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Langmuir monolayers as unique physical models

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ABSTRACT

Physico-chemical processes at air/liquid interfaces are of paramount importance in nature. The Langmuir technique offers the possibility of forming a well-defined monolayer of amphiphilic molecules under study at the air/liquid interface, with a unique control of the area per molecule and other experimental conditions. Despite being a traditional technique in Colloid and Interface science, there is an ever growing interest in Langmuir studies. Herein, recent developing fields of research currently taking advantage of the Langmuir technique are reviewed, comprising the interfacial structure of: water, biomolecules and inorganic/organic hybrids. The good state of the Langmuir technique at present and the foreseeable increase of its usage are discussed.

1. Introduction

Langmuir monolayers have been described more than a century ago, yet Langmuir monolayers are a model system of current and even growing interest in Colloid and Interface Science [1–3]. This review is aimed at highlighting current lines of research in which Langmuir monolayers are making a most important contribution. Of note, this review does not aim to cover the complete range of studies using Langmuir monolayers to any extent.

Langmuir monolayers are single monomolecular layers of a given surface active molecule at the air/liquid interface. The typical experimental procedure for the formation of Langmuir monolayers is rather simple. The deposition of the amphiphilic molecules onto the liquid surface is done by gently placing a defined amount of a solution of the surface active molecules in a volatile organic solvent which is not miscible with water but has a high spreading coefficient. After the evaporation of the organic solvent on time scales of minutes, the polar headgroups of the surfactants stay in contact with the liquid subphase, and the non-polar hydrocarbon chains point to the air. The Langmuir monolayer can be compressed to given values of area per molecule. The changes in the surface tension of the air/liquid interface are monitored by a Wilhelmy plate microbalance.

The unique features of the Langmuir technique are a) a precise control of the available area per molecule at the air/liquid interface, b) an impressive plethora of techniques for extensive characterization of the molecules at the air/liquid interface, and c) simplicity of the physical model. These features make Langmuir monolayers a most useful platform for the detailed study of intermolecular interactions at hydrophobic/hydrophilic interfaces.

Langmuir monolayers have been extensively used with great success for in situ characterization of surfactant molecules at the air/liquid interface since the seminal work by Langmuir [4] inspired by previous findings of Pockels [5]. Indeed, the number of publications concerning Langmuir monolayers has been continuously growing in recent decades, see Fig. 1. Two interesting points are highlighted in Fig. 1. First, a relatively small increase on the number of publications is observed between 1980 and 1990, see arrow 1. An almost exponential growth of the number of publications with time has been registered in the period between 1990 and 1999, indicated by arrows 1 and 2, coincident with the development of novel in situ methods at the air/liquid interface, mainly UV–vis reflection spectroscopy [6], InfraRed Reflection Absorption Spectroscopy (IRRAS) [7], surface selective Sum Frequency Generation (SFG) Spectroscopy, Brewster Angle Microscopy (BAM) [8,9] and most important X-ray diffraction and reflectivity [10]. This period is of course coincident as well with an increase on the absolute number of publications in research journals, but the general trend is still valid. Second, right after the previously mentioned period a stabilization of the increasing rate of publications concerning Langmuir monolayers with time is observed. The growing trend changes from exponential to linear after 1999 up to the present moment, with a positive slope indicating the ongoing interest of the research community in the Langmuir technique.

The Langmuir technique is currently used for a wide variety of purposes under different perspectives. The statement of an exhaustive

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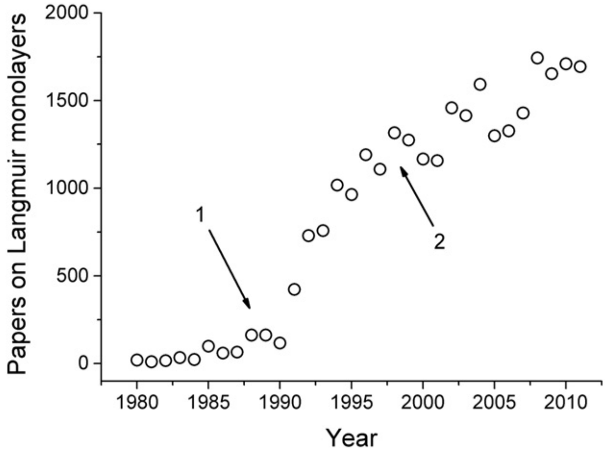

Fig. 1. Number of publications per year including the keywords "Langmuir monolayer" obtained using ISI Web of Knowledge. Search performed on 15/04/2013.

list of research topics using Langmuir monolayers is far beyond the scope of this review. Generally, the Langmuir technique has been proved to be most useful for the study of the arrangement of surface active molecules at the air/liquid interface under a physical chemistry perspective [9,11]. This usage of the Langmuir technique is expected to continue to be of interest in the upcoming years, and undoubtedly interesting contributions will be achieved.

The absence of relevant papers in the reference section is noted. Herein we aim at stating a rather short and comprehensive general highlight of current relevant trends in research based on the Langmuir technique. Therefore, apologies to the colleagues which work is omitted in this review are due.

This review aims at highlighting ongoing fields of research as current cutting-edge areas where the Langmuir technique might offer unique and most valuable insights, as well as reviewing the recent advances in those directions. These research areas represent the broad range of applicability of the Langmuir technique, being: a) a detailed structure of interfacial water, b) biophysics of peptides at interfaces, and c) interfacial supramolecular tailoring of inorganic/organic composites.

2. Detailed structure of interfacial water

A fine description of the structure of the air/water interface is fundamental for a number of top relevant areas as biophysics, atmospheric chemistry, interfacial chemistry and electrochemistry, yet such a basic question as how is water arranged at an interface is still controversial and unresolved. Therefore, this structural description of the air/water interface is currently pursued, being the focus of different studies [12]. Computational and experimental techniques have been used concerning this topic, being the most commonly used: molecular dynamics in computer simulations [13], SFG spectroscopy [14••] and ElectroSpray Ionization Mass Spectrometer (ESI-MS) in experimental studies [15]. As stated in the Introduction, complete description of the lively ongoing debate on the enrichment of the air/water interface in either hydroxide or proton ions is beyond the scope of this review. On the other hand, some significant recent examples are reviewed herein in the spirit of stating the frame of this inspiring field of research, as well as illustrating the usefulness of the Langmuir technique in this research.

The H-bonding situation of the water molecules in either pure water or any type of solution cannot be extrapolated from the bulk to the air/liquid interfacial region. The classical picture of a bare air/water interface containing no ions has been contested by revealing computational and experimental studies [16].

The group of Allen has made excellent contributions in this area. The core aspects of the bare air/water interface with no surfactant molecules were described by SFG and IRRAS spectroscopy, using different sodium halide solutions as subphase. The broad water band at 3000–3600 cm^{-1} commonly observed in SFG and IRRAS studies was used to monitor the structure of interfacial water. The deconvolution of this broad band allowed the analysis of the different contributions, i.e., stretch vibrations including H-bonds and coordinated water molecules with a variable degree of ordering. The modification of this band by the different halide ions was found to be proportional to the size and polarizability of these halide ions. A large polarizability of a given anion resulted in an increased polarizability of the water molecules coordinated to that anion. A quantitative and highly revealing description of the enriched presence of anions at the air/liquid interface proportional to the polarizability of the anions was given [14••]. Therefore, the study by Allen et al. constitutes a significant step in the understanding of the interfacial Hoffmeister effect [17]. This increase in the surface concentration of anions leads to a larger distortion of the interfacial water molecules compared to the water molecules at the bare air/water interface. The so-called interfacial depth, that is, the thickness of the liquid layer physically different to bulk solution, was found to increase with the addition of highly polarizable anions. Besides the interest concerning the interfacial water structure in aqueous solutions of anions, this result is highly relevant for the general validity of the SFG spectra. Indeed, the results given by SFG spectroscopy have been contested on the basis of an uncertain probing depth, although this limitation is part of an ongoing debate [12]. The idea of a varying interfacial depth with the presence of different ions is most relevant to biological and atmospheric chemistry.

In a related study using vibrational spectroscopy, the effect of divalent cations on the structure of interfacial water was also examined. The key parameter for the three studied cations, i.e., Mg^{2+}, Ca^{2+}, and Sr^{2+}, was the surface charge density. The surface charge density significantly varies proportionally to the variation in the size of each cation. The modification of the structure of the interfacial water was found to increase with increasing size of the cation. The interfacial depth follows this trend. The relative orientation of the water molecules at the air/liquid interface was also modified by the cations [18].

In a further step towards a general picture of the interfacial water, Allen reported on a study concerning interfacial water at Langmuir monolayers of biologically relevant phospholipids. In an elegant approach using either positively or negatively charged phospholipids as the sole component of the Langmuir monolayers, the change of the relative orientation of the water molecules in layers close to the lipid headgroups was described, see Fig. 2. A negatively charged headgroup in the Langmuir monolayer is able to orient the interfacial water molecules with the hydrogen atoms directed to the Langmuir monolayer, whereas a positively charged headgroup in the Langmuir monolayer leads to an orientation of the oxygen atom pointing to the Langmuir monolayer. This phenomenon was observed for anionic phospholipids, i.e., DPPA, DPPG, and DPPS. The interfacial water at the zwitterionic DPPC Langmuir monolayer shows a similar ordering as in the case of negatively charged monolayers, albeit to a less extent. The general trend of the ordering of interfacial water was also indicated by the surface electrostatic potential. Indeed, by adding Ca^{2+} cations to the subphase the binding of these cations to the DPPC headgroups resulted in a significant dehydration of the polar headgroups. Therefore, the Ca^{2+} cations partially reduced the effect of the DPPC headgroups in the ordering of interfacial water [19••].

The structure of interfacial water is pertinent as well in the interactions of biomolecules, as DNA, with the cell membrane. This topic is of special relevance for the rational design of lipids designed for gene therapy. In a SFG spectroscopy-based study from the group of Bonn, the SFG signal arising from the interfacial water is deeply discussed, the adsorption of the DNA to the phospholipid monolayer