Study of the interaction between cardiolipin bilayers and methylene blue in polymer-based Layer-by-Layer and Langmuir films applied as membrane mimetic systems

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An increase of the reports involving mimetic systems has been observed. Briefly, these systems use biological phospholipids to exploit specific interactions between membrane-models and drugs. Here, the Layer-by-Layer (LbL) and Langmuir techniques were used to investigate the interaction between cardiolipin (CLP – negative phospholipid) and a cationic-like drug methylene blue (MB). Supported by a cationic polyelectrolyte (PAH), LbL films containing PAH/(CLP+MB) and PAH/(CLP+MB+AgNP) were grown up to 14 bilayers. The optical microscopy analysis exhibited in Figure 1 revealed a decrease of the CLP vesicle sizes in the presence of MB as a possible consequence of the MB action onto the mechanical properties of the CLP membrane. From FTIR spectra, changes mainly related to peak position and band intensity and shape were observed in the spectra from PAH/CLP when in the presence of MB. The latter supports that the interactions between the phosphate and amine charged groups from CLP and PAH, respectively, established during the LbL film fabrication, besides the CLP hydrocarbon environment, are influenced by the presence of MB. Using the micro-Raman technique, a chemical mapping was build based on MB spectrum by resonance Raman scattering (RRS) and surface-enhanced resonance Raman scattering (SERRS). The later phenomenon was activated by Ag nanoparticles (AgNPs) trapped within the LbL film allowing collecting spectra for a single bilayer of PAH/(CLP+MB+AgNP), as show in Figure 2. A rough estimation showed a SERRS amplification of 10^3 in comparison to RRS spectra. As a complementary approach, Langmuir films of CLP in the presence of co-spread MB were investigated through surface pressure *vs* mean molecular area (π-A) isotherms. The results showed that for concentrations of MB below 100 mol%, the drug is expelled to water subphase for high values of surface pressure (condensed phase). For concentration at 100% and higher, the MB keeps bound to CLP floating monolayer.

Key words: SERS, LbL films, phospholipids, methylene blue.
Work supported by FAPESP

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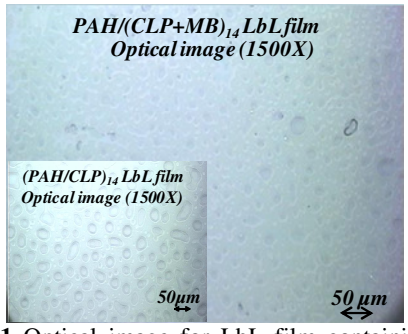

Figure 1 Optical image for LbL film containing 14 bilayers of PAH/(CLP+MB). The inset shows an optical image for 14 LbL bilayers of PAH/CLP.

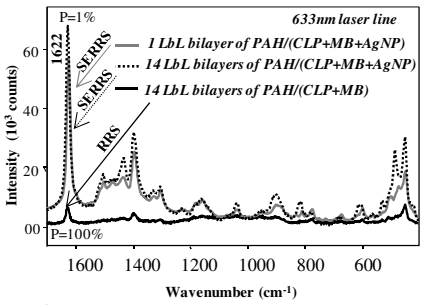

Figure 2: RRS spectra recorded for 14-bilayer PAH/(CLP+MB) LbL film and SERRS spectra recorded for both 1 and 14-bilayer PAH/(CLP+MB+AgNP) LbL films.