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Quantification of deexcitation processes for analyzing liquid surfaces

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ABSTRACT

In the last two decades the mathematical tools for quantitative data evaluation have been developed for several surface spectroscopic techniques like Angular Resolved X-ray Photoelectron Spectroscopy (ARXPS), Neutral Impact Collision Ion Scattering Spectroscopy (NICISS) and Metastable Induced Electron Spectroscopy (MIES). Provided that the experimental data are of good quality, quantitative data processing can add a lot to the information that can be gained from surface spectroscopy. We give a selection of references that contain information on these methods. The emphasis of this contribution aims at providing motivation to apply quantitative data evaluation by presenting a few examples. We try to demonstrate, that careful data evaluation may lead to interesting insight into basic concepts as well as to results that are useful for practical applications.

1. Introduction

For many decades the only experimental tool for studying liquid surfaces has been tensiometry [1]. The advent of surface spectroscopy which has been pioneered by Siegbahn [2] has added more detailed information on liquid surfaces, e.g. concentration depth profiles, thus revealing the 3-dimesional structure of liquid surfaces. Surface spectroscopy does not render the conventional method of surface tensiometry superfluous, but in contrast, the combination of spectroscopy and tensiometry allows understanding the properties of liquid surfaces in more depth than has been possible before. The meaningful combination of both pieces of information is made possible by the Gibbs equation [1] which reads for a binary system of components A, B.

$$-d\sigma = \Gamma^e_{\mathrm{A}} \cdot d\mu_{\mathrm{A}} \tag{1a}$$

or

$$-d\sigma = \Gamma^e_{\mathrm{B}} \cdot d\mu_{\mathrm{B}} \tag{1b}$$

where σ denotes the surface tension, Γ^e the surface excess and μ the chemical potential of the components. The surface excess can be determined from the concentration depth profiles $c_A(z)$, $c_B(z)$ and its definition is given here for component A as

$$\Gamma^e_A = \int_0^\infty \left[c_A(z) - \frac{x_A}{x_B} c_B(z)\right] dz \tag{2}$$

Thus, the advent of surface spectroscopy has turned Γ^e into a measurable quantity. In consequence, the chemical potential μ of either or both components can be determined in a straightforward manner from experiment without any model assumptions. This is of particular interest for surfactant solutions, as the low bulk concentration of surfactants renders conventional methods (e.g. variation of the solvent vapor pressure) for measuring chemical potentials invalid. Recently, some progress has been made along this line: for the first time has it been possible to study the mutual influence of two surfactants [3] quantitatively on the basis of experimental data.

The paper is organized as follows. The next section introduces the three experimental techniques, results of which are discussed. The mathematical methods used to end up with quantitative data evaluation are briefly described and references given. Thus, the reader interested in these methods can find detailed information in the literature. The scope of the present paper goes beyond mere data processing. We will observe that in some cases rigorous treatment of surface spectroscopic data can not only yield unexpected information on the entire system, i.e. on bulk properties, but may as well lead to reconsidering theoretical concepts. We will discuss three systems, the first motivating us to inspect the common concept of micelle formation, the second illustrating that the surface of a liquid system may force matter into a very unusual state of matter, and the last system demonstrating that basic considerations may in some cases be closely related to technical applications.

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2. Experimental techniques employed

In the present contribution we will discuss results from three experimental techniques:

1. X-ray photoelectron spectroscopy (=XPS) which has been applied to liquid surfaces for the first time by Siegbahn [2]. The angular resolved version of this technique (ARXPS) has matured into determining depth profiles in great detail without the need to formulate a model structure, e.g. [4]. Based on the concept of a mean free path of the emitted electrons the observation depth varies in a predictable way with the angle under which the electrons are detected. Thus, the spectra vary with emission angle for different species in a different way reflecting the concentration depth profile of every species. In XPS the chemical shift allows to distinguish different chemical environments for one and the same element. Thus, when evaluating XPS data (and thereby ARXPS data) one can identify one and the same element in different chemical environments as different species. Accordingly, concentration depth profiles can be reconstructed separately for different molecular groups, even if one deals e.g. with hydrocarbon compounds. Carbon atoms within a saturated hydrocarbon chain have a binding energy of ca. 284 eV while a carbon atom pertaining to a carboxylic acid has a binding energy that is ca. 3.4 eV higher. Compared to the energy resolution of the technique that can easily be tuned to be better than a few tenth of an eV, the two species can be unambiguously distinguished. This method has been employed in Ref. [4] for exploring the surface of the solution TBAI/FA (tetrabutylammonium iodide dissolved in the polar solvent formamide) by exploiting the chemical shift between carbon atoms within the solvent and carbon atoms within the solute. The careful evaluation of the experimental spectra is, however, only the first step towards the reconstruction of a reliable concentration depth profile, as has been described in Ref. [4]. Several authors content themselves with observing qualitatively whether a given component is enriched in the surface or not, e.g. [5–7]. In the present contribution we will demonstrate that careful quantitative data evaluation can lead to interesting information that sometimes may even invoke a challenge to theoretical concepts.
2. Neutral impact collision ion scattering spectroscopy (NICISS) is based on the backscattering of projectiles (often He^+ ions with a kinetic energy of several keV). Recording energy loss and scattering angle allows calculating the mass of the target atom that has been hit. NICISS is a reliable technique to determine depth profiles of selected elements in the surface near range in case of amorphous samples. Thus, this method can be used to check results from ARXPS and vice versa. Even though the spectra measured in NICISS allow for a coarse estimate of the concentrations depth profiles without data processing, the detailed quantitative data evaluation requires several steps. First of all, one has to separate the signal caused by the reflected projectiles from the background due to recoiled light atoms. This can be done because the reflected projectiles yield a structured pattern while the recoil signal from light atoms (usually hydrogen) forms a broad unstructured background. Further, the kinetic energy distribution of the projectiles broadens the spectra. The last aspect that has to be taken into account rests in the statistical nature of the stopping power. All three influences can be mathematically handled to good accuracy. If so, very detailed information about the (laterally averaged) concentration depth profile can be obtained, see Ref. [8,9].
3. Metastable Induced Electron Spectroscopy (=MIES) is distinguished by perfect surface sensitivity and, thus, complements the first two techniques. MIES allows determining the composition of the top layer, but is as well sensitive to the orientation of the molecules in this layer. The mathematical tools for quantitative evaluation of MIES data are described in Ref. [10]. In particular the decomposition of spectra from inhomogeneous surfaces into contributions from separate, identifiable species is discussed in this review article.

3. Results and discussion

3.1. Solution of a nonionic surfactant in a polar solvent: challenge to common understanding of micelle formation and to familiar thermodynamic concepts

The surface properties of the solution of the nonionic surfactant 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) in the polar solvent 3-hydroxipropionitrile (HPN) have been investigated by the surface spectroscopy NICISS and by surface tensiometry. The data can be found in Ref. [11]. The spectroscopic measurements allowed determining the surface excess of the surfactant. Combining these results with surface tension data via the Gibbs equation, the chemical potential μ_{POPC} of the surfactant could be determined over a large range of concentrations, starting at more than one order of magnitude below the critical micelle concentration (CMC) to an order of magnitude above the cmc. Inspection of the chemical potential shows that up to the cmc the solution displays ideal solution behavior. Above the cmc the chemical potential and the surface tension remain constant, cf. [11]. Insofar, the behavior of the system follows the expected behavior. However, in a small range above the cmc an unusual feature could be observed. The surface tension displays a local minimum which leads via the Gibbs equation to a local maximum of the chemical potential μ_{POPC}. The literature knows two different comments with respect to this phenomenon, cf. Ref. [12]. Several authors claim that the occurrence of a local minimum in the surface tension is an unambiguous indication for the presence of a surface active impurity. As this impurity is to be understood as impurity with respect to the surfactant, its concentration is much smaller than the surfactant concentration and, thereby, extremely low. Thus, it escapes detection by bulk related analytical techniques. The only method to get rid of such an impurity is the observation of purification protocols. The ability to employ surface spectroscopy gave an advantage in this respect: a surface active impurity is best identified by means of surface spectroscopy. No trace of such impurity could be found, cf. [11]. If an impurity was present, its properties had to be almost identical to the properties of the surfactant POPC. Thus, an explanation of the phenomenon without reference to an impurity has been sought. It has been formulated a few years later in Ref. [13]. The treatment in this paper assumed a hindrance against micelle formation. Not all surfactant molecules exceeding the critical micelle concentration lead to the formation of micelles. Thus, micelle formation is delayed to concentrations larger than the nominal cmc. A later experimental paper reported the same effect for the somewhat different surfactant 1,2-dioleoyl-*sn*-glycero-3-phosphochline (DOPC) dissolved in the same solvent HPN [14]. This time the effect was identified by the spectroscopic technique MIES and was found to be even more pronounced than in case of POPC/HPN. Again, the theory from Ref. [13] proved fruitful in describing the effect. (see Fig. 1).

The systems discussed are characterized by the presence of altogether three phases: the bulk monomer solution, the surface and the micelles. The micelles are comparatively small (about 17 POPC molecules per micelle) such that the total area of the interface between monomer solution and micelles is extremely large.

This goes along with an inhomogeneous distribution of matter. Thus, strong capillary forces are present. One may conclude that