POLARIZED RAIRS STUDY OF ANTICORROSION LB FILMS

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Introduction

Langmuir-Blodgett nanolayers are potential replacements for traditional surface inhibitors, which could decrease the synthetic chemical burden on the environment [1]. Nanolayers of hydroxamic acids can control microbial attachment more effectively than those of phosphonic acids, which is very important in case of microbiologically influenced corrosion. IR spectroscopic techniques (ATR and IRRAS) are accepted methods for studying LB layers, since they provide information on the binding mode of the nanolayer to the surface and on molecular conformation and orientation.

The Langmuir-Blodgett (LB) film technique which enables the fabrication *(Figure 1)* of organized thin films of controllable thickness at the molecular level was considered for the anti-adhesive strategy in microbial attachment [2].

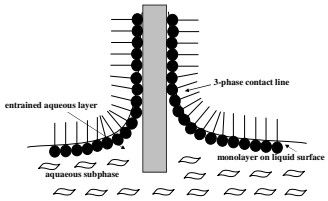


Figure 1. *Deposition of a floating monolayer on a solid substrate*

Different types of LB multilayers can be produced by successive deposition of monolayers on the same substrate *(Figure 2)*. The most common one is the Y-type multilayer which is produced when the monolayer deposits to the solid substrate in both up and down directions. When the monolayer deposits only in the up or down direction, the multilayer structure is called either Z-type or X-type.

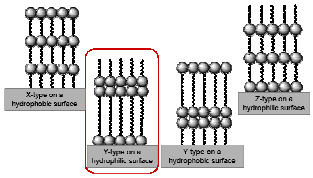


Figure 2. *Different types of deposited LB films*

These nanolayers which reduce the corrosion of metals *(Figure 3)*, will prevent and control biofouling and biocorrosion though mitigation of adhesion of corrosion-relevant microorganisms at an early stage.

Figure 3. *Control copper substrate (left) and copper with 11 monolayers of C18N in LB film (right)*

Experimental

Here we report on measurements and analysis of polarized RAIRS spectra of mono- and multilayers of octadecanoylhydroxamic acid, $CH_3(CH_2)_{16}C(O)NOH$

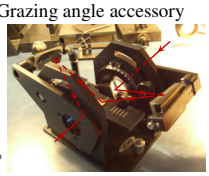
Figure 4. *Structural formula of octadecanoylhydroxamic acid (C18N)*

(designated as C18N, *Figure 4)* prepared on smooth copper and iron surfaces *(Figure 5)*.

Figure 5. *Solid metal substrates: copper and iron*

Instrumentation

- Nicolet Magna 750 FTIR spectrometer
- Specac 19650 Monolayer/Grazing angle accessory
- MCT-A detector
- 512 scans
- 2 cm^{-1} resolution
- Au/KRS-5 polarizer
- Angle of incidence: ~71,5°



References

[1] J. Telegdi, T. Rigó, E. Kálmán, *J. Electroanal. Chem.* **582** (2005) 191.
[2] J. Telegdi, T. Rigó, J. Beczner and E. Kálmán, *Surface Engineering*, **21** (2005) 2.
[3] T. Takahashi, P. Miller, Y. M. Chen, *J. Polym. Sci. B: Polym. Phys.* **31** (1993) 165.

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Results and Discussion

The most prominent absorption bands were observed in the CH stretching region (3000-2800 cm^{-1}), that served for determination of the orientation of the hydrocarbon chains on the metal surface. The tilt angle, Θ, between the molecular axis and the surface normal was calculated from the band intensities of the *s* and *p* polarized spectra (Fig. 6), A_s and A_p, using the formula proposed by Takahashi et al. [3]:

$$\frac{A_s}{A_p} = \frac{\sin^2\Theta}{\cos^2\phi - \sin^2\Theta + 2\sin^2\phi\cos^2\Theta}$$

where A_s and A_p are the absorbances from the *s* and *p* polarized spectra respectively, Θ is the tilt angle of the molecules relative to the substrate normal (the induced dipole moment), and ϕ is the angle of incidence of the IR beam.

In case of monolayers on copper or iron substrates, the molecules are perpendicular to the surface, while in case of multilayers (up to N_L=9), the average tilt angle is around 23° *(Figure 7)*.

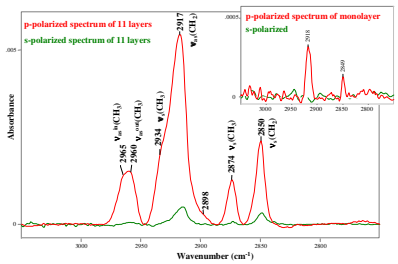

Figure 6. *s- and p-polarized RAIRS spectra of C18N in the C-H stretching region as absorbed LB layers on copper*

- **Tilt angle (Θ)**
  in the case of copper substrate:
  1 layer: ~0°
  3 layers: ~23°
  9 layers: ~19°
  11 layers: ~22°
- **Tilt angle (Θ)**
  in the case of iron substrate:
  1 layer: ~0°
  3 layers: ~26°

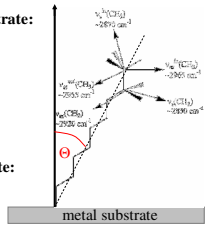

Figure 7. *The tilt angle of the molecules relative to substrate normal*

Practically linear relationship was observed between the number of layers (N_L) and the asymmetric and symmetric CH_3 stretching band intensities (with R^2 = 0.9992), see *Figures 8 and 9*.

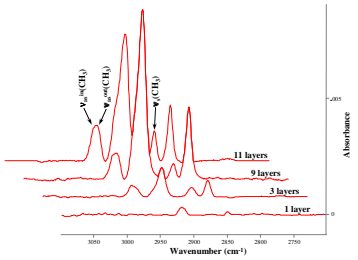

Figure 8. *RAIRS spectra of C18N in the C-H stretching region as adsorbed LB layers on copper; N_L= 1, 3, 9 and 11.*

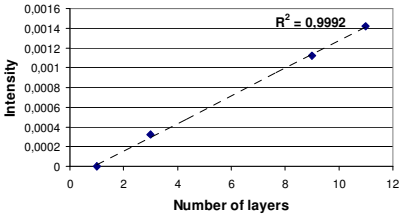

Figure 9. *Relationship between the number of layers and the asymmetric CH_3 stretching intensities (at 2965 cm^{-1})*