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ABSTRACT: Specular neutron reflectometry is a powerful technique to resolve interfacial compositions and structures in soft matter. Surprisingly however, even after several decades, a universal modeling approach for the treatment of data of surfactant and phospholipid monolayers at the air/water interface has not yet been established. To address this shortcoming, first a systematic evaluation of the suitability of different models is presented. The result is a comprehensive validation of an optimum model, which is evidently much needed in the field, and which we recommend as a starting point for future data treatment. While its limitations are openly discussed, consequences of failing to take into account various key aspects are critically examined and the systematic errors quantified. On the basis of this physical framework, we go on to show for the first time that neutron reflectometry can be used to quantify directly *in situ* at the air/water interface the extent of acyl chain compaction of phospholipid monolayers with respect to their phase. The achieved precision of this novel quantification is ~ 10%. These advances together enhance significantly the potential for exploitation in future studies data from a broad range of systems including those involving synthetic polymers, proteins, DNA, nanoparticles and drugs.

Introduction

Specular neutron reflectometry (NR) is an experimental technique that can be used to provide a direct measure of the surface excess of a surfactant or phospholipid monolayer at the air/water interface thanks to the use of isotopic contrast variation.[1,2] It can also be used to reveal the intefacial composition and structure of more complex systems through the application of a common physical model to data recorded in multiple isotopic contrasts. An important reason for the use of isotopic labeling is that deuterium scatters neutrons strongly and in a different phase to hydrogen, so the incorporation of deuterium atoms in a species enhances its sensitivity selectively, and mixtures of H_2O and D_2O can be used to tune the scattering of an aqueous subphase. Recent advances in instrumentation have meant that it is now possible to resolve the surface excess of a single deuterated species on the second time scale and the composition of a binary mixture involving only one deuterated component on the minute time scale.[3,4,5]

Nowadays, NR provides routine insight into complex systems in soft matter and biology.[6,7] It is most common to treat experimental reflectivity data through fitting models using the optical matrix or Parratt formulism for stratified media.[8] Surprisingly, however, the approach to model even a system as simple as a surfactant or phospholipid monolayer at the air/water interface is far from universal. Variations in the approach include whether to account for changing monolayer coverage by varying its thickness or density, which itself appears to be related to the need to include surface roughness, whether to have one or more layers, and whether to account for a change in density of a phospholipid with respect to its phase.

A model where changing coverage is accounted for principally by a change in density rather than thickness, while effects of surface roughness are neglected, appears to date back to an early NR study on Langmuir monolayers of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) in 1994.[9] It was stated that surface roughness was not included in the model as it did not improve the quality of the fits. In work soon after on Gibb's monolayers of sodium dodecylsulfate (SDS) in 1995,[10] the applied model involved a single layer with a thickness close to the all-*trans* conformation of the alkyl chains and different volume fractions. This model, with the molecules standing rigidly on end, was applied even at monolayer coverage of < 10%. While the physical basis of such a model may be reasonably questioned, good agreement with the data, although notably in only one isotopic contrast of the subphase, was demonstrated. Zero[11] or rather low[12] layer roughness values have continued to be used in some studies, and inclusion or not of the parameter in applied models is not even mentioned in others to this day.[13,14] Such an approach may have originated as a result of the lower neutron flux over the accessible range in the momentum transfer normal to the interface, Q_z, on early instruments and/or the assumption that inclusion of roughness in a model is simply a consequence of not having split the system into enough layers.[15]

Such an approach is seemingly in contradiction to the capillary wave roughness of ~ 2.8 Å for a bare air/water interface resulting from thermal fluctuations,[16,17] and its inverse square root dependence on the surface tension