Supporting Information for

Experimental Depth Profiles of Surfactants, Ions, and Solvent at the Angstrom Scale:

Studies of Cationic and Anionic Surfactants and their Salting Out

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This document contains two sections:

Part 1: Procedure for converting He arrival times to He backscattering energies and then to depths of the target element.

Part 2: Procedure for determining He backscattering energy at zero depth for elements in the absence of gas phase measurements.

The elemental concentration depth profiles in the main text rely on the conversion of arrival time \( t \) in the He TOF spectra to He backscattering energy \( E \) and then to the depth \( z \) of the target element.\(^1\) These conversions are carried out below.

1.1 Conversion from He arrival time to He backscattering energy

The conversion from \( t \) to \( E \) is given by

\[
E = \frac{1}{2} m_{\text{He}} \left( \frac{L}{t} \right)^2,
\]

where the flight path \( L \) is 1.35 m. The main text describes how zero arrival time is determined from photon emission as the He\(^+\) ion is neutralized upon impact with the surface. Correspondingly, the He atom TOF signal \( S(t) \) (after removal of the H atom sputtering background\(^2\)) is converted to \( S(E) \) by

\[
S(E) = S(t) \left| \frac{dt}{dE} \right|,
\]

where \( \left| \frac{dt}{dE} \right| = t/2E \). The signal \( S(E) \) is proportional to the backscattered He atom flux per unit energy interval.

1.2 Conversion from He backscattering energy to elemental depth

The trajectories of backscattered He atoms that are detected at our 165° backscattering geometry (Figure 2 of main text) can be divided into three segments. This division is illustrated in Figure SI.1: (1) The He atom passes through the solution and loses energy through electronic excitations and small-angle collisions with solvent and solute atoms, (2) a single head-on collision with an atom reverses the He atom trajectory back toward the vacuum, and (3) the outgoing He atom again loses energy through electronic excitations and small angle collisions. The energy loss in step 2 depends mainly on the mass of the target atom and the energy losses in steps 1 and 3 depend on the length of the helium atom trajectory, which is determined by depth of the target atom.
Figure SI.1: Example trajectory of an He$^+$ ion, neutralized at the surface, undergoing small angle scattering (step 1), backscattering from a Br$^-$ ion (step 2), and emerging into vacuum after further small angle scattering (step 3). The liquid is divided into parallel layers to calculate the He energy losses in each layer.

**Step 1: Energy loss of the incoming He atom**

We divide the solution into layers of thickness $\Delta z = 3$ Å, where this value is a small but arbitrarily chosen layer thickness, and recursively calculate the energy loss of the incoming He atom at layer $n$ from its energy at layer $n-1$:

\[
E_n^{\text{in}} = E_{n-1}^{\text{in}} - \Delta z \times \left(\frac{dE}{dz}\right)_{n-1}
\]

where $<dE/dz>_{n-1}$ is the average stopping power (energy loss per depth) at the kinetic energy of the projectile while passing through layer $n-1$. The initial He energy, $E_0^{\text{in}}$, is 5000 eV in our experiments. The stopping power is not constant but varies with $E^{1/2}$. This empirical relation is found to be

\[
\left(\frac{dE}{dz}\right)_n = 0.0445 \sqrt{E} + 0.8451
\]

with energy $E$ in units of eV and depth $z$ in units of Å. The coefficients are determined by fitting
data obtained for He atom backscattering from alkanethiolate monolayers, where the stopping powers were measured to be $2.3 \pm 0.2$ eV Å$^{-1}$ for 1.07 keV He atoms and $3.7 \pm 0.6$ eV Å$^{-1}$ for 4.12 keV He atoms.\textsuperscript{5} At our initial energy of 5000 eV, the stopping power is computed to be $4.0 \pm 0.7$ eV Å$^{-1}$. Over a 30 Å (10 layer) depth, the mean energy loss is 109 eV, lowering the initial He atom energy from 5000 to 4891 eV.

**Step 2: Head-on Collision between He and target element**

At a depth $z$, the He atom collides with the target element and loses kinetic energy according to the kinematic relation:

$$E_{n}^{\text{out}} = E_{n}^{\text{in}} \times \left( \frac{\cos \theta + \sqrt{A^2 - \sin^2 \theta}}{1 + A} \right)^{2} = K \times E_{n}^{\text{in}}$$  \hspace{1cm} \text{(S1.3)}

where $A$ is the mass ratio $m_{\text{element}}/m_{\text{He}}$ and $\theta$ is the backscattering deflection angle of 165°. For $^{79}\text{Br}$ atoms, $E_{\text{out}}/E_{\text{in}}$ is 0.819 and for O atoms it is 0.366. The loss in energy of the He atom upon collision with a $^{79}\text{Br}^-$ ion at a depth of 30 Å is $(1-K) \times E_{\text{in}} = 884$ eV. Because the backscattering energy is not precisely the same as predicted by the kinematic relation above, an offset $Q'$ is introduced to account for this difference:

$$E_{n}^{\text{out}} = K \times E_{n}^{\text{in}} - Q'$$  \hspace{1cm} \text{(S1.4)}

The term $Q'$ is a combination of physical and experimental factors, summing over the energy loss due to electronic excitations during the head on collision with the atom from which the He projectile is backscattered and any offsets in the incident He$^+$ energy or flight path. It may therefore be positive or negative. For bromine, oxygen, and sulfur, $Q'$ is determined as the difference between the kinematic prediction of the backscattering energy an incident energy 5000 eV and the peak energy of the corresponding measured gas-phase spectrum. Part 2 of this SI describes the procedure to determine $Q'$ for elements without a gas-phase measurement, which applies to carbon and sodium in our study.

In our experiments, $Q'$ is measured to be -79 eV for He-Br$^-$ collisions at 5000 eV (for He-
O and He-S collisions, \( Q = -13 \text{ eV and } -12 \text{ eV} \). Using our example of a He-Br\(^{-}\) collision at a depth of 30 Å, \( E_{n}^{\text{out}} \) equals \( K \times E_{n}^{\text{in}} - Q = (4891 - 884) - (-79) = 4086 \text{ eV} \). We emphasize that the two components of \( Q \), the electronic inelasticity and the experimental offset, are not measured individually. Only the sum \( Q \) is determined by comparison with gas-phase measurements. The \( Q \) values are listed here to provide a sense of their magnitudes, and will change with each new set of experiments.

### Step 3: Energy Loss of Outgoing He Atom

The backscattered He atom again loses energy through multiple small angle deflections given by

\[
E_{n-1}^{\text{out}} = E_{n}^{\text{out}} - \Delta z' \times \left( \frac{dE}{dz} \right)_{n}
\]

where \( \Delta z' = \Delta z / \cos(15^\circ) = 1.035 \Delta z \) because the outgoing trajectories detected in the 165° backscattering geometry are not perpendicular to the surface. The outgoing energy loss is 104 eV starting at the 30 Å depth considered above. The overall energy loss summed over the three steps is 109 + 805 + 104 = 1018 eV, dominated by backscattering from the Br\(^{-}\) ion. The He atom ideally emerges from solution with an energy of 3982 eV.

We note that the He energy loss of 109 eV in the incoming trajectory is similar to the 104 eV value in the outgoing trajectory. This similarity is accidental and will be different following a head-on collision of He with an O atom instead of with a Br\(^{-}\) ion. In the case of an He-O atom collision at 30 Å, eq S1.3 yields \( E_{n}^{\text{out}} = 1790 \text{ eV} - Q = 1803 \text{ eV} \). Additionally, eq S1.4 yields 77 eV, which is significantly lower than the outgoing 104 eV energy loss. Together these losses generate a final energy of 1726 eV as the energy with which the He atom will be detected.

### Step 4: Empirical Correlation between the Observed Backscattering Energy and Elemental Depth

The individual energy losses arising from steps 1, 2, and 3 sum to the observed He backscattering energy \( E_{\text{final}} \) following collision with a target atom at depth \( z \) and penetration
through the solution. We tabulate this overall energy loss every 3 Å and fit it by a quadratic function \( z(E_{\text{final}}) = \alpha E_{\text{final}}^2 + \beta E_{\text{final}} + \delta \), which is found to match the tabulated energy losses well. Table S1.1 lists the coefficients for Br, O, C, S, and Na.

<table>
<thead>
<tr>
<th></th>
<th>Br</th>
<th>S</th>
<th>Na</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>7.387\times10^{-6}</td>
<td>1.187\times10^{-5}</td>
<td>1.612\times10^{-5}</td>
<td>2.588\times10^{-5}</td>
<td>4.353\times10^{-5}</td>
</tr>
<tr>
<td>( \beta )</td>
<td>-0.2023</td>
<td>-0.2449</td>
<td>-0.2760</td>
<td>-0.3301</td>
<td>-0.3982</td>
</tr>
<tr>
<td>( \delta )</td>
<td>718.1</td>
<td>644.2</td>
<td>597.6</td>
<td>520.0</td>
<td>440.1</td>
</tr>
</tbody>
</table>

Finally, the quadratic function is used to convert the measured backscattering energies \( E \) to depths \( z \), along with the transformation \( S(z) = S(E) \left| \frac{dE}{dz} \right| \), which is given by eq S1.2. The last step in creating the molar concentration depth profiles is the conversion of \( S(z) \) to molar concentrations \( c(z) \), as described in the main text.

### 1.4 Energy Loss Straggling

The quadratic \( z(E_{\text{final}}) \) formula above represents the average energy loss and does not imply that there is a one-to-one relation between the observed backscattering energy \( E \) and depth \( z \) of the target atom. Because of the diversity of small angle and backscattering collisions, and because of inelastic energy exchange through electron excitations during collisions between He and the target atom, there is a range of backscattering energies that correspond to a single depth \( z \) (and vice versa). This dispersion around the mean value given by \( z(E) \) is called energy loss straggling.\(^1,6,7\) Electronic excitations in the He-target atom collision are the primary contributor to this dispersion and are already present in the measured gas-phase distribution. They are thus automatically incorporated in the genetic algorithm fitting procedure. For example, collisions of a 5000 eV He atom with a Br\(^-\) atom generate a dispersion in energy losses measured in the gas phase to be 110 eV as the FWHM of its Gaussian distribution.
Part 2. Determining the He Backscattering Energy at Zero Depth for Elements in the Absence of Gas Phase Measurements

We report the concentration depth profiles for sodium and carbon in the main text, which require a measurement of the He backscattering energy \( E(z=0) \) at zero depth \( z \), located at the outermost surface of the solution. This energy sets the zero-depth mark for each profile. The values of \( E(z=0) \) are determined for Br, O, and S from the peak kinetic energy measured in gas-phase collisions between He\(^+\) and CHBr\(_3\), O\(_2\), and thiophene, as described in the main text. We do not have gas-phase measurements, however, for the elements C and Na, and we therefore find alternative routes to determine \( E(z = 0) \) for Na and C atoms (the gas-phase carbon signal is too weak to measure and Na is not easily injected into the gas-phase without evaporating pure sodium). These routes are described in the following paragraphs.

**Determining \( E(z = 0) \) for carbon.** We first assume that the oxygen and carbon profiles in glycerol are the same, as confirmed through molecular dynamics simulations.\(^8\) We then compare the carbon profile to the fully calibrated oxygen profile because its gas-phase spectrum has been measured using O\(_2\). As illustrated in Figure S1.2, the carbon profile is first plotted using the estimated kinematic contribution to the backscattering energy predicted by eq S1.3. The oxygen profile is then plotted on the same graph. Because the offset \( Q'_{\text{carbon}} \) is not zero, the two spectra do not coincide. The net offset is found by moving the carbon curve, along with its energy scale, until it overlaps with the oxygen curve. The result is that \( E(z = 0) = 1325 \text{ eV} \), which is the sum \( K_{\text{carbon}} \times E_{\text{in}}^0 - Q'_{\text{carbon}} \), where \( E_{\text{in}}^0 \) is the incident 5000 eV He\(^+\) energy.
**Figure SI. 2.** The carbon profile is shifted along with its energy scale (black) until it overlaps (blue) with oxygen profile plotted on its depth scale (red).

**Determining $E(z = 0)$ for sodium.** Because the sodium depth profile differs from all other elemental profiles, we cannot use the procedure above to determine $E(z = 0)$. As illustrated in Figure SI.3, we can instead use the correlation between the predicted kinematic exit energies from eq 1.3 and the measured gas-phase energies for Br, O, and S, along with the inferred $E(z = 0)$ for C, to roughly predict the $E(z = 0)$ value for Na. The four elements with known $E(z = 0)$ are well aligned on a straight line from which the sodium zero-mark energy can be easily deduced. The differences between the experimental calibration and the kinematic prediction may be caused by electronic excitations in the backscattering collision and by an unknown deviation of the primary beam energy from the acceleration voltage of 5.00 kV. For Na, this procedure was used to determine the zero-depth mark $E_{\text{sodium}}(z=0)$ to be $2511 \pm 40$ eV. This uncertainty in
energy translates into a shifting of the Na profile over ±8 Å, making the relative position of the Na depth profile significantly less determined than the other elements in Figure 13 in the main text.

**Figure SI.3.** Correlation of kinematic (x-axis) and gas-phase experiments for $E(z=0)$ (y-axis) at a primary He energy of 5000 eV. The least-squares equation of the line is $E_{\text{exp}} = (0.959 \pm 0.010) \times E_{\text{kinematic}} + (109 \pm 29) \ (R^2 = 0.99)$. The $E(z=0)$ value of 2511 eV for sodium is read directly from the y-axis.
References


