Supplementary Information: Strong Enrichment of Atmospherically Relevant Organic Ions at the Aqueous Interface: The Role of Ion Pairing and Cooperative Effects

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1 Nitrogen 1s

In Figure 1, one can see the XPS signal at the nitrogen 1s (N 1s) edge of $HexNH_3^+$ in the the single solute $HexNH_3Cl$ solution (blue solid), mixed solute system (black dashed), liquid phase 100 mM hexylamine (green dash-double dotted) and gasphase hexylamine (red dash-dotted). Liquid phase hexylamine intensity is multiplied by a factor of 0.35 to facilitate binding energy comparisons. The gasphase spectrum was acquired at a position where the liquid jet was moved out of the X-ray beam such that no liquid water or liquid hexylamine signal was detected. The gasphase hexylamine spectrum was calibrated against the N 1s peak of residue N_2 gas (not shown in the Figure), positioned at ∼409.9 eV [1]. By comparing the four spectra we can be sure that the binding energy shift for N 1s between the single and mixed solute $HexNH_3Cl$ solutions cannot be due to proton transfer since we then would expect an even larger binding energy shift.
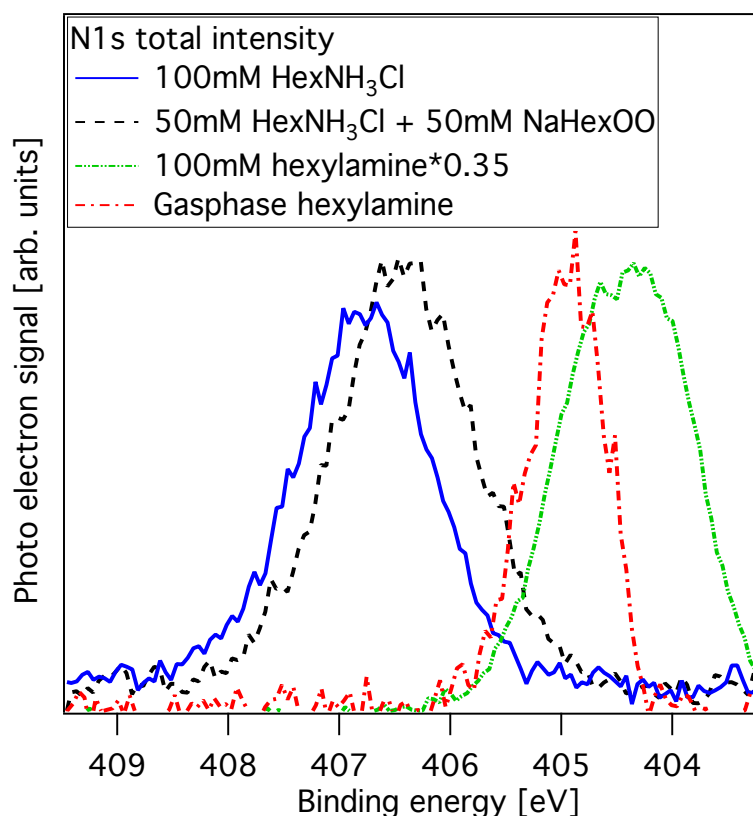

Figure 1: N 1s photoelectron spectra of aqueous 100 mM hexylammonium (blue solid line), aqueous 100 mM hexylammonium + 100 mM hexanoate (black dashed line), aqueous 100 mM hexylamine (green dash-double-dot) and gaseous hexylamine (red dash-dot).
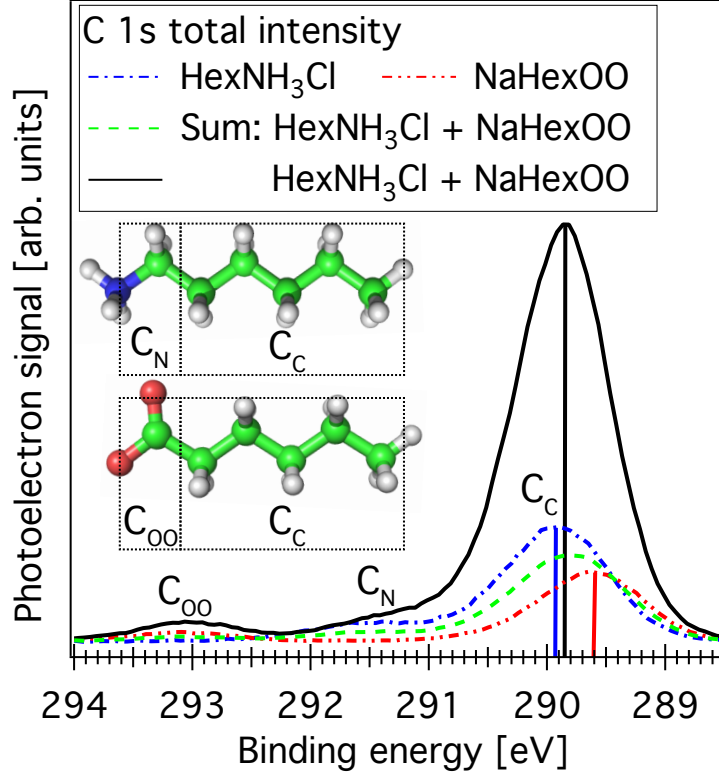
2   In depth analysis of C 1s spectra

Figure 2: The same figure as in the main paper, except the vertical lines that are supposed to highlight the C_C peak position in the different solutions.

Table 1: Intensity ratios from C 1s spectra.

Ratio	Value
Single solute solutions	
$I(C_C)/I(C_N)$	~ 5
$I(C_C)/I(C_{OO})$	~ 10
Mixed solute solution	
$I(C_C)/(I(C_N)+I(C_{OO}))$	~ 9

Due to the spectral overlap of the two C_C peaks in the mixture originating from the two alkyl chains of $HexNH_3^+$ and $HexOO^-$ in Figure 2 it is difficult to disentangle the individual differences in orientation relative to the surface comparing the single solutions with the mixed.

2.1   Single solute solutions

Returning to the C 1s spectra in Figure 2, in the single $HexNH_3Cl$ solution there are two overlapping peaks, one at around 290.0 eV corresponding to the alkyl chain carbons (C_C) which has a different binding energy position compared to the so called α carbon (closest to the NH_3^+-group, C_N) at around 291.5 eV. Intensity-ratio between the two peaks i.e. $I(C_C)/I(C_N)$ is determined to be about 5 for the single solute $HexNH_3Cl$ solution. The value is close to the stoichiometric ratio, which means that the $HexNH_3^+$ ions are laying flat on the surface. Though random orientation would also yield a 5:1 ratio, it is not very likely due to the interaction between the charge of the organic ion and the dielectric field of water. In the case of the single solute NaHexOO solution the spectrum also contains two different peaks: one at 289.6 eV corresponding to the alkyl chain carbons (C_C)

and one at 293.1 eV corresponding to the carbon in the COO$^-$-group (C$_{OO}$), with intensity-ratio I(C$_C$)/I(C$_{OO}$) of about 10. The intensity is larger than the stoichiometric ratio and suggests that the HexOO$^-$ ions are standing up relative to the surface with the alkyl chains outwards. The differences in surface alignment between the two organic ions in the single solute solutions could possibly be due to either differences in ion pairing between the organic ions and their respective counter ion or water interaction.

2.2 Mixed solute solution

All spectral components, C$_N$, C$_{OO}$ and C$_C$, are more intense in the mixed solute solution compared to the single solute solutions. Since some or both of the organic ions have changed their orientation, as will be discussed, a change in for example C$_N$ intensity does not necessarily have a one to one correspondence to the change in surface concentration. If normalizing to bulk concentration the intensity of the C$_C$ peak is about 4 times as high in the real mixed solute solution compared to the artificial sum while the sum of α carbon intensities (I(C$_N$)+I(C$_{OO}$)) is about 3 times as high. At the same time the ratio of C$_C$ and the sum of α carbon intensities, i.e. I(C$_C$)/(I(C$_N$)+I(C$_{OO}$)), is about 9 in the real mixed solute solution. In other words, since the amount of I(C$_C$) have increased more than the I(C$_N$)+I(C$_{OO}$) in the real mixture but the ratio is close to the one of single solute HexOO$^-$, we ascribe the HexNH$_3^+$ ions undergoing a reorientation as the most significant contribution to the change of the intensity ratio.

2.3 Binding energy shifts

We also observe binding energy shifts in the C 1s spectra which we can relate to the ion pairing and support the proposed reorientation of the HexNH$_3^+$ ions. The C$_C$ peak is narrower in the real mixture compared to the artificial sum and is slightly shifted towards higher binding energy. From peak fitting it seems like the binding energy of the C$_C$ peak for HexOO$^-$ has shifted to a higher binding energy while the C$_C$ peak for HexNH$_3^+$ has shifted to a lower binding energy such that they end up at the same binding energy, though the shift for HexNH$_3^+$ is smaller. Both shifts are consistent with the positive charge of HexNH$_3^+$ increasing the binding energy of C$_C$ of HexOO$^-$, while the negative charge of HexOO$^-$ decreases the binding energy of C$_C$ of HexNH$_3^+$. The reason for the binding energy shift of the C$_C$ for HexNH$_3^+$ not being as large might be due to the alkyl chain standing up in the mixed solute solution, resulting in a higher binding energy. Consequently, the net effect could instead be a small shift towards lower binding energy. This would suggest that part of the extra intensity of the C_C would come from a reorientation of the HexNH$_3^+$ ions to a standing up position.

3 Molecular dynamics density profiles

Density profiles calculated from the MD simulations are presented in Figure 3, where 3a displays the HexNH$_3$Cl solution, 3b the NaHexOO solution and 3c the NaHexOO+HexNH$_3$Cl solution.

3.1 Surface enrichment

As discussed in the analysis of the C 1s spectra in Figure 2, the organic ions are both surface enriched in the single solute solutions and even more in the mixed solute solution. This is also confirmed by the MD simulation density profiles shown in Figure 3a-c. In Figure 3a-b both single solute organic ions are enriched (HexNH$_3^+$, blue; HexOO$^-$, red). Both organic ions are even more surface enriched in the mixed solute solution (Figure 3c), at least in relative terms (since the bulk concentration of the ions are half in the mixed solute solution compared to the single solute solutions). It also seems like the HexOO$^-$ ions are more surface enriched compared to the HexNH$_3^+$ ions in the mixed solute solution.

3.2 Orientation

Note that the organic compounds at the interface in Figure 3 all have their alkyl chains pointing out of the surface. This agrees with the experimental results in the case of the single solute NaHexOO solution and the mixed solute solution, while in the case of HexNH$_3$Cl it does not. The HexNH$_3^+$

ions are, as discussed in the main paper, laying flat on the surface at this particular concentration in the single solute solution.

The discrepancies between the MD and XPS results could originate from that our MD simulations and XPS measurements are most likely probing different surface concentrations. It could be that at lower concentrations the $HexNH_3^+$ ions prefer a "flatter" orientation while at higher concentrations with a more crowded surface the $HexNH_3^+$ would be forced into an orientation with the alkyl chains pointing out, as have been seen for alcohols [2]. Another reason could be that the repulsive interactions between the alkyl chains and water is overestimated, which in turn would add to the van der Waals interactions between the alkyl chains as the they would be forced together. A third explanation could be that the MD overestimates the ion-ion interaction between $HexNH_3^+$ and its counter ion, Cl^-. With a strong interaction the Cl^- ions could follow the $HexNH_3^+$ ions to the surface and facilitate a "standing up" position.
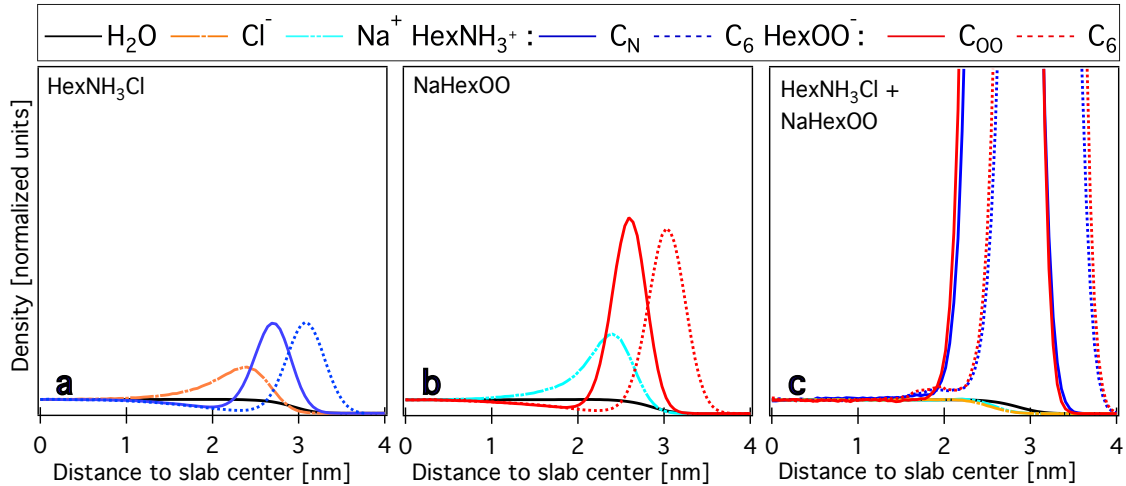

Figure 3: The MD density profiles are normalized to 1 in the bulk (slab center). In all three systems the organic ions are surface enriched and points out of the surface. The surface enrichment is even stronger in the mixed solute solution (c).

4 Cluster structure

In order to understand what the structure of the clusters look like, a distance to angle correlation has been calculated from the MD simulations. In Figure 4c-d, the distance between two headgroups of the same charge (fringe ions) is correlated to the angle they form with headgroup of opposite charge (center ion). The black curve in both graphs is the angle to a segment length in a circle of radius 3.73 Å, i.e. that if the dots end up close to the line the fringe ions are on constant distance to the center ion. The radius of the circle is estimated from the RDF of $N_{HexNH_3^+} \leftrightarrow O_{HexOO^-}$ (Figure 3(b) in the main paper), by taking the mean value distance. Also, we only display correlation points that have distances that are < 5 Å between the fringe ions to the center ions, which makes this a subset of the molecules used to calculate the RDFs (Figure 4a-b).

In Figure 4c the correlation between C_{OO}-C_{OO} distance, r_{OO}, and the angle α formed with the nitrogen of $HexNH_3^+$ is shown. It seems like the $HexOO^-$ ions are distributed along a circle around the $HexNH_3^+$ ion following the black curve, having a preference to be positioned at an angle around $\alpha = 98°\pm22°$ according to the histogram.

The same is done for the nitrogen-nitrogen distance, r_{NN}, similarly correlated to the angle β formed with the closest C_{OO} atom in $HexOO^-$, Figure 4d. Also in this case, the fringe ions are positioned on a circle around the center ion, following the black curve. Interestingly enough, the histogram shows the ions in region A have a distribution of angles around $\beta_A = 71°\pm10°$. This is the same region as in Figure 4b, i.e. the first peak in the RDF curve between nitrogen-nitrogen in the mixed solute solution. The ions in the second peak of the RDF, region B in Figure 4b, have a more even angular distribution along the circle segment line. Region A and B could correspond to two different structural situations, where A could be two $HexNH_3^+$ ions per $HexOO^-$ ion as a part of a chain with alternating ions. The B case could correspond to three $HexNH_3^+$ ions per $HexOO^-$,

where sharing 360° could lead to a distribution around $\approx 120°$, which also falls within the error bars of the fit of the histogram in Figure 4d, $\beta_A = 117° \pm 10°$.

Thus, according to the MD simulations, it seems like the organic ions in the mixed solution are structured within the clusters, with something reassembling a zig-zag chain with alternating ions with angles $\alpha \approx 98°$ and $\beta \approx 71°$.
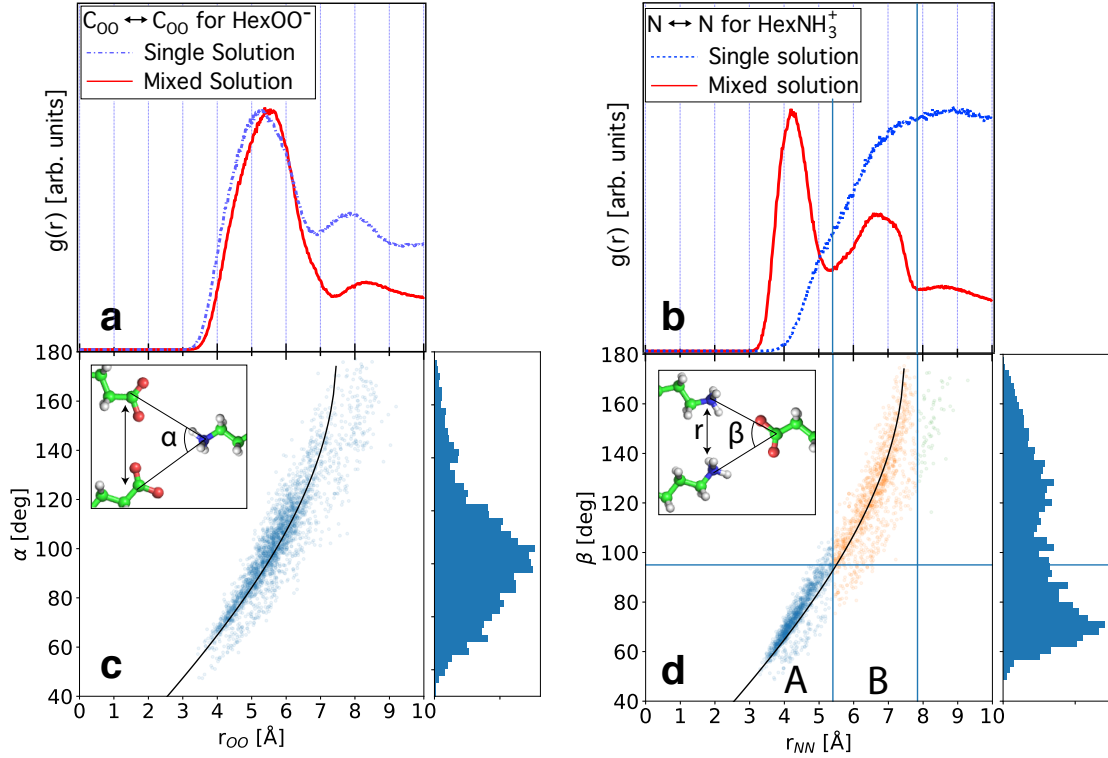

Figure 4: The black curve in c and d is the angle to a segment length in a circle of radius 3.73 Å, i.e. if the dots end up close to the line the fringe ions are on constant distance to the center ion.

References

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