

Aqueous solutions: a look at the surface

Vincenzo Carravetta^a

^a *Institute of Chemical and Physical Processes - CNR, Pisa (Italy)*
carravetta@ipcf.cnr.it

In aqueous solutions the acid-base chemistry at the surface can be quite different from that in the bulk; this aspect is of great importance for several processes. For instance, the presence of surfactant molecules in the atmosphere is known to influence the nucleation process and hence the creation of droplets that ultimately form clouds. Amino acids are water-soluble organic compounds that can play such a role. Originating from phytoplankton and bacteria, they are injected into atmospheric droplets over oceans by bubble bursting.

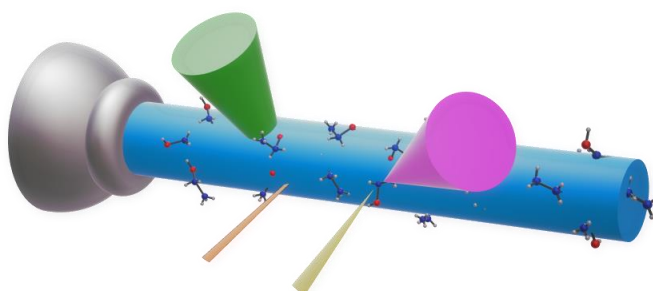


Figure 1: X ray photoemission from a micro-jet of an aqueous solution of cysteine.

By a joint experimental and theoretical study, an aqueous solution of cysteine is here taken as a prototype system to explore distribution and protonation states of such amino acid. It is shown how both properties, which are, of course, strongly affected by the average acidity of the environment, also exhibit large differences between surface and bulk. X-ray photoelectron measurements at N1s and S2p edges are interpreted by means of reactive molecular dynamics simulations for predicting the composition of the aqueous solution at different pH and by quantum calculations for predicting the binding energies and the chemical shifts. At specific pH values, we find that the distribution of the cysteine species at the surface is quite different from that of the bulk, for the appearance in the surface region of species, containing the COOH group, which do not exist in the bulk. Likewise, we predict the occurrence at the surface of “low pH species”, containing NH₃⁺ and SH groups, which do not exist in the bulk of medium/high pH solutions. This finding, however, cannot be used to infer straightforwardly that the surface propensity of H⁺ is different from that of the bulk of the aqueous solution.

References

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