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Surface/bulk partitioning and acid/base speciation of aqueous decanoate: direct observations and atmospheric implications

N. L. Prisle¹, N. Ottosson^{2,*}, G. Öhrwall³, J. Söderström², M. Dal Maso¹, and O. Björneholm²

¹University of Helsinki, Department of Physics, P.O. Box 48, 00014, University of Helsinki, Helsinki, Finland

²University of Uppsala, Department of Physics and Astronomy, Box 516, 75120, Uppsala, Sweden

³University of Lund, MAX-lab, Box 118, 22100, Lund, Sweden

* now at: FOM Institute AMOLF, Science Park 104, 1098 XG Amsterdam, The Netherlands

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Correspondence to: N. L. Prisle (nonne.prisle@helsinki.fi)

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Dilute aqueous solutions of the atmospheric organic surfactant sodium decanoate have been studied using surface sensitive X-ray photoelectron spectroscopy combined with synchrotron radiation. We studied the decanoate/decanoic acid speciation and preferential adsorption at the vapor–liquid interface, and the responses to mixing in solution with some of the most common atmospheric inorganic ions, Na^+ , NH_4^+ , Cl^- , and SO_4^{2-} . We observe no influence of Na^+ , Cl^- , or SO_4^{2-} ions on neither the relative speciation nor the individual adsorption properties of decanoate and decanoic acid. In particular, the anticipated salting-out effect due to common Na^+ cations of the organic and inorganic salts was not observed. On the other hand, mixing with NH_4^+ cations resulted in a pronounced surface enhancement of decanoic acid, which is attributed to surface specific acid–base chemistry. These changes in surface/bulk partitioning and speciation may significantly affect properties of aqueous droplets containing decanoate/decanoic acid, and potential implications for several processes critical to the climate effects of atmospheric aerosols are discussed.

1 Introduction

Aerosol effects still constitute the greatest uncertainties in assessing anthropogenic contributions to global climate change (IPCC, 2007). Both direct and indirect climate effects of atmospheric aerosol particles are governed by their numbers, sizes, and chemical properties. Particles in the atmosphere are typically mixtures of both organic and inorganic species (O’Dowd et al., 2004; Murphy et al., 2006; Zhang et al., 2007). In addition, particles may absorb water from the air, to maintain equilibrium of condensed phase water activity (a_w) at a given ambient humidity, according to the generalized Raoult’s Law (Prisle et al., 2010, e.g., and references therein). Including interactions with water, as well as effects of mutual interactions between individual particle compo-

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



nents within the aqueous phase, is therefore essential to considerations of atmospheric aerosol properties.

Many of the organic compounds identified in the atmospheric particle phase are known, or expected from their molecular structures, to be surface active in aqueous solutions. This means that these molecules preferentially adsorb at the surface, where they may reduce the surface tension, compared to pure water. Such surface active molecules (surfactants) have been observed in bulk samples of atmospheric cloud and fog waters, as well as in aerosol samples and their aqueous extracts, from a wide range of environments. Fatty acids ($\text{CH}_3(\text{CH}_2)_n\text{COOH}$) and their carboxylate anion corresponding bases ($\text{CH}_3(\text{CH}_2)_n\text{COO}^-$) constitute an important class of atmospheric surfactants (Facchini et al., 1999, 2000; Mochida et al., 2002; Cheng et al., 2004; Kiss et al., 2005; Dinar et al., 2006). Their surface activity in aqueous solution stems from hydrophobic interactions of the aliphatic carbon chain with the polar water molecules.

The surface activity of dissolved components in aqueous aerosol and the nature of functional groups present at the solution–air interface may significantly affect a number of climatically important aerosol properties. For example, the cloud droplet formation of organic aerosols is affected by surface activity via both the influence of surface/bulk partitioning on bulk phase water activity, and the resulting surface tension reduction in aqueous droplets (Sorjamaa et al., 2004). These mechanisms are however intricately and non-linearly connected, and the overall influence of surface activity on cloud droplet activation and resulting cloud properties is not readily anticipated (Prisle et al., 2008, 2010, 2012). Analogously, properties of solutes dissolved in the bulk phase can also be expected to influence the freezing of aqueous droplets in the atmosphere. The mechanisms involved however still remain to be properly constrained. Surface adsorption of aerosol constituents with varying chemical functionalities may in turn influence heterogeneous chemistry at the particle surfaces, towards both gas phase and aerosol condensed phase reactants. Formation of organic films on aqueous aerosol surfaces may in addition affect gas–particle mass transfer of semi-volatile aerosol components. All of these processes ultimately affect the formation, composition, microphysics, pro-

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



cessing, transport, and eventual removal of atmospheric organic aerosols, and consequently both the direct and indirect aerosol climate effects.

For these aerosol systems, an important aspect of the aqueous-phase interactions between organic and inorganic components are manifested in the salting-out or -in of organics with finite solubility by inorganic salts (Gill et al., 1983; Lin et al., 2005; Tuckermann, 2007). Such phenomena are anticipated to further affect the properties of mixed atmospheric aerosols (Tabazadeh, 2005; Vanhanen et al., 2008) and have therefore on occasion been invoked to explain deviations from simple thermodynamic predictions observed for ambient or experimental model aerosol systems. However, the underlying molecular level interactions are not sufficiently well-known for the relevant aqueous solution compositions, from either experimental or theoretical approaches. The detailed nature and magnitude of salting-out effects in atmospheric aerosols thus remain speculative.

In this work, we studied the speciation of an atmospheric organic surfactant, sodium decanoate ($\text{CH}_3(\text{CH}_2)_8\text{COONa}$; DecNa), in terms of the relative abundances of the decanoate anion ($\text{CH}_3(\text{CH}_2)_8\text{COO}^-$; Dec⁻) and the corresponding decanoic acid ($\text{CH}_3(\text{CH}_2)_8\text{COOH}$; DecH) in the aqueous solution surface phase. We further investigate how these abundances are affected by mixing in the aqueous phase with salts comprising some of the most common inorganic ions found in atmospheric aerosols (e.g., Seinfeld and Pandis, 2006), specifically sodium chloride (NaCl), sodium sulfate (Na_2SO_4), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium chloride (NH_4Cl). The surfactant DecNa has sufficiently high water solubility and low vapor pressure to facilitate the experimental handling, and sufficiently high surface activity to for us to anticipate detectable effects of the investigated mechanisms. Of many potentially interesting compounds, we therefore chose DecNa for this study, based on knowledge from prior studies of an advantageous combination of properties making it a good model system for the present purposes (Prisle et al., 2008, 2010).

The bulk-phase distribution between the two corresponding carboxylic acid/carboxylate forms depends on intrinsic acid strength, as given by the acid

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



constant

$$K_a(\text{DecH}) = \frac{[\text{Dec}^-]_{(\text{aq})}[\text{H}_3\text{O}^+]_{(\text{aq})}}{[\text{DecH}]_{(\text{aq})}} \quad (1)$$

according to the protolysis equilibrium



5 as well as solution concentration, pH, and general mixing state. The Dec^- and DecH forms have different bulk solubilities and surface adsorption properties; DecH being much less soluble and much more surface active than Dec^- . These properties may in turn be affected differently for Dec^- and DecH, respectively, upon mixing with inorganic solutes in the aqueous solution.

10 2 Methods

Aqueous solution surfaces were studied *directly* using synchrotron radiation based X-ray photoelectron spectroscopy (XPS), a highly surface and chemically sensitive spectroscopic technique (Hüfner, 1995). Due to their high vapor pressure, aqueous systems have been difficult to study with XPS, which needs to be performed in vacuum. These problems were recently solved with the liquid jet technique (Winter and Faubel, 2006, e.g., and references therein), thus allowing XPS to be used for the study of systems with compositions immediately resembling those of aqueous atmospheric aerosol. For the present study, XPS is in particular capable of discriminating between signals originating from the protonated and deprotonated carboxylic groups (Ottoisson et al., 2011), respectively, and hence between the two different molecular forms comprising the corresponding decanoate/decanoic acid pair. Detected photoelectrons originate mostly from the topmost molecular layers in the surface region of the solution. The method

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



is therefore ideal for probing adsorption of dissolved surfactant species at the vapor-liquid interface.

To illustrate the chemical sensitivity of XPS, an idealized spectrum for an aqueous mixture of Dec⁻ and DecH, based on earlier results for carboxylic acids (Ottosson et al., 2011), is shown in Fig. 1. The ordinate gives the electron binding energy in the C1s region (note that the scale increases from right to left). For the energy region displayed, signals of detected electrons are shown (using an arbitrary scale) on the abscissa, originating from the chemically inequivalent aliphatic (methyl and methylene), carboxylate, and carboxylic carbons, respectively. The C1s electron binding energy of the carboxylic acid group is larger than that of the carboxylate group, because the C1s electrons are more tightly bound in the neutral environment of the protonated carboxyl group than in the negatively charged de-protonated carboxylate group.

The liquid-jet photoelectron experiments were performed at the Swedish national synchrotron facility MAX-lab in Lund, at the soft X-ray undulator beamline I411 (Bässler et al., 1999). The experimental setup has previously been described in detail (Bergersen et al., 2007). Briefly, the liquid samples were injected into an evacuated experimental chamber as a 20 μm jet, travelling at a velocity of approximately 25 ms⁻¹. The ionization occurred within a few millimeters after injection, and eventually the liquid jet was frozen out in a liquid nitrogen cold trap. The expelled electrons entered the analyzer through a circular opening with a diameter of 0.5 mm, situated approximately 1 mm from the liquid surface. This allowed for good differential pumping of the spectrometer, while a sufficient fraction of the photoelectrons were passed through the vapor without undergoing inelastic scattering which would change their apparent binding energy. A Scienta R4000 hemispherical electron analyzer was mounted perpendicular to the flow of the liquid jet, at 54.7° (the magic angle) relative to the polarization plane of the linearly polarized synchrotron radiation, in order to minimize angular distribution effects on the resulting spectra (Hüfner, 1995). The total experimental resolution (as determined from the width of the gas phase water 1b1 state) at the photon energy of 360 eV used for the C1s measurements was better than 250 meV. This is significantly

Surfactant XPS

N. L. Prisle et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

less than the inherent width of the investigated photoelectron lines for the aqueous species in question, meaning that the experimental resolution is not a limiting factor of the measurements.

The investigated systems were aqueous solutions of sodium decanoate, as pure solute (binary), and mixed solute (ternary) with one of the inorganic salts sodium chloride, sodium sulfate, ammonium sulfate, and ammonium chloride. Each solute or solute mixture was studied at two different aqueous concentrations, corresponding to approximately 25 mM of DecNa (close to the critical micelle concentration or solubility limit observed for DecNa in the ternary solutions upon sample preparation) and 10 mM of DecNa, respectively. Specifics of the organic and inorganic solutes are given in Table 1 and properties of the investigated solutions in Table 2.

Experiments were conducted at two occasions, during October 2010 and February 2011. In the first set of experiments, ternary solutions comprising NaCl and $(\text{NH}_4)_2\text{SO}_4$ were prepared to be approximately equimolar in the organic and inorganic salts. For the next experiments, ternary samples with Na_2SO_4 and NH_4Cl were prepared such that the individual ammonium and sulfate ion concentrations matched those of the previous experiments. The main results presented in this paper were reproducibly observed in both sets of experiments. Details of the sample preparation procedure are given in the Supplement.

3 Results and discussion

Results of the liquid-jet experiments are shown in Figs. 2 and 3. Each figure presents core photoelectron spectra recorded in the energy region relevant for the carboxylate and carboxylic acid C1s electrons. The spectra display photoelectron signal intensity (on an arbitrary scale) as a function of core electron binding energy. The measured spectra are presented in two separate figures due to experimental conditions; for the spectra in Fig. 2, alignment of the XPS setup was maintained between the individual experiments presented in each panel and the recorded photoelectron signal intensities

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



can therefore be immediately compared. The spectra in Fig. 3 are on the other hand measured with a different alignment than those shown in Fig. 2, and the alignment was not maintained between recordings of the individual spectra in Fig. 3. Normalization of these spectra is therefore arbitrary, such that no quantitative inferences of relative signal intensities can be made, and only the *shapes* of spectral features can be compared between different measurements.

3.1 First set of experiments

Figure 2 shows the spectra recorded for the reference binary aqueous solutions of sodium decanoate, together with those recorded for ternary aqueous mixtures of DecNa with equimolar amounts of NaCl and $(\text{NH}_4)_2\text{SO}_4$ salts, respectively. The left panel (a) shows the more dilute solutions (approximately 10 mM in each of the salts), and the right panel (b) shows the spectra measured for the more concentrated (approximately 25 mM) solutions.

Comparing the X-ray photoelectron spectra for binary DecNa to those for the ternary mixtures with NaCl and $(\text{NH}_4)_2\text{SO}_4$ in Fig. 2, it is immediately evident that no change occurs in the decanoate/decanoic acid C1s spectrum from the binary solution upon addition of equimolar amounts of NaCl, in neither the more dilute, nor the more concentrated, solutions. On the other hand, at both concentrations, mixing with $(\text{NH}_4)_2\text{SO}_4$ leads to a pronounced change of the spectral shape in the Dec⁻/DecH C1s region. The XPS spectra for the ternary DecNa- $(\text{NH}_4)_2\text{SO}_4$ solutions have been fitted with two Gaussian peaks; in each case, the carboxylic (protonated) signal appears to the left (at higher electron binding energies) of the carboxylate (de-protonated) signal. The positions of the C1s peaks clearly demonstrate that the change in spectral shape for the ternary $(\text{NH}_4)_2\text{SO}_4$ mixtures is in accordance with a large enhancement of the corresponding DecH feature, at more than 1 eV higher binding energies, compared to Dec⁻.

In the more dilute ternary $(\text{NH}_4)_2\text{SO}_4$ solutions, the Dec⁻ signal itself is also enhanced, compared to the spectra for either the binary DecNa solutions or the ternary

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5 mixtures with NaCl. A similar enhancement is not seen for the more concentrated so-
lutions, and this is therefore interpreted as an indication that the surfaces of the more
concentrated binary solutions are already saturated with Dec⁻. This is consistent with
observations of these solutions being close to the bulk solubility limit during sample
10 preparation (see Supplement). In the dilute solutions, the surface phase is more likely
not fully saturated and more Dec⁻ may consequently adsorb in response to changes
in solution properties. The absolute photoelectron signals for the more concentrated
solutions are indeed consistently more intense than for the more dilute solutions, sug-
gesting that surface abundances of the emitting surfactant species are enhanced in the
former, compared to the latter. Increased surface adsorption with increasing concentra-
15 tion is anticipated until surface saturation is reached, according to Gibbs adsorption
theory (Szyskowski, 1908; Gibbs et al., 1928).

Notably, in neither the more dilute, nor the more concentrated, ternary (NH₄)₂SO₄
solutions does the Dec⁻ feature *decrease*, compared to either the corresponding binary
20 DecNa solutions or the ternary NaCl mixtures. The large enhancement of DecH in the
surface phase therefore does not occur at the expense of the adsorbed Dec⁻ and
consequently more organic molecules in total (both Dec⁻ and DecH) are present in the
surface region of the ternary (NH₄)₂SO₄ solutions.

3.2 Second set of experiments

25 To investigate whether the changes occurring in the solution surface upon addition
of ammonium sulfate are caused specifically by NH₄⁺, SO₄²⁻, or the combination of
these ions, we conducted the second set of experiments in which the combinations of
cations and anions in the inorganic salts were interchanged. The corresponding XPS
spectra measured for the ternary aqueous DecNa mixtures with NH₄Cl and Na₂SO₄
are shown in Fig. 3. In each case, the relevant spectra from Fig. 2 are included again
for comparison. The two upper panels in Fig. 3 show the spectra for ternary Na₂SO₄
mixtures, together with the ternary NaCl mixtures and the reference binary DecNa
30 solutions, for the more dilute solutions (approximately 10 mM of DecNa) in the left panel

(a), and the more concentrated solutions (approximately 25 mM DecNa) in the right panel (b). The lower panels in Fig. 3 show the measured spectra for ternary NH_4Cl mixtures, together with ternary aqueous $(\text{NH}_4)_2\text{SO}_4$ mixtures and binary DecNa, for the dilute solutions in the left panel (c), and the concentrated solutions in the right panel (d).

Comparison of the spectral shapes for ternary mixtures with Na_2SO_4 and NH_4Cl in Fig. 3 to the original spectra for binary aqueous DecNa and the ternary mixtures with NaCl and $(\text{NH}_4)_2\text{SO}_4$ from Fig. 2 clearly illustrates that the additional DecH feature arises specifically upon addition of NH_4^+ ions. The shapes of the carboxylate/carboxylic acid C1s spectra measured for ternary Na_2SO_4 mixtures are fully consistent with those of binary aqueous DecNa and ternary NaCl mixtures at the same respective concentrations, whereas the spectral shapes of ternary NH_4Cl mixtures look very similar to those of the corresponding ternary $(\text{NH}_4)_2\text{SO}_4$ mixtures, with the same strong enhancement of the DecH feature in the surface region.

In an aqueous solution of either Dec^- or DecH, there will always be some of the corresponding acid or base present, due to the protonation/protolysis equilibrium given in Eq. (2). According to the acid strength of decanoic acid, as expressed by the acid constant $\text{p}K_a(\text{DecH}) = 4.9$ (Stahl and Wermuth, 2002), the vast majority of the Dec^-/DecH system will be on the basic (Dec^-) form in a solution of DecNa close to neutral pH (~ 7). Above the solubility limit (or possibly the critical micelle concentration), either of the corresponding Dec^-/DecH forms will be enhanced in the surface phase, if the respective activities ($a = \gamma_c c$, where γ_c is the activity coefficient according to the concentration scale c in question) are increased (as follows from the Szyskowski equation). This may result from increased bulk-phase concentrations, or from non-ideal interactions increasing organic activity coefficients. If more decanoic acid is formed in the solution, enhanced surface abundances can therefore subsequently be expected. Decanoic acid is intrinsically considerably more surface active than the corresponding decanoate ions (Wen et al., 2000; Fainerman et al., 2002; Lide, 2004), which would further contribute to the effect.

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



When the bulk solubility of a solute is decreased due to the addition of salts to the solution, it is often referred to as “salting-out”. Disregarding any specific changes in surface adsorption properties arising directly as a consequence of the change in mixing state, a decrease in bulk-phase solubility of a solute may be expected to increase the activity corresponding to a given concentration of this solute, below the solubility limit (or the critical micelle concentration), and may in turn also lead to enhanced surface adsorption. For an ionic solute, such as DecNa, this can formally occur, either from the additional salt increasing the individual sodium and/or decanoate ionic activities by increasing the overall solution ionic strength (I , see Eq. 3 below), or from the common sodium counter cations decreasing the specific contribution of the decanoate anion concentration to the DecNa solubility product.

We will now proceed to critically discuss these and other possible explanations for the experimental observations.

3.3 Ionic strength and salting-out

The ionic strength (on a molar concentration scale) of a solution is given as

$$I = 0.5 \sum_{i=1}^n c_i (z_i)^2 \quad (3)$$

where c_i is the molar concentration (in $[M] = [\text{mol l}^{-1}]$) of ion i , calculated from the concentration of undissociated salt and the number of ions per formula unit, by assuming complete dissociation of each salt, z_i is the charge number of that ion, and the sum is taken over all ions (n) within the solution considered. The ionic strength can be regarded as a first order approximation of the total activity of dissolved ionic solutes, and is as such an indicator of the overall strength of non-ideal solute-solute interactions in solution. However, the concept is based on considerations strictly applicable to small inorganic ions and for bulky organic ions, such as Dec⁻, with both polar and non-polar moieties, further (and non-trivial) considerations are generally needed to determine

ionic activities more accurately. It must also be noted that DecH is also expected to be affected by solution non-ideality, but as a molecular solute does not enter directly into the simplified considerations regarding ionic strength.

Calculated ionic strengths for the investigated solutions are listed in Table 3, first by including the total amount of ions present, inorganic as well as organic carboxylate ions, (I_{tot}) and second for inorganic ions – but originating from dissociation of both organic and inorganic salts – only (I_{inorg}). Solution ionic strength is enhanced relatively more in (NH_4)₂SO₄ mixtures, compared to other ternary solutions of equimolar inorganic concentrations, due to the greater number of ions per formula unit of undissociated salt and the higher ionic charge of the sulfate anions. From these considerations, it is clear that appearance of the DecH signal from the aqueous surface is not simply caused by salting-out from increased ionic strength in ternary solutions: Increasing I_{inorg} (in mM) in the more concentrated solutions from 28.6 in binary aqueous DecNa to 57.2 mM and 98.0 in ternary NaCl and Na₂SO₄ mixtures, and in the more dilute solutions from 9.8 mM in binary aqueous DecNa to 19.8 mM and 40.0 in ternary NaCl and Na₂SO₄ mixtures, makes virtually no difference in the shape of photoelectron spectra and notably does not lead to any increased intensity of the weak DecH feature.

Curiously, the often speculated salting-out of Dec⁻ from enhanced concentrations of common Na⁺ counter cations upon mixing with either NaCl or Na₂SO₄ is clearly *not* observed. In the spectra of Fig. 2, the shape and intensity of the Dec⁻ feature is unaffected by the addition of NaCl doubling the concentration of Na⁺, and Fig. 3 furthermore shows how the spectral shape is invariant between each of the binary DecNa and ternary NaCl and Na₂SO₄ solutions. This is somewhat surprising, since Na⁺ might be expected to have a salting-out effect on DecNa via the solubility product, even in the absence of unfavorable non-ideal ($\gamma_c > 1$) interactions. Poorly constrained salting-out phenomena have occasionally been invoked to explain experimental observations regarding aqueous aerosol systems. For the solutions investigated here, however, such mechanisms are clearly not at work.

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Surfactant XPS

N. L. Prisle et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The enhanced Dec⁻ surface abundance seen in Fig. 2 does indicate a salting-out effect of decanoate anions upon mixing with sulfate ions in the more dilute ternary (NH₄)₂SO₄ solutions, which may stem from the increased ionic strength in these solutions. The inorganic ionic strength is more than doubled, going from the ternary NaCl to (NH₄)₂SO₄ mixtures. Salting-out of the organic decanoate anions in solutions of higher ionic strength would in turn be evidence of non-ideal solute-solute interactions affecting aqueous solution properties, even at these rather low concentrations. This is particularly interesting in an atmospheric context, because non-ideal interactions are often assumed to be negligible for such aqueous systems as activating cloud droplets. Unfortunately, the effect cannot be verified for the ternary Na₂SO₄ solutions, owing to the lack of quantitative comparison of the XPS spectral intensities.

3.4 Equilibrium considerations

At the core of making the XPS feasible for aqueous systems is the continual renewal of the sample using the liquid jet (Winter and Faubel, 2006). This means that a new surface is formed continuously, within a time frame of the order of 10⁻⁴ s from leaving the nozzle to measurement. It is now generally accepted that this time scale is sufficiently long for the surfaces of solutions of inorganic ions and small molecules to equilibrate (Winter and Faubel, 2006). Long-chain fatty acids and their corresponding anionic bases, such as the Dec⁻/DecH pair investigated here, have however in some cases been observed to display very long equilibration time scales in dynamic surface tension measurements. These long equilibration times are nevertheless thought to be related to structural rearrangements occurring within the surface phase, rather than arising from slow molecular diffusion from the bulk to the surface, which is considered to be much faster (Prisle et al., 2008, and references therein). Still, we cannot a priori exclude that the aqueous surfaces probed in the liquid-jet experiments in this work have not equilibrated in terms of surface adsorption of either surfactant species. Naturally, this could affect the relative Dec⁻/DecH surface abundances inferred from the measured XPS spectra in Fig. 2.

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Along these lines, it would then be conceivable that insufficient equilibration times, from generation of the liquid jet and until detection of the emitted photoelectron signal, could explain our failure to observe Dec⁻ salting-out upon mixing with Na⁺, in that any potential enhanced surface adsorption of the surfactant is not captured within the time frame of the measurements. However, the ternary (NH₄)₂SO₄ mixtures do in fact show enhanced surface adsorption, compared to the binary DecNa solutions, at both the investigated concentrations. The identities of the adsorbing surfactant species (Dec⁻ and DecH) are the same, as are the concentrations, diffusion distances and experimental time scales, in these different experiments. We therefore conclude that for the present case, just as for solutions of inorganic ions and small molecules, absence of enhanced Dec⁻ surface abundances is not caused by insufficient equilibration. By the same argument, we also consider the lack of appearance of a significant DecH signal for solutions without NH₄⁺ to not be an artefact resulting from the limited time scale of the experiments.

3.5 Surface vs. bulk-phase protonation?

The decanoic acid and the ammonium cation may act as Brønsted acids (proton donors) in aqueous solution, and the decanoate and sulfate anions as Brønsted bases (proton acceptors), whereas the sodium and chloride ions have practically no acid/base properties in this respect. Mixing with NH₄⁺, and not increased solution ionic strength, is clearly the cause of the greatly enhanced DecH feature observed for the ternary (NH₄)₂SO₄ and NH₄Cl mixtures. We therefore conclude that the strong enhancement of DecH in the solution surface is due to acid-base chemistry, where a proton from NH₄⁺ is (directly or indirectly) transferred to the Dec⁻ carboxylate group, forming the corresponding carboxylic acid according to the net reaction:



This is supported by the observation of a weak nitrogen N1s XPS signal from the gas phase, originating from molecular ammonia (NH_3) evaporated from the aqueous surface.

To gain further insight into whether the observed Dec^-/DecH protonation effects are caused by changes in bulk-phase pH, or by chemistry pertaining strictly to the solution surface region, we measured the pH in the remainders of the solution samples after each liquid-jet experiment. When possible, we made parallel determinations using two different pH instruments (a portable Thermo Scientific meter and a Hanna/Mettler Toledo meter). In a few cases, there was unfortunately not enough sample available for the pH measurements to be performed. Measured pH values for the investigated solutions are listed in Table 4. None of the solutions, neither the more concentrated, nor the more dilute, had a pH significantly different from neutral, as expected from the overall dilute nature of the solutions and the fairly modest acid/base strengths of the different organic (and inorganic) solutes involved. The Thermo Scientific meter consistently gave slightly higher readings than the Hanna/Mettler Toledo, and both meters consistently showed a slightly lower pH for the more dilute (10 mM) than the more concentrated (25 mM) solutions. From the variation in the measured pH values, the accuracy of these measurements is expected to be at least within ± 0.05 . The bulk solution pH is in each case sufficiently far from the decanoic acid $pK_a (= 4.9)$ to strongly indicate that the appearance of the DecH feature in the XPS spectra must be a purely surface-specific effect.

We also performed supporting bulk- ^1H NMR measurements which confirm the interpretation of surface-specific chemistry. The individual DecH and Dec^- forms are clearly distinguishable in the proton NMR spectra. For solutions equivalent to those investigated in the XPS experiments, the ^1H NMR spectra show a bulk-phase signal which is nearly identical to that of pure DecNa in water, thus essentially devoid of any signal from the DecH form, and in complete agreement with the measured pH values. This excludes a significant change in solution bulk-phase composition as NH_4^+ donate

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



protons to Dec^- , and thus confirms that what we see in the XPS measurements is indeed a surface-specific effect.

3.6 Atmospheric implications

As mentioned, adsorption of carboxylic compounds in aqueous surfaces, and their speciation from protonation and protolysis, may have significant implications for a number of important atmospheric processes involving aqueous aerosol particles. Here we briefly describe some of these anticipated mechanisms, related to (1) heterogeneous reactivity in the condensed aerosol surface, and thus aerosol mass formation and atmospheric chemical processing, and (2) thermodynamics of atmospheric phase transformation, in terms of aerosol hygroscopic growth and cloud drop and ice nucleation. These processes in turn govern aerosol mass, properties, lifetimes and influence on atmospheric composition, and thus intricately connect to various major climate impacts of atmospheric aerosols. The list of processes and their interrelations is by no means exhaustive, just as the evaluation of the relative and overall magnitudes of their effects is left for future studies.

The total amount of organic mass adsorbed in the aqueous droplet surfaces, and in this case specifically the relative speciation of a carboxylate/carboxylic acid pair, could affect the immediate (potentially non-equilibrium) aerosol heterogeneous reactivity towards gas-phase species with (Brønsted) acid/base character, for instance ammonia (NH_3) and higher order amines ($\text{R}_n\text{NH}_{3-n}$). This will in turn affect the atmospheric processing of these species, in particular the reactive uptake to the aerosol phase and hence the formation of aerosol mass. Furthermore, reaction rates and pathways for chemical processing of organic species in the atmosphere may be greatly affected by their uptake to the condensed phase, as opposed to remaining in the gas phase. These processes and their surface specificity are in turn expected to depend on aerosol pH and the acid strength of adsorbed surface active organic species.

As an example, depending on the relative rates of diffusion and the different chemical reactions involved, NH_3 generated from NH_4^+ in the aerosol surface according to

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Surfactant XPS

N. L. Prisle et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Eq. (4) could be lost to the gas phase, as was indeed observed in the present XPS experiments, and subsequently replaced by larger organic amines forming substituted ammonium ions ($R_nNH_{4-n}^+$) that dissolve into the aqueous aerosol bulk phase. Ammonia lost by out-gassing would then on the other hand be available for atmospheric chemical “recycling”. The original aerosol mass loss from out-gassing of generated NH_3 is not expected to be dramatic, in case of similarly low solute concentrations, in particular of organics with low water solubilities. However, dissolved $R_nNH_{4-n}^+$ salts generated from gas-phase species with bulky substituents (R) could add significant mass to the aerosol phase, facilitated by much higher expected aqueous solubilities of the ions compared to the corresponding molecular forms.

Increased aerosol mass, especially dissolved aqueous ion concentrations is expected to affect aerosol hygroscopicity and cloud condensation nuclei (CCN) and ice nuclei (IN) activity from an increased Raoult effect (Pruppacher and Klett, 1997). However, the effect on water activity of non-ideal interactions in the aqueous phase remains to be firmly constrained for many of the solutes comprised in atmospheric aerosol. Furthermore, the thermodynamic framework for the various ice nucleation processes awaits further development in order to evaluate the effect of chemical composition and aqueous phase interactions. Aerosol hygroscopicity and cloud drop and ice nucleation may in turn greatly influence the addition of aerosol mass from uptake of gas-phase water, as well as formation of cloud droplets and ice crystals, and their eventual removal by precipitation, and thus the total atmospheric suspended aerosol burden.

The extent of organic surface adsorption will also affect aerosol hygroscopic and cloud and ice forming properties, by influencing the corresponding total amount of dissolved species remaining in the aqueous bulk-phase and hence the bulk water activity. The amount of adsorbed surfactant and the speciation onto different chemical forms also affect the aqueous droplet surface tension; the different forms of long-chain corresponding carboxylate/carboxylic acid pairs may have significantly different surfactant properties, in terms of both surface adsorption and surface tension reducing potential. In addition, synergetic effects on solution surface tension may arise from the simulta-

neous adsorption of several surfactant species. The resulting hygroscopicity and CCN activity could be either enhanced or impeded by the combined effects on total surface adsorption and aqueous surface tension, depending both on the relative magnitudes of these mechanisms, as well as other intrinsic aerosol characteristics (Prisle et al., 2010, 2011, 2012). Similar effects on aerosol IN activity have to our knowledge not yet been investigated.

These implications pertain to the current level of understanding and description of mechanisms affected by surface adsorption properties and speciation, from the process-level to the global scale. For example, activating cloud droplets are typically such dilute aqueous systems that non-ideal interactions are assumed not to affect their CCN properties. Here, we nevertheless see evidence of non-ideality for solutions of compositions immediately comparable to dilute droplets in the atmosphere. To properly capture non-ideal organic/inorganic solute interactions, process-level models of cloud microphysics would need to use multi-component surface tension parametrizations, or in other ways account for the enhanced organic activity coefficients in droplet solutions. Furthermore, fatty acids and their salts are found in atmospheric aerosol from all environments, whereas the common inorganic salts sodium chloride and ammonium sulfate are often related to marine and continental/urban environments, respectively. Differences in surface adsorption and speciation of organic surfactants, when mixed with these different inorganic salts, may affect properties of atmospheric aqueous aerosol, such as CCN activation, in environment-specific ways that are not accounted for in current state-of-the-art atmospheric models.

The atmospheric system is generally not in equilibrium, on either the chemical and microphysical process-level, or even on regional scales. The actual atmospheric implications of these speculated effects will all be crucially dependent upon the relative time scales of the numerous processes involved. Correct predictions of general circulation atmospheric and climate models are therefore innately limited by their ability to properly capture such processes and their relative importance on the various time scales in question. For the investigated solutions as model systems for atmospheric aerosols,

Surfactant XPS

N. L. Prisle et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Surfactant XPS

N. L. Prisle et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

directly probing the aqueous surface phase is greatly advantageous, compared to approaches based on inferring surface composition and properties from bulk-phase measurements. No implicit assumptions regarding equilibrium between the surface and bulk phases, or validity of specific adsorption isotherms, are imposed upon obtaining our present results. From a perspective of atmospheric modelling, this will lead to much better constrained characterizations and more robust parametrizations of the properties in question, than those based on results derived from (computationally expensive) iterative procedures.

Our present results provide new insights into the properties of aqueous solution surfaces of immediate atmospheric relevance. This work thus clearly demonstrates the viability of the synchrotron-based XPS technique for studying such systems. Photoelectron spectroscopy even has the potential for probing the detailed interactions responsible for these surface phenomena directly on the molecular level (Ottosson et al., 2011).

4 Conclusions

We have characterized the surfaces of binary aqueous solutions of the organic surfactant sodium decanoate, and ternary mixtures of sodium decanoate with four different inorganic salts, sodium chloride, ammonium sulfate, sodium sulfate, and ammonium chloride, using synchrotron based X-ray photoelectron spectroscopy (XPS). All solutes are common constituents of atmospheric aerosol particles.

We found that the sodium and chloride ions had no influence on the relative speciation of the decanoate anion and its corresponding decanoic acid in the aqueous surface, nor did these inorganic ions influence the individual adsorption properties of the different forms of the organic surfactant. Notably, no salting-out effect from common sodium cations of the organic and inorganic salts was observed. There are indications of decanoate salting-out by increased ionic strength in sulfate solutions, but our present results are not conclusive. Instead, mixing with ammonium cations significantly

enhanced the surface abundances of decanoic acid. This decanoic acid enhancement is caused by surface-specific protonation of decanoate by the weakly acidic ammonium ions, but does not occur at the expense of the decanoate surface abundance. Mixing with ammonium ions thus leads to more surfactant molecules in total being present in the topmost surface region of the solution.

Surface activity of some components in aqueous solution is a central, yet often not well-constrained, property determining the processing of atmospheric organic aerosols. XPS is highly surface and chemically specific, and thus ideal for direct characterization of surfactant properties and speciation in solution surfaces. Here, we have presented results of XPS experiments for aqueous solutions of organic–inorganic mixtures and at dilute concentrations, comparable to those found in the atmosphere. Our results elegantly demonstrate the successful application of XPS to solutions of immediate atmospheric relevance, and yield directly measured characterizations that shed new light to the molecular properties and interactions within the investigated aqueous surfaces. The novel results potentially have significant implications for a number of processes critical to the climate effects of aqueous aerosol, which will be the focus of future work.

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acpd-12-12453-2012-supplement.pdf](http://www.atmos-chem-phys-discuss.net/12/12453/2012/acpd-12-12453-2012-supplement.pdf)**

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



References

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- 30

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Surfactant XPS

N. L. Prisle et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

ACPD

12, 12453–12483, 2012

Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. Basic properties of the organic and inorganic salts used for sample preparation: molecular formula, molar mass (M [g mol^{-1}]), and number of ions per formula unit (ν).

Formula	M [g mol^{-1}]	ν
$\text{CH}_3(\text{CH}_2)_8\text{COONa}$ (DecNa)	194.247	2
NaCl	58.4428	2
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	322.2	3
$(\text{NH}_4)_2\text{SO}_4$	132.1	3
NH_4Cl	53.49	2

Surfactant XPS

N. L. Prisle et al.

Table 2. Measured solutions: Molar concentrations (c [mM]) of organic and inorganic salts, respectively.

Experiment	organic [mM]	inorganic [mM]
10 mM DecNa	9.8	–
10 mM DecNa + NaCl	9.8	10.0
10 mM DecNa + Na ₂ SO ₄	10.0	10.0
10 mM DecNa + (NH ₄) ₂ SO ₄	9.8	10.1
10 mM DecNa + NH ₄ Cl	10.6	23.3
25 mM DecNa	28.6	–
25 mM DecNa + NaCl	28.6	28.6
25 mM DecNa + Na ₂ SO ₄	24.5	24.5
25 mM DecNa + (NH ₄) ₂ SO ₄	28.6	27.9
25 mM DecNa + NH ₄ Cl	25.3	53.1

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Surfactant XPS

N. L. Prisle et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 3. Total ionic strength (I_{tot} [mM]) and ionic strength from inorganic ions (I_{inorg} [mM]) for the studied solutions.

Experiment	I_{tot} [mM]	I_{inorg} [mM]
10 mM DecNa	9.8	9.8
10 mM DecNa + NaCl	19.8	14.9
10 mM DecNa + Na ₂ SO ₄	40.0	35.0
10 mM DecNa + (NH ₄) ₂ SO ₄	40.1	35.2
10 mM DecNa + NH ₄ Cl	33.9	28.6
25 mM DecNa	28.6	28.6
25 mM DecNa + NaCl	57.2	43.0
25 mM DecNa + Na ₂ SO ₄	98.0	85.7
25 mM DecNa + (NH ₄) ₂ SO ₄	112.2	97.9
25 mM DecNa + NH ₄ Cl	78.4	65.7

Surfactant XPS

N. L. Prisle et al.

Table 4. Measured pH for the investigated solutions, with two different instruments: Hanna/Mettler Toledo meter (pH1) and a portable Thermo Scientific meter (pH2)

Experiment	pH1	pH2
10 mM DecNa	–	–
10 mM DecNa + NaCl	7.085	–
10 mM DecNa + Na ₂ SO ₄	6.86	6.94
10 mM DecNa + (NH ₄) ₂ SO ₄	7.06	–
10 mM DecNa + NH ₄ Cl	6.79	6.863
25 mM DecNa	7.07	–
25 mM DecNa + NaCl	6.92	–
25 mM DecNa + Na ₂ SO ₄	7.08	7.135
25 mM DecNa + (NH ₄) ₂ SO ₄	6.83	–
25 mM DecNa + NH ₄ Cl	7.08	7.122

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



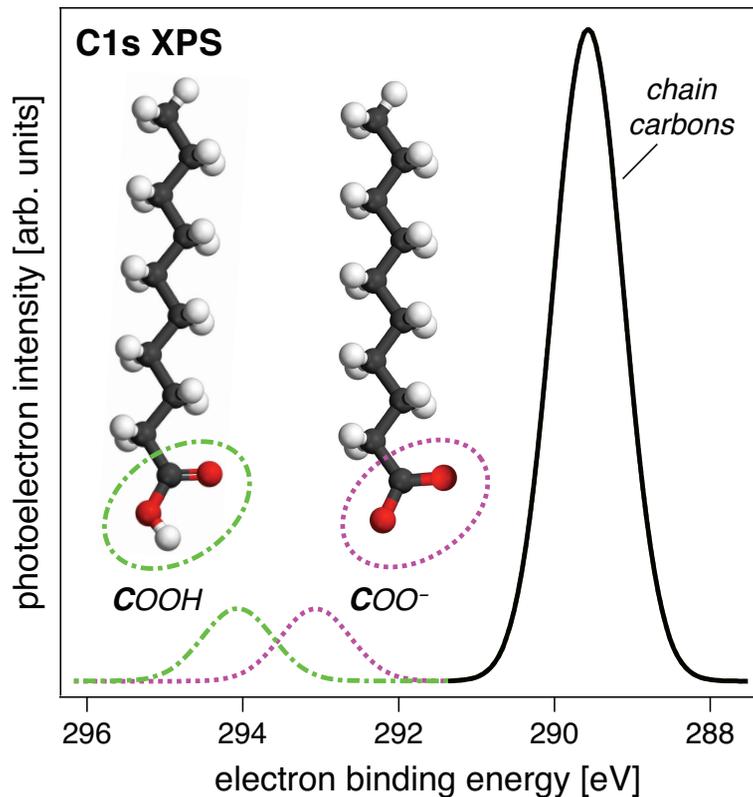


Fig. 1. Schematic representation of an X-ray photoelectron spectrum of aqueous decanoate/decanoic acid in the C1s region, showing, for increasing binding energy (from right to left ordinate), idealized signals (on an arbitrary scale abscissa) originating from aliphatic (methyl and methylene), carboxylate, and carboxylic carbons, respectively. The electron binding energy shifts for the aliphatic carbons are much smaller than for the carboxyl carbon upon (de)protonation, and have been neglected in this figure.

Surfactant XPS

N. L. Prisle et al.

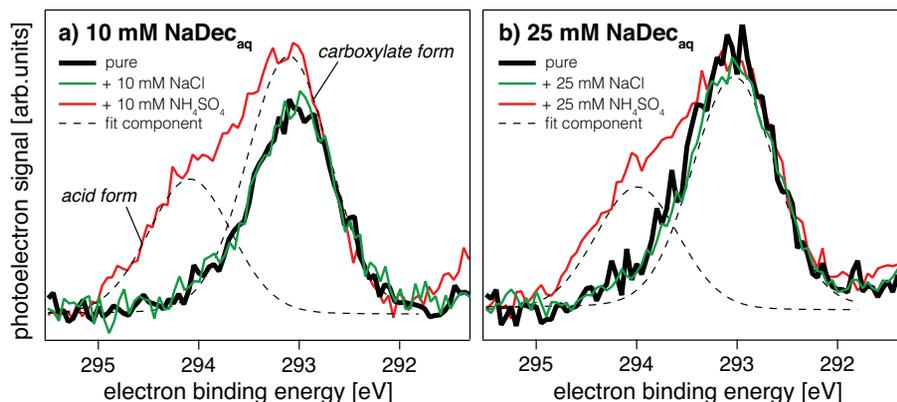


Fig. 2. X-ray photoelectron spectra for binary aqueous DecNa and ternary mixtures with NaCl and $(\text{NH}_4)_2\text{SO}_4$, showing the features in the region relevant for carboxylate and carboxylic acid C1s electron binding energies, respectively. Panel **(a)** shows spectra recorded for solutions of approximately 10 mM in each solute, and panel **(b)** shows spectra for solutions of approximately 25 mM in each solute. No change in the Dec⁻/DecH spectrum from the binary solution is seen upon mixing with NaCl, at either concentration, whereas a strong carboxylic acid feature appears in both ternary mixtures with $(\text{NH}_4)_2\text{SO}_4$. At the lower concentrations in panel **(a)**, the carboxylate signal is furthermore enhanced in the ternary $(\text{NH}_4)_2\text{SO}_4$ solutions.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

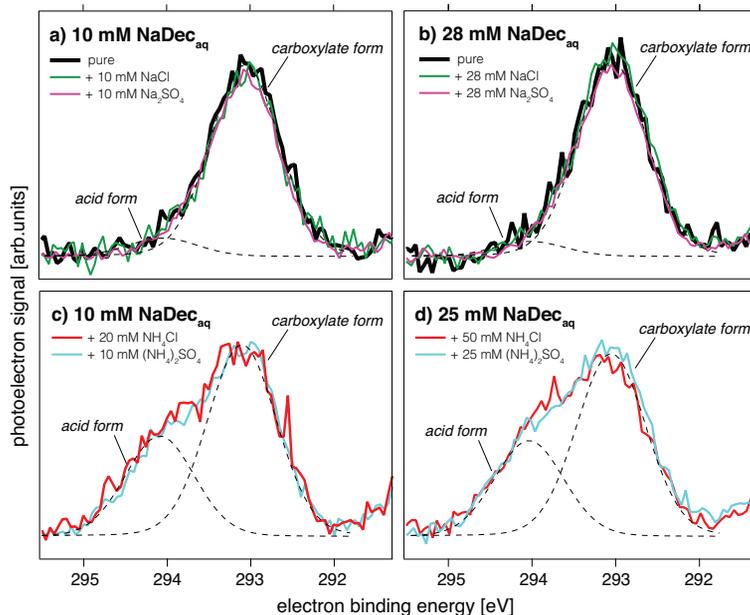


Fig. 3. X-ray photoelectron spectra recorded in the electron binding energy region relevant for carboxylate and carboxylic acid C1s for ternary aqueous DecNa mixtures with NH_4Cl and Na_2SO_4 , shown together with the relevant spectra for binary aqueous DecNa and the ternary mixtures with NaCl and $(\text{NH}_4)_2\text{SO}_4$ from Fig. 2. Spectra are shown for ternary Na_2SO_4 mixtures, together with the ternary NaCl mixtures and the reference binary DecNa solutions, for solutions of 10 mM DecNa in panel (a), and for 25 mM DecNa in panel (b). Spectra for ternary NH_4Cl mixtures, together with the ternary $(\text{NH}_4)_2\text{SO}_4$ mixtures and binary DecNa solutions, are shown for 10 mM solutions in panel (c), and for 25 mM solutions in panel (d). The strong enhancement of the carboxylic acid feature clearly occurs upon mixing with inorganic salts comprising NH_4^+ .

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)
