This work has studied the effect of a covering layer of hexanoic, octanoic and lauric acid, which are present in the Earth's troposphere, on the hygroscopic properties of sodium halide submicrometer particles, which are constituents of sea salt aerosol. Infrared extinction spectroscopy together with particle counting and visualizing techniques has allowed to detect the formation of homogeneously and heterogeneously nucleated particles and the variation of their composition in the presence of variable amounts of gaseous water, leading to the processes of deliquescence and efflorescence. SEM measurements and data deduced from infrared absorbance spectra indicate that
the covering thickness of the obtained salt particles is compatible with an average value of 30 nm. SEM images show that the effect of lauric acid on NaCl is to agglomerate salt particles, producing bigger effective particles. It has not been possible to observe this effect with the other acids, due to experimental inconveniences.

It has been found that the hygroscopic properties of sodium halide particles covered with hexanoic, octanoic or lauric acid change both with the nature of the inorganic salt and the carboxylic acid. The DRH of NaCl aerosol is dependent on the organic acid covering the particles. The deliquescence of NaCl/OA and NaCl/LA systems occurring near RH=56%, considerably lower than in pure NaCl. On the other hand, NaBr covered particles do not substantially alter their water uptake behavior respect to pure salt particles, irrespective of the organic acid. The growth factor of these particles is also unaffected by the organic coating. Finally, organic acid covering on solid NaI particles acts as a barrier to water uptake; NaI pure particles deliquesce at about 15% RH when coated with hexanoic and lauric acid, but the DRH increases remarkably up to 60% RH for octanoic acid covered particles. The general consequence is that the water uptake behavior of sodium halide particles coated with organic acids is dependent on the nature of the anion and the carboxylic acid. This is in accordance with former studies of sodium halides with succinic acid, which showed a salt-specific behavior. Consequently, although it is customary to extrapolate the water uptake behavior of NaCl particles to sea salt aerosol, due to the predominance of this species in marine salt, the detailed picture can be more complex. Regarding efflorescence process, the obtained results indicate that the overall effect of the organic acid cover is to retain higher amounts of water at RH in the 60-90% range with respect to pure NaX particles. In NaCl particles the longer chain acid (LA) achieves the highest water retention, while the shortest one (HA) achieves the lowest. All acids act similarly in NaBr aqueous particles, whereas in aqueous NaI particles OA is the acid that produces higher water retention at RH in the 60-90% range. The results show that this barrier effect is dependent on the nature of the organic acid, and can have important consequences for the troposphere, as the organic species can determine the amount of liquid water in the particles and their phase at a given RH. Finally, the measurements indicate that there is no simple correlation between water uptake of crystallization processes in coated salt particles and the length of the carbonated chain in the carboxylic acid. The complex behavior in hygroscopic properties in the different salts can not be easily attributed to a single effect, and the results point to more specific ion-molecule interactions in the NaX/organic acid/H₂O systems or to the structure of the organic film on the particle.

Several consequences for the atmosphere can be driven from this study: as bromine and iodine ions tend to segregate to the surface of marine aerosol particles, and the effect of fatty acids
on them can be different as compared to the more abundant NaCl species, this may influence the surface properties of the particles not usually taken into account in the models. At a given value of ambient relative humidity, sea salt particles may have an outer core in which NaBr and NaI are more abundant, and if an organic layer having low water solubility is present, the interactions of the organic compound will predominantly take place with bromide and iodide ions. At given conditions of relative humidity in the atmosphere, liquid water amounts and phase of sea-salt particle outer core may vary regard to the expected behavior of pure NaCl particles. This has consequences in the heterogeneous processes taking place between particles and atmospheric gases, such as gas uptake and chemical reactivity.

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**FIGURE CAPTION**

**Figure 1:** Diagram of the experimental setup.

**Figure 2:** Representative particle size distributions of dry NaCl aerosol. Upper plot has been obtained by imaging particles deposited on a glass slide by SEM technique and counting them with the ImageJ software [rsbweb.nih.gov/ij/]. Bottom plots have been obtained by sizing particles by an aerodynamic particle spectrometer; pure NaCl particles (left) and heterogeneously nucleated particles with hexanoic particles (right) are shown.

**Figure 3:** Infrared extinction spectra of HA, OA and LA in different conditions: bottom spectra are from bulk phase acid; medium spectra corresponds to homogeneously nucleated acid particles; upper spectra are from heterogeneously nucleated acids onto NaCl particles. In all cases, the upper spectra have been increased for clarity (increasing factor: ×Number)

**Figure 4:** SEM images of: (a) pure NaCl particles; (b) pure LA particles; (c) NaCl particles covered with LA.

**Figure 5:** Infrared spectra of NaBr particles after passing through the heated reservoir containing OA and exposed to different RHs.

**Figure 6:** Evolution of the infrared absorption intensity of the C=O band of hexanoic acid with RH in NaBr particles in deliquescence and efflorescence mode. The shaded region indicates the selected area for measuring liquid water abundance in the particles (see text).

**Figure 7:** Deliquescence and efflorescence curves of NaX (X = Cl, Br, I) particles covered with HA, OA and LA. The curves for the pure inorganic salts are shown by lines.

**Figure 8:** $N_{HA}/N_{H2O}$ and $N_{OA}/N_{H2O}$ mole ratios in heterogeneously coated particles at various relative humidities in deliquescence and efflorescence conditions. “del” and “effl” stand for deliquescence and efflorescence. “RH” stands for relative humidity.
FIGURE 1
FIGURE 2

NaCl (SEM)  
$\bar{D} = 0.046 \ \mu m$
$\sigma = 2.00$

NaCl (APS)  
$\bar{D} = 0.77 \ \mu m$
$\sigma = 1.99$

NaCl + Hexanoic Acid (APS)  
$\bar{D} = 0.68 \ \mu m$
$\sigma = 1.96$
FIGURE 3

HA

OA

LA

Wavenumber (cm$^{-1}$)

Extinction (a.u)

0.0 0.2 0.4 0.6 0.8 1.0 1.2

0.0 0.2 0.4 0.6 0.8 1.0 1.2

0.0 0.2 0.4 0.6 0.8 1.0 1.2

0.0 0.2 0.4 0.6 0.8 1.0 1.2

3500 3000 2500 2000 1500 1000

3500 3000 2500 2000 1500 1000

3500 3000 2500 2000 1500 1000

3500 3000 2500 2000 1500 1000

x 10

x 75

x 80

x 85

x 100

x 100
**FIGURE 4**

(a) NaCl

(b) Lauric acid

(c) Lauric-acid-covered NaCl particles
FIGURE 5

Extinction (a.u)

RH=79.6%

RH=61.6%

RH=0.2%

Wavenumber (cm\(^{-1}\))

18
16
14
12
10
8
6
4
2
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
3500 3000 2500 2000 1500 1000
FIGURE 5

Condensed Liquid HA
Gaseous HA

0.00 0.04 0.08 0.12 0.16 0.20 0.24
RH=82.2%
RH=21.0%
RH=13.3%
RH=2.7%

Wavenumber (cm⁻¹)

DELIQUESCEENCE

0.00 0.10 0.20 0.30 0.40 0.50 0.60 0.70 0.80
RH=100%
RH=76.8%
RH=48.4%
RH=24.1%

Wavenumber (cm⁻¹)

EFFLORESCENCE

RH=100%
RH=76.8%
RH=48.4%
RH=24.1%

Condensed Liquid HA
Gaseous HA
FIGURE 6

- NaCl
- NaI
- NaBr

Liquid Water Mass vs. RH for different compounds:

- H. A.
- O.A.
- L.A.
- Pure NaX
FIGURE 7

A bar graph showing the ratio of N(acid)/N(H2O) for different salt solutions (NaI/OAdel, NaBr/OAdel, NaCl/OAdel, NaI/HAdel, NaBr/HAdel, NaCl/HAdel) as a function of relative humidity (RH) from 30% to 86%. The graph illustrates the variation in acidity with different salt concentrations and humidity levels.
### TABLE 1

Physical properties of the studied carboxylic acids

<table>
<thead>
<tr>
<th>Name</th>
<th>#C</th>
<th>Structural Formula</th>
<th>Melting Point (K) (a)</th>
<th>Boiling Point (K) (a)</th>
<th>Water solubilities (20^\circ\text{C}, \text{g/l}) (b)</th>
<th>Vapour pressure (mbar, 25ºC) (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexanoic Acid</td>
<td>6</td>
<td>(\text{\includegraphics[width=1cm]{hexanoic_acid}})</td>
<td>269.7</td>
<td>477±4</td>
<td>9.9</td>
<td>0.272</td>
</tr>
<tr>
<td>Octanoic Acid</td>
<td>8</td>
<td>(\text{\includegraphics[width=1cm]{octanoic_acid}})</td>
<td>289.3±0.7</td>
<td>510±4</td>
<td>0.68</td>
<td>(5.05\times10^{-3})</td>
</tr>
<tr>
<td>Lauric Acid</td>
<td>12</td>
<td>(\text{\includegraphics[width=1.5cm]{lauric_acid}})</td>
<td>317±2</td>
<td>571</td>
<td>0.058</td>
<td>(2.18\times10^{-5})</td>
</tr>
</tbody>
</table>

\(a\): NIST Chemistry WebBook  
\(b\): The Merck Index: An encyclopedia of chemicals, drugs and biologicals (11th Ed.), Merck, 1989  
\(c\): PubChem Compound, NCBI (National Centre for Biotechnology Information)
### TABLE 2

Band position and bandwidth of the C=O stretching band in various conditions for HA, OA and LA. Units in cm⁻¹

<table>
<thead>
<tr>
<th></th>
<th>Hexanoic acid</th>
<th></th>
<th>Octanoic acid</th>
<th></th>
<th>Lauric acid</th>
<th></th>
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<tr>
<td></td>
<td>Wavenumber at maximum intensity</td>
<td>Bandwidth (FWHM)</td>
<td>Wavenumber at maximum intensity</td>
<td>Bandwidth (FWHM)</td>
<td>Wavenumber at maximum intensity</td>
<td>Bandwidth (FWHM)</td>
</tr>
<tr>
<td>gasa</td>
<td>1780</td>
<td>26</td>
<td>1780</td>
<td>62</td>
<td>1790</td>
<td>30</td>
</tr>
<tr>
<td>bulk</td>
<td>1710</td>
<td>20</td>
<td>1713</td>
<td>26</td>
<td>1700</td>
<td>29</td>
</tr>
<tr>
<td>homog. nucl.</td>
<td>1730</td>
<td>26</td>
<td>1700</td>
<td>46</td>
<td>1710</td>
<td>21</td>
</tr>
<tr>
<td>heter. NaClb</td>
<td>1717</td>
<td>27-40c</td>
<td>1707</td>
<td>19</td>
<td>1710</td>
<td>19</td>
</tr>
<tr>
<td>heter. NaBrb</td>
<td>1711-1720c</td>
<td>27-37c</td>
<td>1713</td>
<td>23</td>
<td>1708</td>
<td>26</td>
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<tr>
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<td>1720</td>
<td>33</td>
<td>1713</td>
<td>36</td>
<td>1707</td>
<td>13</td>
</tr>
</tbody>
</table>

aNIST Chemistry Webbook: [http://webbook.nist.gov/chemistry](http://webbook.nist.gov/chemistry)
bDry particles
cDepending on the amount of acid deposited onto the salt particles