

The opposing effect of butanol and butyric acid on the abundance of bromide and iodide at the aqueous solution - air interface

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SUPPORTING INFORMATION

MD simulations - methods

Classical molecular dynamics simulations were employed to study interactions of NaBr and NaI with BuOH and BuOOH. The slab geometry was constructed in which two monolayers, each containing 116 BuOH/BuOOH molecules (Fig. S1), were placed at the two air/liquid interfaces of the water slab, with the -C-OH/-C-OOH head groups immersed in water. The water slab was placed in the center of a prismatic simulation box, elongated along the interface normal in order to create a vacuum layer over both monolayers. Standard 3D periodic boundary conditions were applied. First, a pure monolayer system was simulated to obtain an equilibrated monolayer at

lateral compressions by NVT simulations with 0.12 M of NaBr or NaI ionic solutions. Both systems were constructed with 5.4 nm size in X and Y, which represents a fairly relaxed monolayer. In all cases, the size of the system in Z direction was taken as 15 nm. Following short energy minimization, a 120 ns MD run was performed for scaled systems equilibration from which the last 20 ns were used for analysis. Results obtained for both monolayers were averaged during the analysis of simulation trajectories. MD simulations were performed employing the empirical OPLS all-atom force field (Jorgensen, Maxwell et al. 1996) for the organic molecules and the SPC/E model of water (Berendsen, Grigera et al. 1987). The lengths of bonds were constrained using the SETTLE/LINCS algorithms (Hess, Bekker et al. 1997). The short-range interaction cutoff of 10 Å was employed, while the long-range electrostatic energy was accounted for using the PME scheme. Temperature in all simulations was set to 298 K and controlled using the Nosé–Hoover thermostat with a coupling constant of 1 ps (Nose 1984, Hoover 1985). Each simulation was carried out at a constant volume and a constant lateral cross-section of the simulation box. Equations of motion were integrated using the leap-frog algorithm with a time step of 2 fs. MD simulations were performed using the GROMACS 4.6.7 program package (Hess, Kutzner et al. 2008). The density profile for different groups was calculated based on particle mass at a certain coordinate.

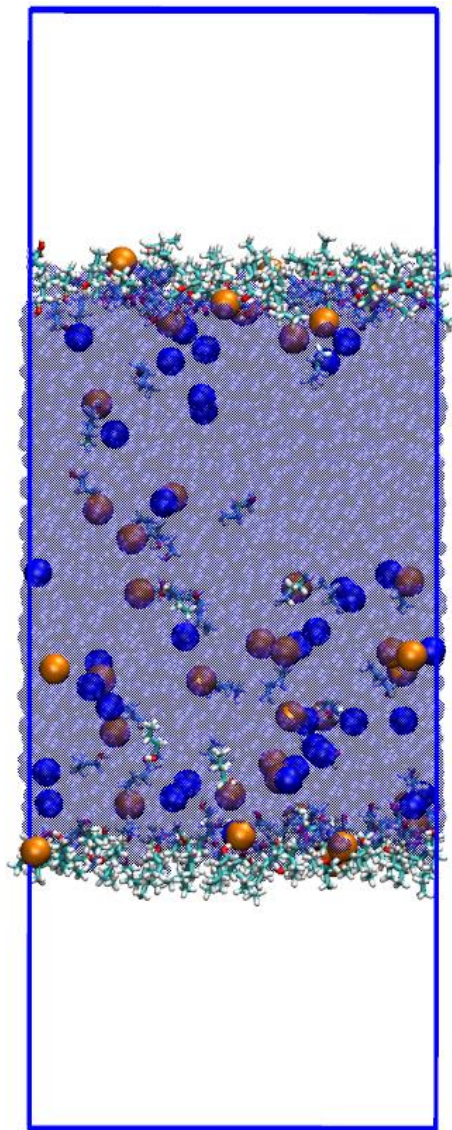


Fig. S1. Last snapshot of the simulation models (120 ns) for BuOH in NaI solution. Water molecules are shown as transparent in light blue, Na^+ ions in dark blue, I^- ions in orange and BuOH molecules which are shown by their elements.

MD simulations – results

To obtain insight into the behavior of bromide and iodide in the presence of BuOH or BuOOH, we performed MD simulations of the solutions studied here. Fig. S2 a,c show the averaged density profiles of halide anions along the normal to the solution/vapor interface for the neat

solutions in absence of organics. Both iodide and bromide ions display a significant surface affinity with high density at the interface with a layer of enhanced Na ion density underneath, which is accompanied by a depletion zone of the halide ions below the interface, consistent with previous studies on neat halide solutions using the same methods. For both solution types, the effect of the organics is to suppress the density of the halide ions at the interface, bromide being more affected than iodide, and butanoic acid having a slightly stronger suppressing effect than BuOH (Fig. S2 b,d). It seems that also in presence of both BuOH and BuOOH, both halide ions remain enhanced at the outermost surface in comparison to the Na cations. The somewhat larger near-surface peak of iodide is accompanied by an also larger Na⁺ ion peak underneath to equilibrate the overall charge of the bilayer.

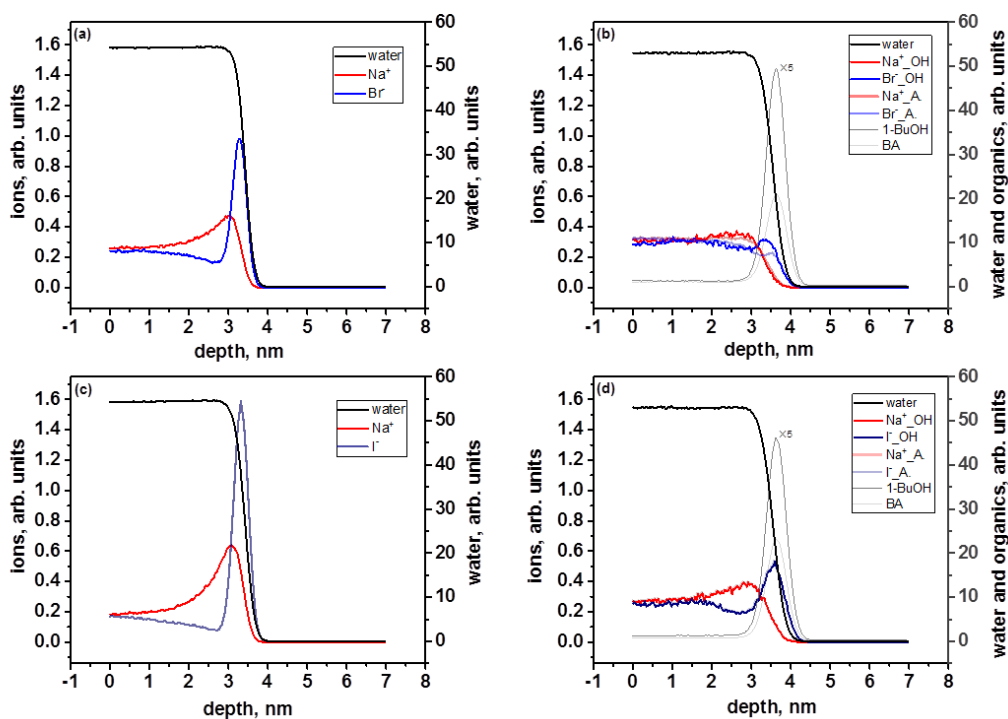


Fig. S2. (a) Density profile of Br (blue), Na (red), and water (black) atoms of aqueous 0.12 M NaBr solution. (b) Density profile of Br (blue with BuOH; light blue with BuOOH), Na (red with BuOH; light red with BuOOH), and water (black) atoms of aqueous 0.12 M NaBr solution in the presence of BuOH (grey) or BuOOH (light grey). (c) Density profile of I (navy), Na (red), and water (black) atoms of aqueous 0.12 M NaI solution. (d) Density profile of I (navy with BuOH; light navy with BuOOH), Na (red with BuOH; light navy with BuOOH), and water (black) atoms of aqueous 0.12 M NaI solution in the presence of BuOH (grey) or BuOOH (light grey).

In order to compare the density profiles returned by the MD simulations with the XPS data, the density profiles were integrated in a similar way as presented by Krisch et al. (Krisch, D'Auria et al. 2007). They used an approach wherein electron attenuation in the solution was modeled by a simple exponential decay with respect to the depth into solution, as described in equation 1:

$$S(\text{KE}) = \int_0^{z(\rho_{50\%})} \rho(z) dz + \int_{z(\rho_{50\%})}^{\infty} \rho(z) e^{-z/\lambda(\text{KE})} dz \quad (\text{equ. 1})$$

S denotes the relative photoemission signal obtained from electrons with a given kinetic energy, KE , $\rho(z)$ is the density profile of the atom the core level (photo)electrons of which contribute to S , z is the distance from the dividing plane placed at the position where the total density reaches half of its maximum value ($\rho_{50\%}$), and $\lambda(\text{KE})$, is the KE-dependent inelastic mean free path of the photoelectrons. The first term is the integral of all surface components lying above the dividing plane for the neat solution $z(\rho_{50\%}) = 3.4$ nm, while for the other solutions $z(\rho_{50\%}) = 3.8$ or 3.7 nm (corresponding to the x-axis in Fig. S2) in the presence of BuOH or BuOOH respectively. Above $z(\rho_{50\%})$ the density is at most 50 % of its bulk value ($\rho_{50\%}$); therefore attenuation of photoelectrons originating from this region is neglected in this simplified approach. The second term describes the exponential attenuation of photoelectrons originating from atoms in the bulk with the density profiles derived from the MD simulation.

The results, depicted in Fig. S3 a (for bromide) and b (for iodide), shows the relative departure of the normalized simulated photoemission signal using equation 1, derived from the density profile of ions, from their value for the neat halide-solutions. The LJ-XPS results for the corresponding solutions are plotted as hollow symbols in both panels. PE signals for sodium, bromide, and iodide at the interface, observed in the aqueous salt solution, were decreasing with increasing bulk BuOH or BuOOH concentration in general. The reduction is more apparent in the presence of BuOOH than BuOH. Qualitatively, this suppression effect also becomes apparent in the simulated signals derived from the MD simulations. At a more quantitative level, clear differences in the relative effects of BuOH and BuOOH on bromide and iodide between simulated and measured signals become apparent. The simulated photoemission intensities clearly indicate opposite response of bromide and iodide to whether BuOH or BuOOH is present, whereas in the measurements, they behaved in parallel. We also note that when in addition

calculating the O1s signal intensities (not shown), the ratio of Br/O signal intensities behave exactly the other way round in response to the presence of BuOH and BuOOH as observed in the measurements (Figure 4c and d of the main text). This relative trend of the simulated photoemission intensities was also independent of the position chosen for the dividing plane, z , used to evaluate equation 1 between 3.0 and 3.6 nm. On one hand, it should be noted that there is significant scatter in the experimental data, especially for the iodide solutions, and the simulations rely on heavily simplified assumptions regarding electron scattering in the strongly structured interface. In turn, these apparent discrepancies between measured signal intensities and those estimated from the MD simulation results might be an indication of the fact that the ionic parameters used in the present work may overestimate the bromide and iodide enhancement at low concentration in the absence of organics as discussed in the main text.

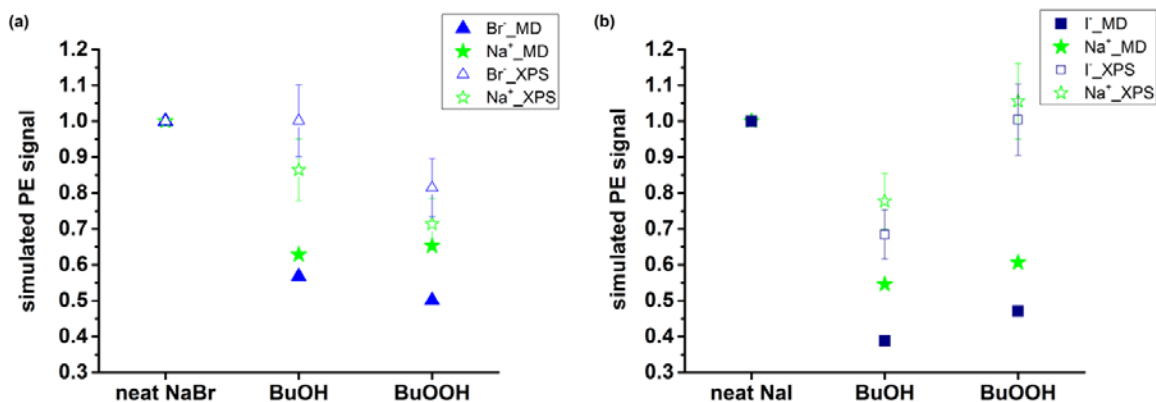


Fig. S3. (a) Normalized changes to the simulated photoemission signal, S , of bromide (blue triangle), sodium (green star) of aqueous 0.12 M NaBr solution as a function of functional group of organics with bulk concentration 0.12 M as derived from the MD simulations using equation (E1). (b) Normalized changes to the simulated photoemission signal, S , of iodide (navy square), sodium (green star) of aqueous 0.12 M NaI solution as a function of functional group of organics with bulk concentration 0.12 M as derived from the MD simulations using equation (E 1). The hollow symbols denote the experimental results for the corresponding solutions in both panel (a) and (b).