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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Surface/bulk partitioning and acid/base speciation of aqueous decanoate: direct observations and atmospheric implications" *by* N. L. Prisle et al.

N. L. Prisle et al.

nonne.prisle@helsinki.fi

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Final author reply to anonymous referee comments.
We thank the referees for their careful revision of our manuscript *Surface/bulk partitioning and acid/base speciation of aqueous decanoate: Direct observations and atmospheric implications*. Preparing a manuscript concerning an interdisciplinary study for a wide audience poses significant challenges and the comments and suggestions of the referees have provided a valuable aid in directing the focus of the discussion of our results. Below, we address the individual comments in detail.

Reply to Anonymous Referee # 1
The paper under discussion takes advantage of an excellent experimental approach to study an important issue. There is a severe lack of clear experimental data examining the surface structure of mixed solutions with compositions characteristic of atmospheric aerosol so this type of experiment is badly needed. A convincing set of experiments of this type and on this system would definitely warrant publication here. However, in the opinion of this reviewer, the authors do not present a large enough set of data to convincingly characterize a system of this complexity. For this reason, I do not feel that the manuscript warrants publication as a full article without, at minimum, substantial revision. It is possible that some of the needed data has been collected and not shown; the extent to which this is true is not immediately clear from the paper. Although the paper is generally well structured and clearly written, discussion of the data would also be strengthened by consideration of a body of relevant literature that is not well referenced. These points are elaborated below.

1. One of the major weaknesses of the paper is that it attempts to characterize a multicomponent system by looking at only a portion of the carbon signal. It is not clear to this reader why no data on other elements is presented. The paper makes allusions to nitrogen signal, but never shows it. This should definitely be included, since it is important to the explanation of what causes the enhancement of the DecH at the surface. I was left wondering what the solution N signal looked like, as well as wondering if the authors looked for XPS signal from the other salt components. Several things could be changing at the interface simultaneously that might contribute to an explanation of the observed results.

A: The aim of the paper is not to perform a complete characterization of the multi-component system, but rather to present the observation of a surface-specific protonation reaction affecting the speciation of the decanoate/decanoic acid system.

The atoms most influenced by changes in the protonation state of the decanoic acid are the oxygen atoms of the carboxylic/carboxylate group, but these are not useful in the present case, as the XPS O1s signal from these overlap with the strongly dominating signal from the solvent H2O. The C1s region of the carboxylate group, however, is well suited to monitor possible changes in the protonation state of the decanoic acid as the carboxylate carbon is much more influenced by this than the aliphatic carbons (as previously shown for acetic acid, see eg. reference Ottosson, 2011, 2012). By monitoring the C1s region of the carboxylate group, we show that this reaction is not induced by chloride, sulfate and sodium ions but by ammonium ions. Since ammonium is thus the case of interest, we have now in response to the referee added N1s spectra to the revised manuscript, showing that existence of a gas phase NH3 produced in the reaction.

2. I am concerned that the results might be obscured or thrown off by sample contamination, which can be a big issue in the XPS carbon region. Although the authors describe the solution preparation with care, this does not ensure that there was no contamination detectable at the level of detail capable with this technique. A surface active contaminant may by visible via XPS even after careful filtration. There are two clear ways that this could be checked. The first is to run control experiments examining the carbon spectra of water plus each added salt component. This would give the reader a way to gauge whether the salts might be bringing in adventitious carbon in the carboxylate or carboxylic acid region.
Secondly, the ratio of the fits to the aliphatic carbon signal and the combined carboxylate and carboxylic acid carbon signals could be checked (at present, the aliphatic signal is cut out of the figures). This ratio should be relatively invariant between experiments if the solutions are clean. It is possible that there could be some variation in this ratio due to changes in composition of the interface and/or orientational changes that affect the electron scattering in solution, but these effects are unlikely to be major (and can also be estimated).

A: As the referee points out, sample contamination can be a major issue in the XPS carbon region. The reason for this is that XPS is sensitive to what is on the surface, and carbon-containing contaminants are common on solid surfaces. These contaminants often arise from either carbon segregating to the surface from impurities in the sample bulk or from CO molecules in the rest gas of UHV systems adsorbing (and dissociating) and accumulating on the sample surface. In the present case, we have a continuously renewed liquid surface, minimizing the contamination from the ambient environment. The water and chemicals used for sample preparation are of highest commercially available purity, minimizing the contamination from the solution itself. As the referee points out, control experiments examining the carbon spectra of water with the salt but without the decanoate, could be done to check whether our precautions have been sufficient. For the critical case of ammonium sulfate, we have added a figure to the Supporting Material of the revised manuscript, showing such a control experiment. This was carried out with 1M of ammonium sulfate instead of the 28 mM used in combination with decanoate. Even with this 35-fold increase of the ammonium sulfate concentration no carbon signal could be detected in the control experiment. We conclude that the carbon contribution from the ammonium sulfate/water solution is below our present detection limit, and that the observed changes in the spectra are NOT due to any such contaminations.
The referee also brings up the ratio between the C1s signal of the aliphatic carbons and the carboxylate/carboxylic carbon. We have checked this, and find that it is not affected by addition of the inorganic salts. We do, however, find a small but significant difference in this ratio between the low and high decanoate concentrations. This can be interpreted as due to the molecules having a more lying-down orientation in the low concentration case, and a more standing-up orientation in the high concentration case. This would in turn be consistent with the surface being (close to) saturated in the high concentration case, but not in the low concentration case. We have added a discussion about this in the revised manuscript, and we thank the referee for this

helpful suggestion.

3. I have concerns about the reproducibility of the results. Although the authors state that, “the main results presented in this paper were reproducibly observed in both sets of experiments,” it is not clear to this reader that any of the systems examined were looked at more than once. The spectra presented from different visits to the synchrotron all appear to be of different solutions, which are then re-plotted together for easier comparison. These are complicated experiments and the study would be much stronger with some check on reproducibility. It is entirely possible that the authors did take multiple measurements of the same spectra but did not present them. If so they should present and describe the replicates in some way. A clear way to present this would be to give some idea of the reproducibility in the data fits, something about which no quantitative information is given in the paper. From the writing, it sounds as if the authors did not have the information, such as flux measurements, necessary to normalize the data for direct comparison between different runs. However, the reproducibility of fits to the carboxylate and carboxylic acid regions of the carbon spectra could be checked by looking at the ratio of fits to the two regions.

A: We realize that we may have been unclear in our description of the experimental procedure in the respect. On the the qualitative level, i.e. whether the effect exists or not for a particular added salt, the measurements have been performed several times during separate beamtimes and with separate preparations without any significant differences between these independent runs. We understand the referee’s concern for the reproducibility on the quantitative level, as some similar set-ups in the world are operated in ways that make quantitative determinations less reliable. We have therefore developed a methodology to go beyond the qualitative level, and to properly quantify the effect. For this, special care has to be taken to ensure stable measurements conditions, including both achieving, maintaining and monitoring stable conditions regarding the liquid jet and the synchrotron radiation, as well as to perform

intensity calibration measurements using reference samples. Taking this special care makes the measurements more complex, but we have nevertheless undertaken them on separate occasions to successfully confirm the reproducibility of the measurements.

4. A supporting NMR experiment is mentioned but not shown. I recommend that this be described in the Methods section and the spectra collected shown in the paper, so that the readers can better evaluate it.

A: In this case we have used a standard NMR instrument to perform a double check to confirm well-known bulk solution chemistry. Since the results are not not unexpected but relevant for the case, we mention them in the main text, and added the NMR spectra and the method description in the Supporting Material of the revised manuscript, so that interested readers may evaluate them without disrupting the main text.

5. I think that the paper, and especially the discussion, would benefit from putting these results in the context of the existing literature. There has been a lot of recent work examining acid/base speciation as well as multi-component solution structure at the liquid-vapor interface of solutions. Very little of the more molecular measurements seem to be referenced. Some groups have used XPS specifically to study this (for instance the Hemminger and Winter groups-although I note that there are some Winter group references but not some of the most relevant ones on acids). Other groups have used methods as varied as scattering from liquid jets (Nathanson) and non-linear spectroscopy (Saykally, Schultz, Allen, Richmond groups). These issues are also a source of much interest in the theory community. It is not clear to me why so little of this previous work from other groups is referenced, as it seems directly relevant to what is presented in this paper. More consideration of how this result fits in to other surface sensitive studies would enhance the discussion. The authors do a nice job, in contrast, of referencing studies with a more macroscopic approach to the same issues.

A: We have expanded the discussion on previous and most recent relevant literature in the revised manuscript, as suggested by the referee.

Reply to Anonymous Referee # 2
In this paper the authors use X-ray photoelectron spectroscopy combined with synchrotron radiation to probe the behaviour of organic surfactant sodium decanoate at the vapour-liquid interface. Directly observing the distribution of surfactant compounds in a solution is a very interesting capability and could help to resolve a long standing issue about the true effect of surfactants in atmospheric aerosol.
The paper presents the general area in a well balanced manner and results presented are seemingly caveated enough given the danger of extrapolating from proxy systems to atmospheric impact. I think the paper is appropriate for readership in this area. Whilst I do not have minor specific comments, as the paper is quite small, i do have a few observations which should be addressed before publication. I think the paper would benefit from some additional presentation of detail.

1. Page 12456. The authors chose Sodium decanoate based partially on 'sufficiently high water solubility'. Can the authors comment on what range of solubilites this technique might be restricted to?

A: The lower and upper bounds of the useful solubility range for the XPS + liquid jet technique have very different origins. The minimum concentration possible to study depends on factors such as surface propensity and ionization cross section. Ionization cross sections vary with several orders of magnitude between different elements, different orbitals in the same element and photon energy (see i.e. Yeh and Lindau, Atomic and Nuclear Data Tables 32, 1-155 (1985)). For the case of C1s and no surface enrichment of the investigated species, a minimum concentration

for practical measurements of 0.05 M may be fair, and if the species is surface enriched the minimum concentration may be as low as 0.001 M. Such low aqueous concentrations however also involve very small amounts of solute material used for sample preparation, which eventually limits the precision of the results.
There is no similar upper concentration limit, but in practice solutions which are 'too close' to the bulk solubility limit often cause the nozzle used to create the micro-jet setup to become clogged. Aqueous bulk solubility for many solutes decrease with decreasing temperature and as the liquid jet is gradually cooled in the evacuated chamber, solutes may cross the solubility limit and precipitate. We therefore mostly have to restrict the measurements to concentrations below ∼80% of the respective bulk solubility limits.
Atmospheric organics display wide ranges of aqueous bulk solubilities, but quantitative information on the exact values and their variation with mixing state in the aerosol phase and temperature is scarce. As a further complication, it is often uncertain if the values found represent the actual solubility (the maximum concentration of solute that can remain dissolved without precipitating a separate condensed phase) or rather the critical micelle concentration (the concentration above which additional dissolved molecules will start to assemble into aggregate structures, micelles, instead of remaining dissolved as individual entities). A miscibility gap may commonly exist between water and organics, separating the stable regions of their mixing diagram into an organic phase with water dissolved and an aqueous phase with dissolved organics (see e.g. Prisle et al., Geophys. Res. Lett., 37, L01802, 2010).
The liquid jet technique is targeted specifically at the aqueous region of organic-water miscibility. The upper concentration limit for the measurements is thus highly dependent on the bulk water solubility of the investigated species. The binary aqueous solubility of decanoic acid at 20°C is reported as 0.015 g/100 g H2O, corresponding to 0.77 mM (Handbook of Chemistry and Physics, 85th edition). For sodium decanoate, a binary aqueous critical micelle concentration of 94 mM at 25°C is given by A. N. Campbell and G. R. Lakshminarayanan, Canadian Journal of Chemistry, 43, 1729–

1737 (1965), and in agreement with aqueous surface tensions reported by others (see e.g. V. B. Fainerman, R. Miller and H. Möhwald, Journal of Physical Chemistry B, 106, 809–819, 2002). To our knowledge, no values are available for corresponding ternary mixtures of decanoate or decanoic acid with inorganic salts, but we observe during sample preparation that the more concentrated solutions of about 25 mM decanoate are close to the solubility limit for those mixtures. These samples therefore represent the upper concentration bound for the XPS + liquid jet measurements of the present systems. However, for other organics with higher aqueous solubilities, much more concentrated solutions can be studied.
We have added an elaboration of this aspect to the revised manuscript.

2. It would be nice to see the corresponding NMR data which dosent appear anywhere in the manuscript. Whilst the authors discuss these 'supporting' measurements it is difficult to ascertain just how helpful they were.

A: Please see reply to Anonymous Referee # 1, 4.

3. Would it not be possible to attempt prediction of the distribution of material between the bulk and surface layer in this system? This would help the reader take some qualiattive understanding on how 'bad' our predictions might be, even without a detailed thermodynamic model. The authors reference papers in which similar calculations are peformed. If these calculations cannot be made the reasons must be stated. That would be an unfortunate problem as presently we are left with measuring the potential effect of bulk/srface partitioning indirectly through single particle measurements.

A: The referee is addressing a very important point. A quantitative understanding of the amount and speciation of organics adsorbed at the aqueous surface and the surface enhancement of different species in response to changes in solution mixing

state would be the ultimate outcome of our work. Nevertheless, it is not immediately clear to us what similar calculations the referee is referring to. We reference previous work where calculations of bulk-surface partitioning in activating droplets have been made using isotherms based on measured relationships between total concentrations of dissolved organic solute and bulk aqueous surface tensions. By assuming e.g. Langmuir adsorption characteristics, the surface enhancement of organic can be estimated for binary aqueous solutions by fitting such surface tension measurements to semi-empirical relations like the Szyskowski equation, where the fitting parameters can be attributed specific physical significance. The referenced studies have iterated surface enhancement in ternary solutions from similar bulk composition-surface tension relationships. But what we exactly demonstrate in this work is that for some of the investigated organic-inorganic aqueous mixtures, a significant change in the surface composition results from surface-specific chemistry without any corresponding change in the solution bulk phase. If the changes in surface adsorption of organic species influences aqueous surface tension, as we indeed expect it might, the underlying mechanism will not be captured by the macroscopic measurements and therefore not easily resolved by relations fitted to such data. For example, based on the present findings, we would expect surface tensions to remain unchanged from those of binary aqueous sodium decanoate upon addition of equimolar amounts of NaCl, for the the more concentrated 25 mM solutions where no surface enhancement of either decanoate or decanoic acid is observed. And from the unchanged decanoate feature and enhanced decanoic acid signal upon mixing with ammonium sulfate, we would anticipate a simultaneous decrease of aqueous surface tension. The origin of such a surface tension reduction would however not be evident from the macroscopic approach and if surface adsorption was to be inferred from measured surface tension isotherms, it would be attributed to enhanced decanoate adsorption, arising from salting out by ammonium sulfate! The generation and co-adsorption of an additional surfactant species would not be captured, since there is no change in bulk solution properties following sample generation.

We nevertheless fully agree that comparison of our present result to measured surface tensions would be most useful. Surface tensions of aqueous sodium decanoate solutions is reported in the literature (see e.g. V. B. Fainerman, R. Miller and H. Möhwald, Journal of Physical Chemistry B, 106, 809–819, 2002 and A. N. Campbell and G. R. Lakshminarayanan, Canadian Journal of Chemistry, 43, 1729–1737, 1965). To our knowledge, there is however no corresponding reports of the ternary sodium decanoate–salt mixtures investigated here. These ternary surface tensions have in fact been measured earlier by Prisle and co-workers, but publication has been halted by unresolved disagreement between parallel measurements using different methods. Surface tension measurements are tedious and time consuming and we have been hesitant to perform more measurements until the discrepancies in the existing extensive data set had been resolved. This seem to now be the case. What we can say with our best conviction from this unpublished data, however, is that we do measure consistently lower surface tensions in ternary sodium decanoate solutions with ammonium sulfate than with NaCl in the transition region between pure water surface tension and the cmc/solubility point value, and both ternary solutions have lower surface tensions than binary sodium decanoate in this transition region. Above the cmc/solubility concentration, solutions converge on similar saturated surface tension values.
We are looking into ways of estimating organic surface adsorption from measurements of ternary aqueous surface tensions and will elaborate on this in the revised manuscript. In addition, we will during our next beamtime 29/10–4/11 carry out additional measurements that will allow us to quantitatively estimate the surface enrichment. The results of this and a description of the method will be added to the revised manuscript.

Reply to Anonymous Referee # 3
The work presented by Prisle et al. addresses a very interesting and important

topic that is highly relevant to timely questions on aerosol composition and resulting properties. The authors use a powerful experimental approach and I was excited to see this work. However, I am not convinced there are enough experiments nor is the discussion detailed enough on some of the technical aspects. In this reviewer's opinion, these additional details can (likely) easily be added by the authors but I would suggest additional experiments as suggested below.

1. I was a little surprised to see only 2 concentrations, and those quite dilute compared to aerosol in this study. I am not sure whether 2 concentrations are sufficient to extrapolate results. It would also be useful to add the ionic strength to table 2 and 3 for the discussion of salting in/out. I would strongly recommend that experiments at higher concentrations are conducted, especially if results are discussed within the context of aerosol (see point 8).

A: As we explain in the reply to Anonymous Referee # 2, 1, the 25 mM solutions are close to the solubility limit of decanoate and as the upper limit for stable aqueous solutions of these mixtures therefore aso represent the upper limit for XPS measurements using the liquid jet technique. To study highly concentrated solutions of water in organic-inorganic mixtures at the other stable end of the solute mixture-water miscibility range with XPS, radical and non-trivial changes of the experimental procedure are required. We agree with the referee that such investigations would be most interesting and we are in fact planning them for future work. These measurements are however still in the developmental stage and certainly outside the scope of the present work concerning the XPS + liquid jet technique.
In the present work, we have studied 5 different solute compositions, each at 2 different concentrations, and thus a total of 10 systems. Adapting the well-established setup to the surfactant systems and performing the XPS measurements has not been straight-forward and involved a considerable effort. The measurements involve significant technical challenges and consequently have a rather low success rate. We

therefore do not feel that the amount of data presented in this manuscript is small. The studied concentrations give a representative span of concentration region where measurements are feasible and yield a good signal, and furthermore give a good representation of the transition region with respect to aqueous surface tension.
We completely agree with the referee that an extrapolation of our present results to other organic surfactants, mixing states, and to concentrations orders of magnitude higher or lower than the ones investigated here are not trivial, and may likely be futile in many cases. We are not attempting such an extrapolation, but simply to report the unequivocal demonstration, using a new application of an established microscopic technique, of a phenomenon which may significantly affect predictions of properties, such as surface tensions, for aqueous systems of compositions we find to have immediate atmospheric relevance, via mechanisms that are not captured by conventional macroscopic approaches.
The atmospheric relevance of the studied systems is discussed below under point 8.
We shall be happy to include the ionic strength to Tables 2 and 4 (as we assume is meant, since they are given in Table 3), if the journal setup allows this.

2. Were calibrations of spectra undertaken? This would help evaluate the changes in the spectra quantitatively and also the degree of surface coverage. It was not clear to me whether the authors know that degree of surface coverage, which could perhaps also be evaluated with surface tension measurements (point 7) or whether it is estimated, which relates to the next point.

A: The spectra are calibrated for absolute binding energy, and relative intensities. The present intensity calibration allows us to determine whether the surface coverage changes or not. We will during our beamtime 29/10-4/11 carry out additional measurements that will allow us to estimate the absolute surface enrichment, i.e. how much higher the surface concentration is compared to the bulk concentration. The results of this and a description of the method will be added to the revised manuscript.

3. One very important technical detail, that it is not mentioned, unless I overlooked this, is the probe depth of the XPS measurement. It is mentioned that the method is surface- sensitive but the surface selectivity is another critical aspect in order to evaluate to what degree the observations really reflect only the surface. Although this is likely obvious to experts in this field it is not necessarily clear to myself and perhaps not the ACP audience.

A: This is a good point and we will elaborate in the revised manuscript. The probing depth of the XPS measurement depends on the kinetic energy of the outgoing photoelectrons. If these undergo inelastic scattering, and thereby lose energy, they will not contribute to the studied peaks but to a featureless background at lower kinetic energies. The attenuation of the signal with depth is often discussed in connection with the 'universal curve', which describes the inelastic mean free path of electrons in condensed matter. For kinetic energies in the 50-150 eV range, i.e. the one used in this case, the electron inelastic mean free path is typically in the order of 'a few Ångström'. This means that 25-75% of the signal will come from the outermost molecular layer, and the rest, 75-25%, from deeper down in the sample, however the vast majority of the signal that does not originate from the first 'few Ångströms' will still originate from molecules at the most a few nm from the Gibbs surface (Reference: C.J. Powell and A. Jablonski, Nuclear Instruments and Methods in Physics Research A 601, 54–65, 2009).

4. Liquid jets have the potential for charging to occur (Faubel et al.), which could affect the surface (e.g., hydronium concentrations) differently than the bulk, I imagine, but I am unsure whether this effect was excluded for the experimental conditions. This charging effect may depend on electrolyte content. A brief mention that charging is not important for the experiments, if that is the case, would be helpful.

A: The charging problems discussed by Faubel et al. in their earlier publications seems to largely have been due to the use of pure liquids as samples, i.e. insulating liquids without any ionic charge carriers. These charging problems disappear with the addition of small amounts of some salt, which gives the liquid jet sufficient conductivity to be grounded and thus remain uncharged. In the present cases, all sample solutions fulfilled these criteria.

5. Another piece of information that would be helpful is the temperature of the liquid jet bulk and surface. I imagine that evaporation into vacuum occurs, which should cool the surface. Are the temperatures atmospherically relevant and/or how does temperature potentially affect the results.

A: The liquid jet has a temperature of ~10°C as it leaves the nozzle, after which it starts to cool. It does remain liquid at least until the jet breaks up into droplets, and as the measurements are performed on the jet part and not the droplet part, we estimate the temperature of the liquid to be 5±5°C, i.e. in the liquid water range and thus atmospherically relevant. We expect the surface propensity in both this and other cases to be temperature dependent: Increasing temperature would probably reduce any concentration differences between bulk and surface. We have added this information to the revised manuscript.

6. There is also literature discussing that the concentration of hydronium ions is enhanced at the surface (Petersen et al. 2005), although this might be controversial (Winter et al. 2009). Could this be useful for the discussion of surface protonation, i.e., the idea that NH4+ is enhanced at the surface?

A: As the referee states, the surface enhancement of hydronium is not unambiguously demonstrated, and even the claimed hydronium surface enhancements are very weak. We do not wish to speculate whether such a weak and possible surface

enrichment of hydronium may be relevant for ammonium. As we see it, the important surface enrichment in the present case is that of decanoate/decanoic acid.

7. I would expect that surface tension measurements could have provided helpful information. If not it would be helpful to discuss briefly why they were not conducted. One would expect that the observed effects (of ammonium on surface DecH concentration) should affect surface tension. In fact, this is exactly, one of the reasons the findings matter, i.e., the effect on surface tension and resulting effects on aerosol properties.

A: Concerning the performance and availability of surface tension measurements, please see our reply to Anonymous Referee # 2, 3. We indeed expect that the findings of this work will affect surface tensions and via mechanisms that are not captured by isotherms based on macroscopic measurements. Finding means to quantify and account for this in predictions of aqueous aerosol surface tensions is a priority, but not trivial. We will discuss this in the revised manuscript.

8. The authors in the discussion and as part of their motivation extrapolate/discuss their results in the context of aerosol. However, aerosol electrolyte concentrations are typically orders of magnitude higher and I don't believe that an extrapolation of the findings reported in the manuscript to aerosol concentrations is straightforward. Are the effects, such as salting out, already clearly visible at 25 mM concentration or only at concentrations closer to aerosol conditions.

A: We do find the aqueous systems studied in this work to be of immediate atmospheric relevance. Atmospheric measurements of aerosol compositions from around the globe show a remarkable resemblance in terms of a roughly even distribution between organic and inorganic components (see e.g Zhang et al., Geophys. Res. Lett., 34, L13801, 2007). Granted, there is indeed significant variation in the results.

Furthermore, these measurements using aerosol mass spectrometry are made on a mass-composition basis, and in this work we have studies equimolar organic-inorganic mixtures which are not identical to such equal-mass compositions, since the molar masses of typical organics and inorganics found in the atmosphere are different.

As an example taken from previous work (but not published in this form, see Prisle et al., TellusB, 2008), a spherical aerosol particle, comprising pure sodium decanoate and with a diameter of 50 nm, was crudely estimated to reach the point of cloud activation for a droplet size of 100–150 nm. We here chose the smaller droplet size for a conservative estimate. Calculations assume volume additivity of the components upon forming the aqueous phase. With a molar mass of 194.25 g/mol and a mass density of 1 g/cm3 for sodium decanoate, this corresponds to a binary aqueous solution of about 0.64 mM. If half of the initial aerosol mass was instead ammonium sulfate, with a mass density of 1.769 g/cm3 and a molar mass of 132.14 g/mol, the 100 nm droplet would be a ternary solution of 0.32 mM sodium decanoate and 0.84 mM ammonium sulfate. However, droplets comprising inorganic solutes tend to activate as even more dilute solutions than those containing only organics. We therefore find that the investigated concentrations are highly representative of aqueous droplets involved in cloud formation, precipitation, and cloud processing in the atmosphere. More detailed calculations using the comprehensive thermodynamic model described by Prisle et al. (Atmos. Chem. Phys. 10, 5663–5683, 2010) will be discussed in the revised manuscript.

It must be noted, however, that this previous work has also demonstrated how surface partitioning of organic surfactants can significantly change the bulk phase mixing ratio of organic and inorganic solutes in activating cloud droplets with large surface areas, leading to much higher inorganic ratios than expected from the total droplet composition. Therefore we do agree with the referee that ternary solutions with larger inorganic solute fractions should indeed be investigated. This is certainly possibly within the context of XPS + liquid jet measurements, as ammonium sulfate and other inorganic salts are generally orders of magnitude more water soluble than organics

like decanoate. As stated above, the liquid jet experiments with surfactant solutions are elaborate. Different systems in terms of organic surfactants, organic-inorganic solute mixing ratios and total aqueous concentrations will be studied in future work.

Van den Bogaert and Joos (J. Phys. Chem., 84, 190–194, 1980) measure surface tensions of 45-60 mN/m for binary aqueous sodium decanoate in the concentration range investigated in this work. This is exactly the transition region and therefore where effects of salting out would be seen, if present.

9. Why did bulk phase pH measurements need to be conducted. I would have thought the composition should determine that in a straightforward manner.

A: The referee is completely right in that the composition determines pH. We conducted the pH measurements as a quick and easy way to exclude some possible errors.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 12453, 2012.