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The interaction of water with Langmuir films of amphiphilic amines as a function of pH probed by π-A isotherms and SFG spectroscopy

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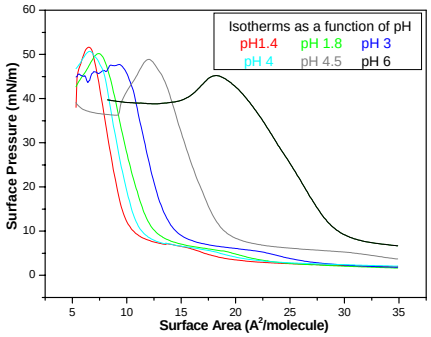
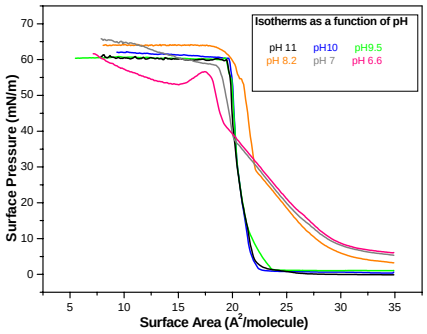
Abstract – Amine groups are found in various forms in nature, such as amino acids, proteins, vitamins and alkaloids. Using Langmuir films of amphiphilic amines as model systems, we investigate the interaction of amine groups with water by surface pressure isotherms and nonlinear optical vibrational spectroscopy. Preliminary results on the stability of octadecylamine Langmuir films as a function of the pH of the aqueous subphase and their characterization by pressure-area isotherms will be presented. SFG vibrational spectroscopy is used to infer the degree of ionization f the amine groups and the corresponding water structure at the interface.

The interaction of organic molecules with water is fundamental to several areas of science, such as chemistry and biology. Proteins, vitamins and amino acids are prominent constituents of living systems. Since all of them contain amine groups, the investigation of the amine-water interaction is highly relevant to our understanding of biological processes *in vivo* and in biosensors. In this work we will investigate such interaction using a long-chain amine Langmuir film [1] as a model system. Surface pressure *vs* area per molecule (π-A) isotherms and vibrational spectroscopy by sum-frequency generation (SFG spectroscopy) were used to investigate the structure of the amine monolayer and its interaction with water, similarly to previous studies with fatty acids.[2] The π-A isotherms allow us to determine at which pH value there is an appreciable ionization of the amine, and verify the stability of the Langmuir film at low pH values. SFG vibrational spectroscopy provides direct information on the structure of the amine film and its interaction with the underlying water layer. In SFG spectroscopy [3], the signal can be generated only at the interface between two media with inversion symmetry, such as gases, liquids and amorphous solids. Therefore, it is possible to study with SFG spectroscopy the layer of water interacting directly with the Langmuir film. It is also to determine molecular orientation at the interface and alkyl chain conformation. The main goals of this work are the study of i) the degree of ionization of the monolayer as a function of subphase pH and ionic strength; ii) the water-amine interaction; iii) comparison between Langmuir and Langmuir-Blodgett films of octadecylamine ($C_{18}H_{37}NH_2$). The figure below presents results on the ionization and stability of octadecylamine Langmuir films as a function of pH of the aqueous subphase, investigated by pressure-area isotherms. A significant expansion of the isotherms as the pH is reduced below 9.5 indicates that the amine groups become significantly ionized, increasing electrostatic repulsion among headgroups. For pH values below 6.0, the degree of ionization increases and the film solubility is so high that the isotherms are no longer stable. Preliminary SFG vibrational spectra of the amine groups and interfacial water will also be presented.



Isotherms with acidic sub-phases



Isotherms with basic sub-phases

References

[1] M. C. Petty, *Langmuir-Blodgett Films*, Cambridge University Press, 1996.
[2] P. B. Miranda, Q. Du, Y. R. Shen, *Chem. Phys. Lett.* **286**, (1995).
[3] P. B. Miranda and Y. R. Shen, *J. Phys. Chem. B* **103**, 3292 (1999).