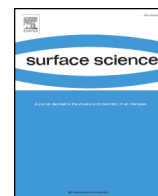




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# Adsorption behavior of the ternary system of phospholipid 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine in 3-hydroxypropionitrile with added tetrabutyl ammonium bromide

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## ABSTRACT

The adsorption behavior in a ternary system composed of the non-ionic surfactant POPC (1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine) and the ionic surfactant TBABr (tetrabutyl ammonium bromide) in the polar solvent HPN (3-hydroxypropionitrile) is investigated utilizing surface tension measurements and ARXPS (angular resolved X-ray photoelectron spectroscopy). The latter technique allows evaluating the surface excess of both surfactants. The combined experimental information (i.e. surface excess and surface tension) allows the determination of the chemical potential and thus the activities of both surfactants by virtue of the Gibbs equation. While the activity coefficient of TBABr is hardly affected by the presence of POPC, the activity coefficient of POPC strongly depends on both, the concentration of POPC and the concentration of TBABr. We observe the activity coefficient  $f_{\text{POPC}}$  to vary by more than 3 orders of magnitude in the 2-dimensional parameter space ( $C_{\text{POPC}}, C_{\text{TBABr}}$ ). This finding reflects and explains the surprising behavior of the surface tension: adding TBABr to the binary system POPC/HPN may increase or decrease the surface tension, depending on the POPC concentration. Inspection of these results suggests that mixed POPC/TBABr aggregates are formed at low POPC concentrations while the typical features of micelle formation are absent in this ternary system even at very low TBABr concentration.

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## 1. Introduction

Understanding the interaction between the molecules at the liquid surfaces plays a vital role in research of new surface materials and in development of products and processes. In many cases, the properties of well-chosen mixtures of surfactants can be tuned to give an improved match for practical applications [1]. The progress in various chemical reactions can be monitored well if we know with accuracy the properties of their surface. In the case of mixtures of surfactants, the surface composition is different from that one of the bulk and can be characterized by the surface excess.

Tensiometry is widely established for the investigation of surfactants. In addition, spectroscopic tools have been applied for microscopic study of surfaces. A particular group of surface sensitive spectroscopic techniques require high vacuum (HV) conditions. These include neutral impact collision ion scattering spectroscopy (NICISS) [2], electron energy loss spectroscopy (EELS) [3], X-ray photoelectron spectroscopy (XPS) [4], ultraviolet photoelectron spectroscopy [5] and metastable induced electron spectroscopy [6]. All of these techniques, with the exception of EELS, provide explicit information about the molecular composition and structure

of surfaces. NICISS [2] and XPS [7] are suited to unambiguously determine concentration depth profiles of all the elements present in a sample near the surface, except hydrogen.

In the present work, we have used ARXPS for analyzing the unexpected behavior of the ternary system which first has been observed by surface tension measurements. With this technique, the fractional contributions of components near the surface are evaluated and then concentration depth profiles are reconstructed with the help of a genetic algorithm [7]. From the depth profiles the surface excess of the surfactants can be obtained.

## 2. Experimental

### 2.1. Materials

The phospholipid POPC was purchased from Avanti Polar Lipids Inc. and was dried in vacuum to weight constancy. HPN was obtained from Merck (98%) and was purified by vacuum distillation. The boiling temperature was ~350 K at a pressure of ~2 mbar. TBABr was purchased from Fluka with a purity of  $\geq 99.0\%$  and was used without further purification. The concentration of POPC in HPN ranged from  $1.00\text{E}-05$  to  $6.58\text{E}-04$  mol/kg. The concentration of TBABr in HPN ranged from 0.1 to 1.3 mol/kg. The structural formulae of both surfactants and the solvent are shown in Fig. 1.

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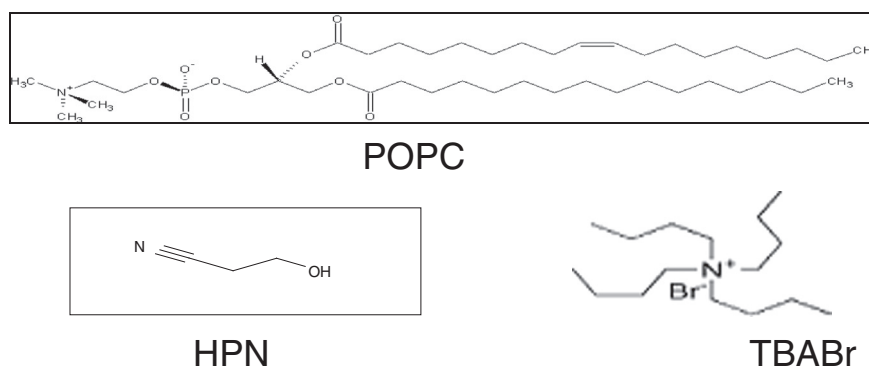


Fig. 1. Structural formulae of POPC, TBABr and the solvent HPN.

## 2.2. Surface tension measurements

The surface tension measurements were carried out with the Tensiometer K100, manufactured by Krüss (Hamburg, Germany). The stated uncertainty is given as  $\pm 0.1$  mN/m. The principle of the tensiometer is based on the Wilhelmy plate method. The measuring temperature was kept at  $-6 \pm 0.1$  °C. During measurements, the sample was protected by an atmosphere of dry nitrogen in order to eliminate the effect of water vapor from the air.

## 2.3. ARXPS measurements

The XPS machine used was made by SPECS (Berlin). The anode of the X-ray source is made of aluminum. The liquid target is a small reservoir with a rotating stainless steel disk as shown in Fig. 2. When this rotating disk emerges from the liquid, it passes the skimmer. This creates a fresh liquid surface that has a thickness of a few tenths of a millimeter. The surface age is controlled by the speed of rotation of the wheel which in turn is driven by a mini motor. The orientation of the rotating disk with respect to the spectrometer can be adjusted around the vertical axis. Thus, the photoemission angle can be varied.

The core level C1s signal was chosen to identify solvent and POPC. Due to a distinct chemical shift, the C1s signals of HPN and POPC can be distinguished very clearly, cf. Fig. 3a, b, such that their areas can be quantified separately without any influence from the other. The peak area pertaining to the ester group was selected to show the quantity of POPC. TBABr contributes to the C1s signal as well, but

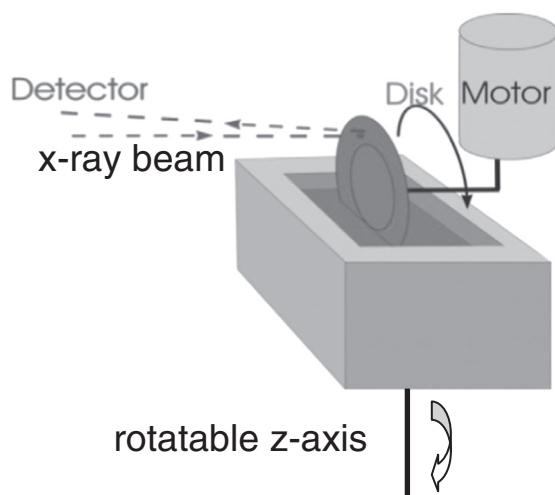


Fig. 2. Schematic figure of the liquid target. The angle between the direction to the detector and the X-ray beam is fixed. The photoemission angle can be adjusted by rotating the z-axis which is vertical to the ground.

this contribution is buried under the remaining peaks, cf. Fig. 3c. Therefore, the peak area of Br3d<sub>5/2</sub> was chosen to represent the quantity of TBABr, cf. Fig. 3d. As for the surface tension measurements, the solution was kept at  $-6$  °C in order to reduce the evaporation of solvent. The signals were recorded under six photoemission angles, namely 0°, 30°, 40°, 50°, 60° and 70°. At photoemission angles higher than 70°, the elastic scattering of photoelectrons can lead to a severe quantitative deviation of the signals in comparison to the sample composition [10]. The signals of C1s and Br3d<sub>5/2</sub> are shown in Fig. 3. The peaks of C1s and Br3d<sub>5/2</sub> were fitted with Gaussian and Lorentz functions.

It is obvious that the C–(O)–O–Signal used for the evaluation of the POPC depth profile is very small and may thus underlie large errors. Therefore, the overall quantities of both surfactants were used to calculate a corresponding aliphatic carbon signal. The fit of the spectra was optimized, such that the deviation between the calculated and the measured aliphatic carbon peaks was minimized.

## 2.4. Evaluation of depth profiles by the genetic algorithm

The relative signal intensities of chemical species as function of the angle  $\theta$  are used to obtain the fractional concentration depth profiles. The detailed procedure for evaluation of the fractional concentration depth profiles is explained elsewhere [7–9]. Therefore, only a short description is given here: the surface near range is conceived to consist of thin homogeneous layers with different compositions. From these model data, the signal intensities for different species and different angles are evaluated. If they fit their experimental counterparts within the experimental error bar, they are regarded as possible solutions. By averaging over all accepted possible solutions, the final solution including the uncertainties is computed.

From the depth profiles, the surface excess of both surfactants has been evaluated. Under the assumption that the partial volumes of the components do not vary with the composition of the surface phase, the products of the layer thickness and the mole fraction in each surface layer for surfactants are added up and their surface excess obtained.

## 3. Results and discussion

The surface tension of pure HPN amounts to 51.74 mN/m, cf. Fig. 4. For the binary systems POPC/HPN the surface tension drops swiftly with increasing POPC concentration. A critical micelle concentration (cmc) has been observed at a POPC concentration of  $2.8E-04$  mol/kg [12], cf. Fig. 4.

Similarly, the surface tension of the binary mixture TBABr/HPN decreases by addition of TBABr, but no cmc can be determined in the concentration range up to saturation as shown in Fig. 5. The data show that POPC is much more surface active than TBABr in binary systems.

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