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Measuring concentration depth profiles at liquid surfaces: Comparing angle resolved X-ray photoelectron spectroscopy and neutral impact collision scattering spectroscopy

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ABSTRACT

Measuring concentration depth profiles is important for analyzing surfaces. The surface excess, the change in concentration from the surface to the bulk and separation of the constituents are some of the features that can be derived from concentration depth profiles and are most important in particular for analyzing liquid surfaces. Angle resolved X-ray photoelectron spectroscopy (ARXPS) and neutral impact collision ion scattering spectroscopy (NICISS) are methods used for determining concentration depth profiles at liquid surfaces. Here we compare concentration depth profiles determined with both methods from the constituents of a solution of the ionic surfactant tetrabutylphosphonium bromide in the polar solvent formamide. ARXPS is performed with a laboratory X-ray source and NICISS with 4.5 keV helium ions. Agreement is found in the surface excess and in the shape of the cation concentration depth profiles. Disagreement was found in the shape of the anion concentration depth profiles. The separation of charges as found with NICISS for projectiles with low kinetic energies could not be reproduced. The advantages of each of the methods and the criteria for selecting the projectile energy in NICISS are discussed.

1. Introduction

The composition and molecular structure determines the function of all kinds of interfaces like biological membranes, surfaces of detergent solutions, catalysts, electrodes or droplets in the atmosphere. Measuring concentration depth profiles is one of the most important approaches to investigate both the composition and the molecular structure of surfaces. Concentration depth profiles inform about the composition of the surface and the gradual change from the surface to the bulk. A number of methods have been developed to measure concentration depth profiles. One approach in measuring concentration depth profiles is applying a surface sensitive method alternating with sputtering the samples; thus removing the upper layers stepwise. Such an approach can be chosen in case the constituents of a sample have such a low mobility that diffusion is much slower than the sputtering process. This approach can be applied to a number of solid samples but cannot be applied to surfaces where the species have a high mobility like liquid surfaces as the constituents would rearrange too quickly while the sample is sputtered. Thus the mobility of the constituents forming a sample has a large influence on which methods can be used to analyze the respective surfaces.

Another feature in which liquid and solid surfaces differ is their surface roughness. The roughness of a solid surface depends not only on the nature of the materials but also on the method of preparation. A liquid surface, however, has a surface roughness which is given only by capillary waves [1]. Capillary waves have a low ratio between the amplitude of the waves and the wavelength and thus show inherently a low surface roughness. Capillary waves with a wave length of a few nanometers have to be treated separately. However, at this wavelength surface roughness has to be treated as local topography rather than a capillary wave as will be discussed later.

There are a few methods which are capable of directly determining concentration depth profiles at liquid surfaces. The reflectivity methods like Neutron Reflectivity (NR) [2–5] or X-ray Reflectivity (XR) [3,6,7] are used to determine concentration depth profiles by measuring how the refractive index changes with the depth. As the refractive index depends on the scattering length density of the neutrons or the X-ray, both methods require that there is sufficient contrast in scattering length density between the constituents of a sample.

A second class of methods is electron spectroscopy. Of particular interest for determining concentration depth profiles is X-ray Photoelectron Spectroscopy (XPS). The method is surface sensitive due to the limited mean free path of electrons in matter which is in the

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order of a few nanometers. Concentration depth profiles can be determined either by changing the angle of observation of the emitted photo electrons or by changing the kinetic energy of the photoelectrons. In the first case the distance the electrons are traveling through matter is varied and thus the depth from which the electrons can escape the sample is varied. In the second case the fact is used that the mean free path of the electrons changes when the energy of the electrons is changed. A variation in electron energy is achieved by changing the energy of the X-ray irradiating the liquid surface [8]. The challenge of this method is to quantify the electron mean free path.

The third class of methods are ion scattering techniques ranging from kinetic energies in the order of MeV (Rutherford Backscattering (RBS)) to around 100 keV (Medium Energy Ion Scattering Spectroscopy (MEIS)) to a few keV (Neutral Impact Collision Ion Scattering Spectroscopy (NICISS)). The depth information of these methods relies on the energy loss processes of the projectiles on their trajectory through the sample. The depth resolution and range of these methods is given by the inelastic energy losses during backscattering, the energy loss straggling and blurring of the scattering angle due to the low angle scattering. Medium and high energy methods have been used to investigate surfaces of ionic liquids [9,10] while the low energy method NICISS was used in particular to determine the surface excess of solutes [11] and preferential adsorption at surfaces.

Both the ion scattering methods and the electron spectroscopy techniques are vacuum based techniques. Thus the question arises whether or not the evaporation of the liquid in the vacuum chamber influences the surface structure. It has been shown by means of computer simulations that the diffusion constant of the solvent molecules in the liquid phase is in general that large that evaporation is much slower than the diffusion of solvent molecules in the bulk [12]. Thus, even though the liquid surface in vacuum is strictly speaking not in equilibrium, the structure of the liquid surface is that close to that in equilibrium that the differences are negligible.

Though measuring concentration depth profiles at surfaces with the described methods is well established, how different methods compare is still discussed [13]. Here we want to compare ARXPS and NICISS. The subject of the investigation is the surface of surfactant solutions. Surfactant solutions have two advantages over solid surfaces for such a comparison. Firstly liquid surfaces do not have a large but also well known surface roughness as the roughness of the surface is given only by capillary waves [1] and the local environment around the species [14]. As long as the angle of observation of the applied method is not too close to the direction parallel to the surface, the surface roughness has negligible influence on the spectra. Secondly, the only prerequisites for reproducibly preparing a liquid surface are that the concentration investigated is reproducible and that there are no surface active impurities in either of the components. The solution of tetrabutylphosphonium bromide (Bu_4PBr) in formamide we have investigated here fulfills these conditions very well. The amount of solute can readily be determined with any standard balance. Surface active impurities can be detected with both methods and while each has its own strength and weakness, when combined they are able to detect any significant amount of a surface active impurity. An amount of impurities has to be considered as significant when it changes measurably the surface properties. Examples for changing measurably the surface properties would be changes in surface composition for a few percent or a measurable change in surface energy or surface tension. Depending on the properties of an impurity, the bulk concentration of such impurities could range from being not measurable to a few percent in concentration. While NICISS is able to detect traces of an element at the surface with an accuracy in the order of 0.1% [15], XPS is capable of detecting the presence of an element in a chemical state other than that of the intentionally added constituents. The accuracy of XPS in detecting impurities is element specific but for most elements in the order of one to a few percent.

The aim of this work is to compare depth profiles determined with ARXPS and NICISS. This has not been done before. Such comparisons make it possible to decide what the strengths and the weaknesses of each method are and to what degree they can be used complementary. The quantities we can derive from the concentration depth profiles are a) the surface excess, b) the gradient of concentrations between the surface and the bulk and c) the relative position between the maxima of the cation- and anion-distribution. The order of this list reflects what degree of accuracy is required in determining the concentration depth profiles while the demand in accuracy increases from the first to the third quantity in the list.

We have used helium projectiles for the NICISS experiments in this study with a kinetic energy of 4.5 keV. The kinetic energy of 4.5 keV is not the optimum energy in a NICISS experiment to achieve the best depth resolution at the surface. However, the higher energy allows a larger range of the concentration depth profile. Solutions of Bu_4PBr in formamide or similar solutions have been studied before with ARXPS and NICISS. However, in the ARXPS study in reference [16] the anion profile has not been investigated and in the previous NICISS investigations a lower kinetic energy of the helium projectiles has been used. Both studying the anion profile with ARXPS and using a higher energy in NICISS aims also to explore the limits of the methods.

2. Experimental

2.1. Methods: ARXPS

In an ARXPS experiment the intensity of photoelectrons is recorded as function of the emission angle. The intensity of the electrons emitted from the species constituting the sample is given in first instance by their concentration depth profiles, i.e. their concentration in the different layers. However, the intensity of electrons emitted is also influenced by their attenuation on their trajectory through the sample due to inelastic interactions of the electron with other charge carriers: the longer the trajectories of electrons through the sample are, the higher is the probability for an inelastic interaction and thus the stronger is the attenuation of the electron intensity. This is related to the angle of emission of the electrons. The larger the angle of emission is, the longer will be the path of an electron in the sample, i.e. the longer will be the distance between the point where the electron is emitted from an atom to the point where the electron passes through the surface. We define here the angle of emission as the angle between the direction of observation and the surface normal. The intensity I of electrons emitted from the constituent i at the angle of observation θ is given by

$$I(i,\theta) = fT(E)\left(\frac{d\sigma}{d\Omega}\right)\int_0^\infty n_i(z)\cdot exp(-z/(\lambda\cdot cos\theta))dz \quad (1)$$

where, n_i is the number density of constituent i, and z the depth. The quantity f is the X-ray flux, $T(E)$ is the transmission function of the electron spectrometer, E the kinetic energy, $d\sigma/d\Omega$ the differential photoionisation cross section of the core level of the respective element, and λ the attenuation length which is approximated by the inelastic mean free path of the photoelectrons in the sample. If the value of the mean free path is known, n_i , the number density of constituent i, can be determined. The intensity of the electrons emitted from deeper layers decreases with an increasing angle of observation.

2.2. Reconstruction of concentration (mole fraction)-depth profiles

Eq. (1) shows, that the XPS signal at a given angle of observation is a sum of the intensity of electrons emitted from all layers. The attenuation of electrons emitted from a particular depth, however, changes when changing the angle of observation. Thus the concentration depth profiles of the species can be determined from a set of measurements recorded at different angles of observation by applying a fitting algorithm based on Eq. (1) as for each angle an equation according Eq. (1) is given. However,