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

S1: Aqueous sample preparation

The aqueous samples were prepared immediately before each XPS experiment. A binary stem solution was prepared by dissolving DecNa in MilliQ water (18.2 MΩcm resistivity). The solid powder dissolved within a minute to form a clear solution. We are therefore confident that the binary solutions were below the decanoate aqueous solubility limit. The stem solution was subsequently divided into individual samples, and ternary mixed DecNa-inorganic salt solutions were prepared by adding the solid inorganic salt to the appropriate binary samples. The inorganic salts also dissolved readily to form clear ternary solutions, however, upon addition to the more concentrated (25 mM DecNa) binary solutions, it was necessary to shake the sample to ensure rapid dissolution. These ternary samples may therefore be close to the solubility limit of the organic. In determining the yielded molar concentrations, is assumed that the inorganic does not increase solution volume upon dissolution (zero mixing volume, or negative excess mixing volume cancelling the added inorganic volume). The remainder of the stem solution was then kept as the binary solution sample.

Even very small amounts of impurities may dramatically affect the surfactant adsorption properties. Therefore, great care was taken to avoid contamination during preparation of the samples. All glassware was carefully cleaned and handled with clean protective latex gloves and samples were kept under lid as consistently as possible. Futhermore, prior to measuring, each sample was filtered (Whatman Puradisc FP30 syringe filters, 1.2 µm) to remove dust and potential precipitates invisible to the naked eye, and sonicated (VWR ultrasonic cleaner) to remove air bubbles, all of which may disturb the flow in the liquid jet and cause the injection system to fail.

S2: Purity control experiment

In the experiments, the water and all the chemicals used were of high purity, and the experimental equipment carefully cleaned to avoid any unwanted carbon-containing contamination. In order to check whether these precautions were sufficient, Figure S2.1 shows the result of a control experiment for the key case of ammonium sulfate. This compares the C1s region recorded for two different solutions: ammonium sulfate + DecNa (blue trace) and only ammonium sulfate (red trace). Note that the control experiment was carried out using 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 spectrum for the solution containing only ammonium sulfate (red trace). 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 of ammonium sulfate + DecNa solutions are not due to any such contaminations.

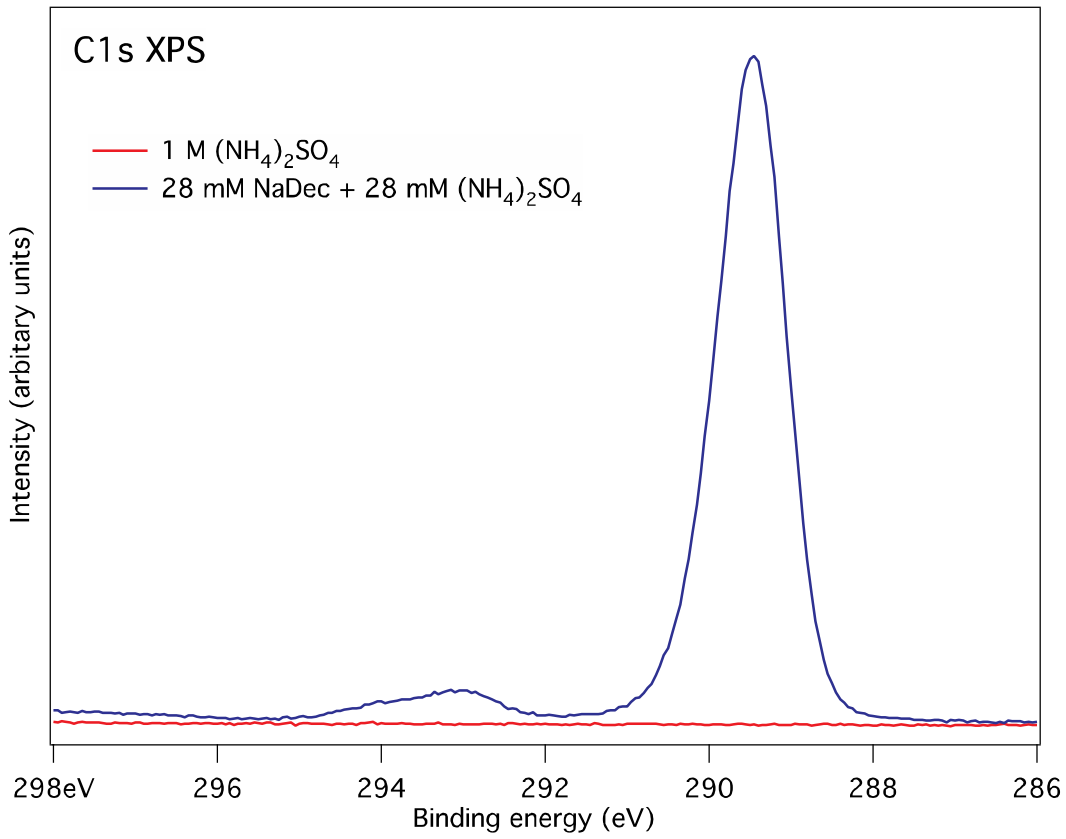

Figure S2.1: Purity control experiment for ammonium sulfate solutions with and without DecNa.

S3: Proton NMR measurements

We performed standard H^1 NMR measurements to determine the bulk Dec/Dec^- speciation. In Figure S3.1 we show H^1 NMR spectra for three different aqueous solutions: pure DecH of approximately 0.1 mM (green trace), pure 25mM DecNa (red trace) and 25 mM DecNa + 50 mM NH_4Cl (blue trace). The NMR spectra of the DecH and Dec^- both contain contributions from different inequivalent protons. Even though the DecH and Dec^- NMR spectra are related, the individual DecH and Dec^- species are clearly distinguishable in the proton NMR spectra. For the solution equivalent to those investigated in the XPS experiments (blue trace), the H^1 NMR spectra show a bulk-phase signal which is nearly identical to that of pure DecNa in water (red trace), thus essentially devoid of any signal from the DecH form, and in complete agreement with the speciation excpected from the measured pH values. This

means that the Dec^- species completely dominates in the bulk, and excludes any significant change in solution bulk-phase composition due to NH_4^+. The NMR measurements thus confirm that what we see in the XPS measurements is indeed a surface-specific effect.

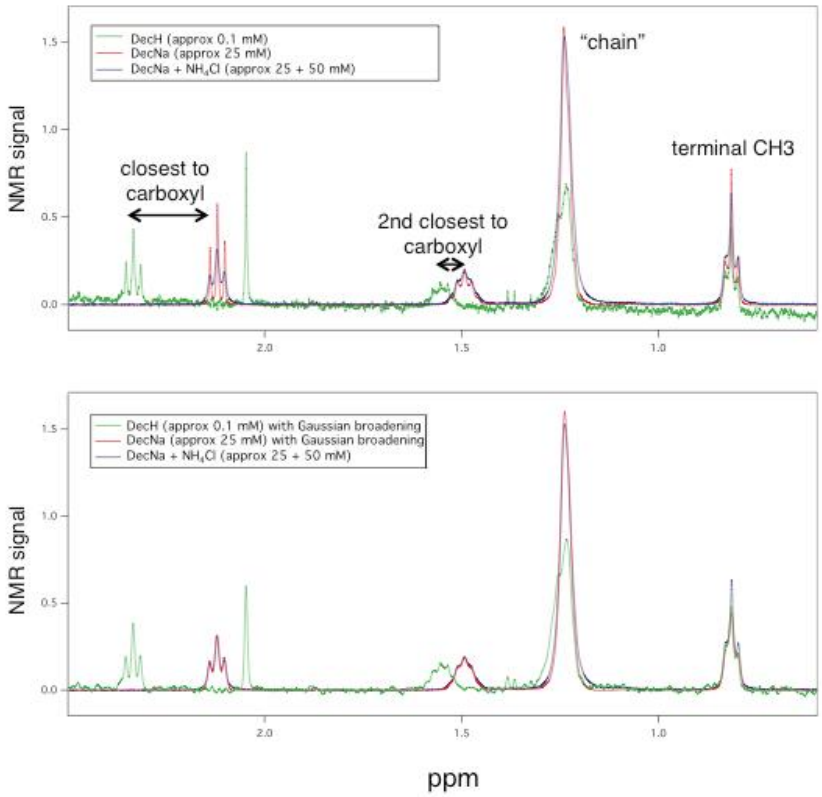

Fig. S3.1. H^1 NMR spectra of pure DecH of approximately 0.1 mM (green trace), pure 25mM DecNa (red trace) and 25 mM DecNa + 50 mM NH_4Cl (blue trace). The low solubility of DecH, causes the corresponding spectra to have not as good statistics as the others. To facilitate comparisons, we present both a raw DecH spectrum (upper panel) and a smoothed DecH spectrum (lower panel).

S4: Relative surface enrichment

To determine the surface enrichment of decanoate/decanoic acid we introduce a simplified model with a surface layer and a bulk. The total intensity of the carboxylate/carboxylic peak, normalized to photon flux and measurement time, is a sum of the contributions from molecules/ions in the bulk and molecules/ions at the surface:

$$I_{total} = I_{surface} + I_{bulk} \qquad (1)$$

The observed bulk and surface intensities depend on the respective concentrations c, and sensitivity factors n (describing the increased sensitivity for the surface layer) and a common constant k (containing cross section, geometric factors etc.):

$I_{total} = k(n_s c_s + n_b c_b)$ (2)

The bulk concentration c_b is known, and we wish to determine the relative surface enrichment c_s/c_b

The bulk contribution $kn_b c_b$ can be estimated using a reference sample of a chemically similar species with negligible surface contribution, i.e. $c_s \approx 0$, for which purpose we have chosen the formate ion:

$I_{total,formate} = kn_b c_{b,formate}$ (3)

We thus approximate the bulk contribution of Dec^- with the bulk contribution of formate:

$kn_b c_b = I_{total,formate}$ (4)

By combining (2) and (4) we obtain an expression for the surface signal:

$kn_s c_s = I_{total} - I_{total,formate}$ (5)

We now have expressions relating experimentally observed total intensities to separate bulk (4) and surface (5) contributions. By forming the ratio between (4) and (5) we obtain and expression for the relative surface enrichment c_s/c_b:

$c_s/c_b = n_b/n_s \, (I_{total}/I_{total,formate} - 1)$ (6)

To estimate the sensitivity factor ratio n_b/n_s we note that for systems without any surface segregation, and at the kinetic energies used here, the surface sensitivity is such that 50±25% of the total signal comes from the surface contribution. Pending more accurate determinations, we thus assume that:

$1/3 < n_b/n_s < 3$ (7)

Using (6) and (7) allows us to estimate the relative surface enrichment c_s/c_b of the decanoate/decanoic acid.

In the experiment we used a NaDec 10 mM solution and a 1 M Na-formate solution. The higher concentration of Na-formate was necessary since the signal from the formate otherwise becomes too weak due to its absence at the surface. The carboxylate region of the C1s XPS spectra, normalized to photon flux and measurement time, of the two solutions are shown in Figure S4.1:

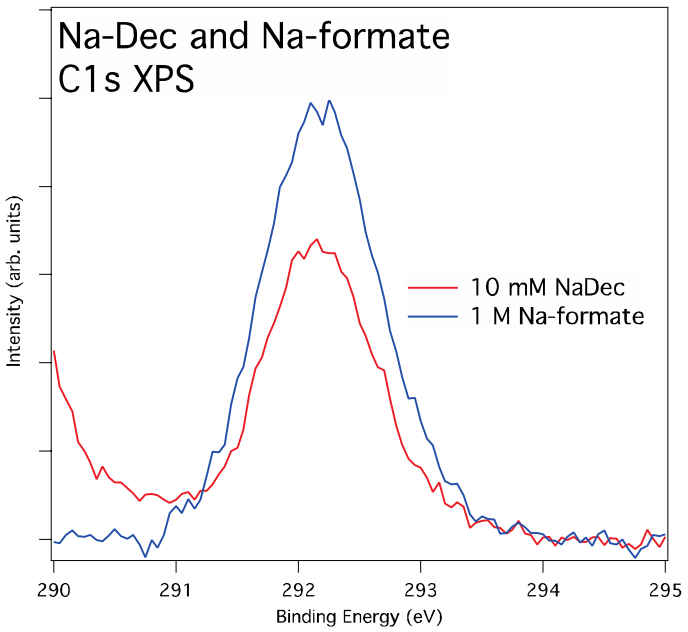

Fig. S4.1. C1s XPS spectra for solutions with NaDec 10 mM and 1 M Na-formate, respectively, normalized to photon flux and measurement time.

From fitting of the normalized spectra we obtain the intensity ratio (NaDec)/(Na-Form)=0.64. Since the concentration of Na-formate was 100 times higher than that of NaDec, the intensity ratio normalized to concentration to be inserted into (6) is $I_{total}/I_{total,formate} \approx 64$. This yields a relative surface enrichment of Dec- as $63 \cdot n_b/n_s$. As noted above, the surface sensitivity factor is not yet as well determined, but is in the range $1/3 < nb/ns < 3$. This implies that the relative surface enrichment of Dec- under these conditions is in the 20-190 range.

To translate the surface enrichment factor into an estimate for the surface adsorption Γ (in mol/m^2) of surfactant, we now further assume that the enriched surface layer has the thickness D. If the molecules all stand up completely straight, D would be equal to the molecular length L, and if they all lie down it is the molecular "thickness". Let's assume that the adsorbed species on average are oriented at a 45 degree angle relative to the surface, so that D=L/sqrt(2). A concentration C (in M=mol/L) in the bulk means that the number of molecules per volume unit is n/V. At the surface we have an enrichment factor K. The number of molecules per m^2 at the surface, n/A, would then be:

$n/A = 6.022 \cdot 10^{23} \cdot 10^3\ (L/m^3) \cdot KCD$, where D is in meters,

and the surface adsorption then becomes:

$\Gamma = 10^3\ (L/m^3) \cdot KCD$.