Contribution of different molecules and moieties to the surface tension in aqueous surfactant solutions

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The calculation of the lateral pressure profile in computer simulations of anisotropic systems is an important problem in various respects; however, it is not a straightforward task at all. The difficulty stems from the fact that pressure is an inherently non-local quantity, which has to be localized in the profile calculation. Further, if an Ewald summation-based method is used to account for the long range part of the intermolecular interactions, the reciprocal space term of this correction is not pairwise additive. We have proposed an accurate and computationally very efficient way of calculating the profile of the lateral pressure, which can also take into account the reciprocal space term when using the sPME method. Further, this way the lateral pressure can be distributed among the interacting atoms in the system as if it were a pairwise additive quantity. Since the surface tension is the integral over the imbalance of the lateral and normal pressure components, and the latter of them is constant, this method allows us to calculate the contribution of the individual particles, molecules and moieties to the surface tension. Recently, we have used this method to determine the surface tension contribution of the different molecules and moieties (i.e., water, headgroup, tail, and, if present, also counterions) in aqueous surfactant solutions. We have considered five different amphiphilic molecules, representative of anionic, cationic and non-ionic (alcoholic) surfactants in this respect. We have found that the headgroups of alcoholic surfactants give a negligible contribution to the surface tension, while the opposite is true for ionic surfactants and counterions, which give much larger (positive and negative) contributions than the total surface tension itself. [1] We investigate the effect of the counterion type and charge sign in this respect. [2,3] Concerning the type of the counterions, the observed trends are qualitatively compatible with the Hofmeister series, with the notable exception of sodium. [3] In the artificial system where the counterion and surfactant charges are inverted in sign, the surface tension contributions of the counterions, surfactant headgroups and water molecules even change their sign. [3] Since the charge inversion makes the counterions considerably harder, the results stress the key role of the hardness of the counterions in this respect. However, the hydration free energy gain of the counterions, occurring upon charge inversion, is compensated by the concomitant free energy loss of the headgroups and water molecules, leading to negligible change in the surface tension of the entire system.

REFERENCES

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