

STRUCTURE AND PROPERTIES OF SOFT ORGANIC-AQUEOUS INTERFACES

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The interfaces formed by water and aqueous solutions with organic soft matter play an important part in nature and technological applications. Good examples are provided by water in contact with surfactants, self-assembled monolayers, polymers, biomembranes, and other biological matter. A characteristic feature of most soft organic-aqueous interfaces is a deep interpenetration of the aqueous and organic phases, resulting in a wide interfacial region that can formally be regarded as an interphase. The anisotropy, inhomogeneity, thermal disorder, and large extension of the interfacial region in width make the structure and properties of such interfaces difficult to study with the available experimental techniques. The situation is particularly complicated in sandwich-like systems, where water or an aqueous solution is nanoconfined between organic phases. This occurs, for instance, when two biomembranes come close together, so that their interfacial regions interact and intersect.

The range of experimental techniques employed in analyzing the structure, chemistry, and dynamics of soft organic-aqueous interfaces includes x-ray and neutron scattering, NMR, nonlinear vibrational spectroscopies (such as sum frequency generation and second harmonic generation), fluorescence spectroscopy, as well as surface force measurements using surface force apparatus, osmotic stress method, and atomic force microscopy. Surface force measurements are particularly important in studies of sandwich-like systems because the measured force-separation dependence is closely related to the structural and dynamic properties of the interfacial region.

Despite the substantial progress in the above-mentioned experimental techniques, their abilities in revealing the detailed molecular organization of soft organic-aqueous interfaces are rather limited. This attaches significance to computer simulations, which provide a molecular level description of the interfaces based on an appropriate model (forcefield) for the potential energy of the system. The diffi-

culties involved in computer simulation of soft organic-aqueous interfaces are mainly associated with a fairly high density and inhomogeneity of the interfacial region, a large size of the molecules forming the soft organic phase, and a large number of the degrees of freedom needed to describe the configurational states of these molecules. All these factors together may lead to ergodic problems in sampling the configurational space of the system. As a consequence, special methods may be required to attain a representative sampling. Unfortunately, this problem has not yet received due attention in computer simulations of soft organic-aqueous interfaces. In particular, there have been only few attempts to check whether the results of a computer simulation are dependent on the choice of the starting configuration of the system.

Another important problem involved in computer simulations of organic-aqueous interfaces is the treatment of mixed interactions, i.e., the interactions between water and the molecules making up the organic phase. The matter is that the water affinity of the organic phase and all related properties are determined by a delicate interplay of the mixed interactions and the interactions between similar molecules. The wide use of ill-grounded combining rules for mixed Lennard-Jones parameters, as well as the combination of partial atomic charges derived for the organic phase molecules and water in different ways (e.g. from *ab initio* calculations for the former and by empirical fitting to experimental quantities for the latter) can hardly be justified for interfacial studies. In this respect, the CHARMM forcefields, where the parameters of mixed interactions were optimized in a more or less independent way, are certainly more preferable.

This In Focus section of *Biointerphases* contains a few representative articles which provide the reader with an idea of the basic problems involved in experimental and computational studies of soft organic-aqueous interfaces.