

Supporting Information

Interplay of the assembly conditions on drug transport mechanisms in polyelectrolyte multilayer films

*Rogério A. Bataglioli**, João Batista M. Rocha Neto, Bruno S. Leão, Luiz Guilherme L. Germiniani, Thiago B. Taketa, Marisa M. Beppu

School of Chemical Engineering, University of Campinas, Avenida Albert Einstein 500, 13083-852, Campinas-SP, Brazil.

*Corresponding author: rogerbataglioli@gmail.com

Number of pages: 7

Number of figures: 6

Number of schemes: 0

Number of tables: 0

Table of Contents:

S1. Polyelectrolyte solution properties and surface morphology of PAA/PAH films

S2. AFM-IR spectra for PAA/PAH films before and after CAL loading

S3. CAL calibration curve in PBS buffer, equilibrium data for CAL loading into PAA/PAH films, and the influence of pH on CAL absorbance spectra

S4. Absorbance spectra for PAA/PAH films after the drug release process

S5. Confocal microscopy images of the axial position of PAA/PAH films with 40 bilayers loaded with CAL

S6. Absorbance spectra for PAA/PAH films loaded with CAL and capped with PEM or phospholipid films

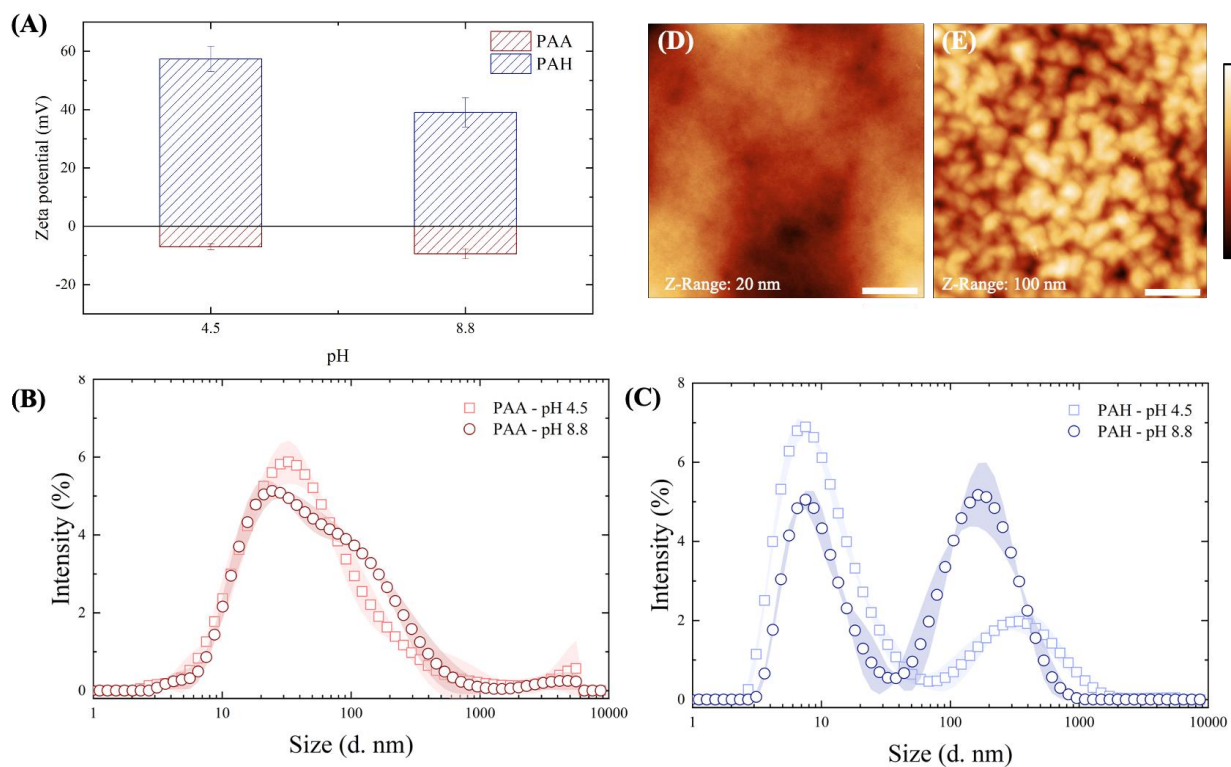


Figure S1. Polyelectrolyte solution properties and surface morphology of PAA/PAH films.

(A) ζ -potential and (B-C) DLS particle size distribution measurements for PAA and PAH solutions under the film assembly conditions. Shaded areas and error bars represent standard error values. Measurements were performed in triplicate. AFM images for PAA/PAH films with 20 bilayers assembled at (D) pH 4.5 and (E) pH 8.8. The correspondent surface RMS values are (3.6 ± 1.0) nm and (14.7 ± 0.2) nm, respectively, for measurements performed in triplicate. Bars in the AFM images correspond to 1 μ m.

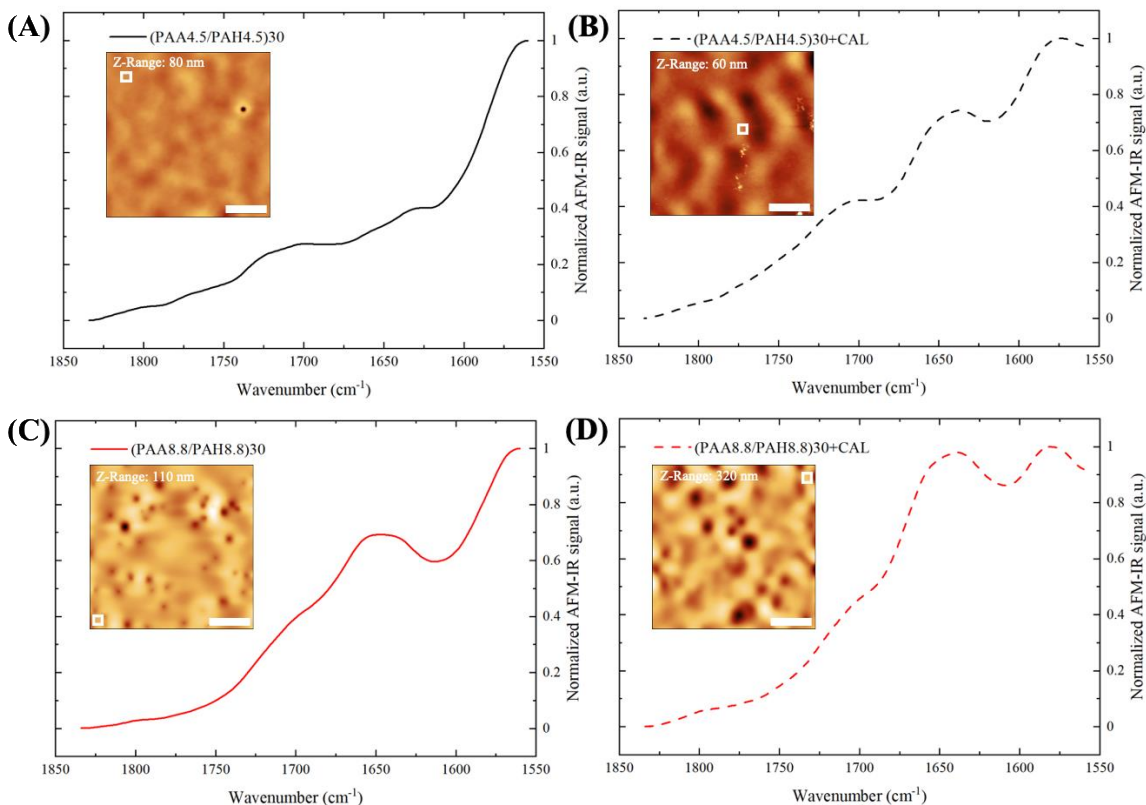


Figure S2. AFM-IR spectra for PAA/PAH films before and after CAL loading. AFM-IR spectra evidence the drug loading into PAA/PAH due to the emergence of the peaks at around 1600 cm^{-1} and 1650 cm^{-1} assigned to C=C stretches in aromatics, and C=O stretches in the carboxylates after the CAL loading process.¹ AFM-IR spectra for (PAA4.5/PAH4.5)30 films (A) before and (B) after CAL loading, and for (PAA8.8/PAH8.8)30 films (C) before and (D) after CAL loading. Bars in the AFM images correspond to $5\text{ }\mu\text{m}$. White squares represent the position where the infrared spectra were recorded.

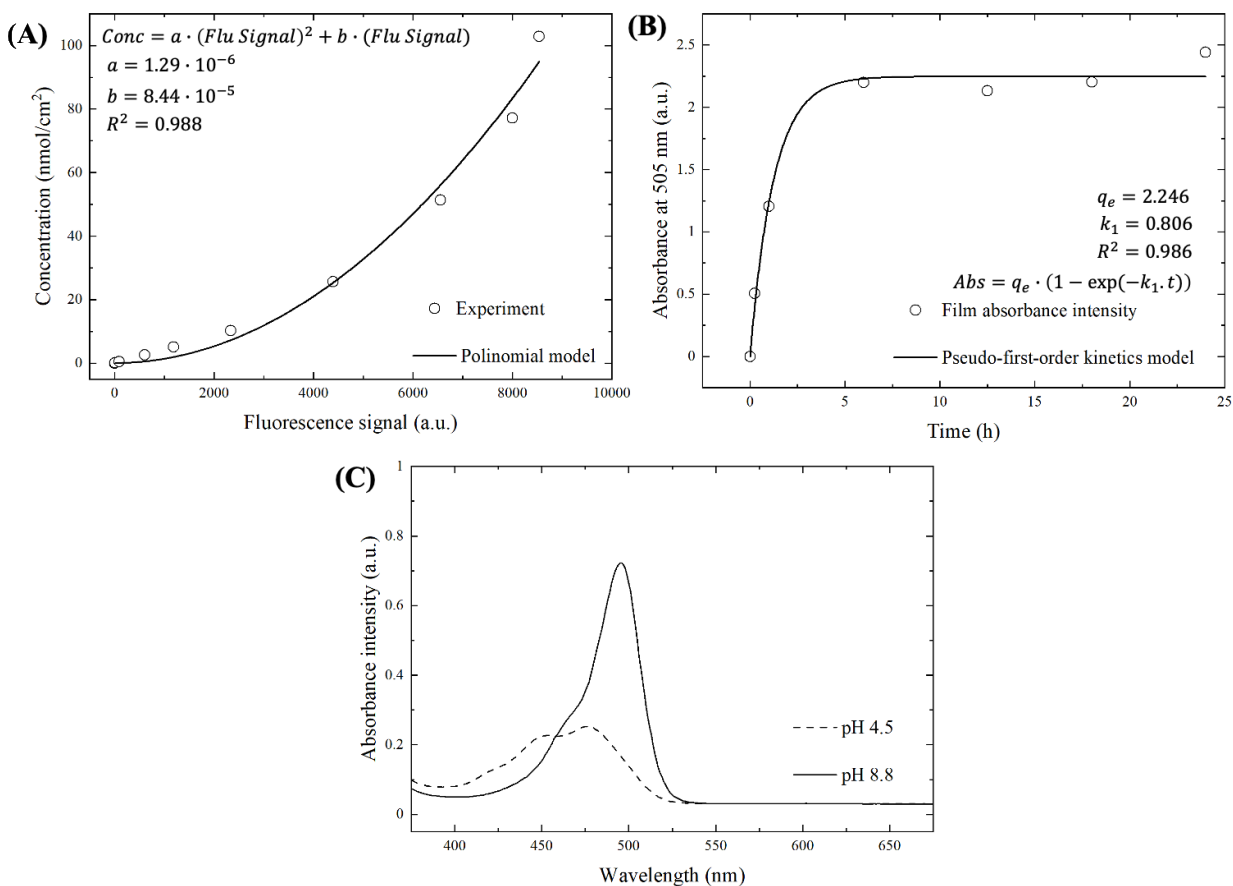


Figure S3. CAL calibration curve in PBS medium, equilibrium data for CAL loading into PAA/PAH films, and the influence of pH on CAL absorbance spectra. (A) Calibration curve for CAL in PBS solution (pH 7.4 and 0.01 M). Fluorescence measurements were performed at excitation and emission wavelengths at 490 nm and 540 nm, respectively. The calibration curve was fitted to a second-order polynomial model with an intercept at 0, and the polynomial constants showed in the plot. (B) Absorbance peak intensity at 505 nm for (PAA4.5/PAH4.5)₄₀ films with postassembly CAL loading over different time intervals. Data were fitted to the pseudo-first-order adsorption kinetics model with parameters presented in the plot. (C) Absorbance spectra for CAL solution (6 mg/L) at the same film assembly pH conditions studied.

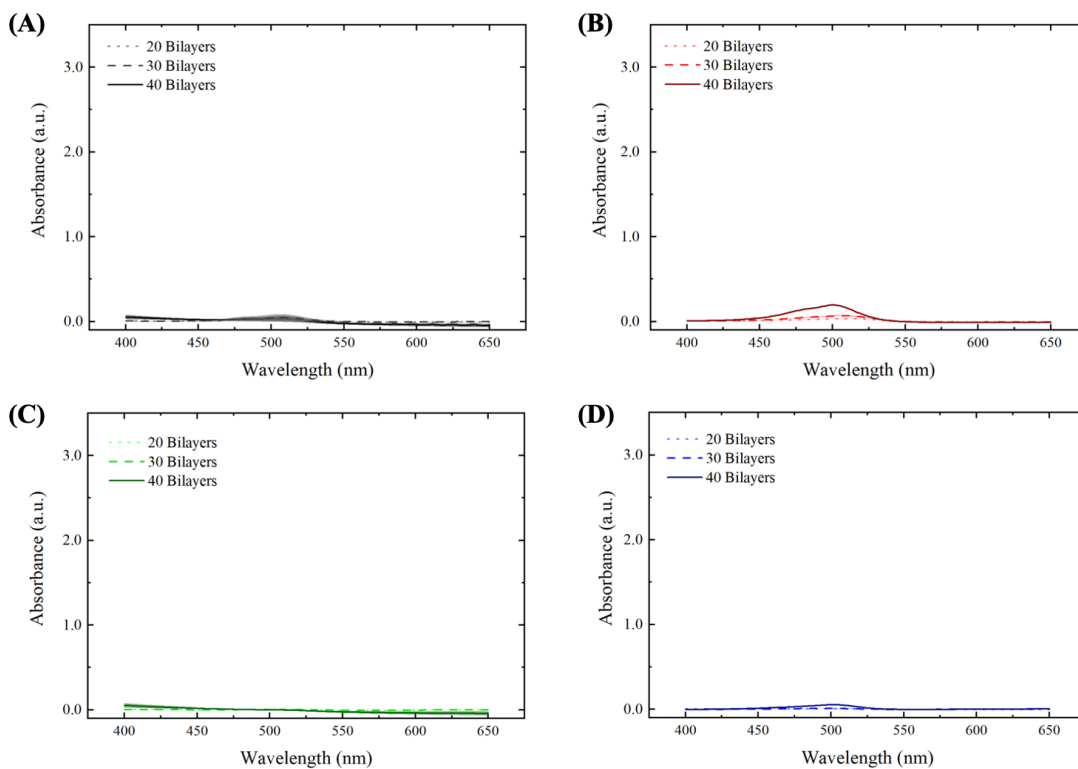


Figure S4. Absorbance spectra for PAA/PAH films after the drug release process. UV-visible spectra for PAA/PAH films assembled at (A) pH 4.5 and (B) pH 8.8 with postassembly drug loading, and at (C) pH 4.5 and (D) pH 8.8 with during-assembly drug loading. Spectra recorded after (A, B, and C) 24 h and (D) 6 days of drug release. Shaded areas represent standard error values.

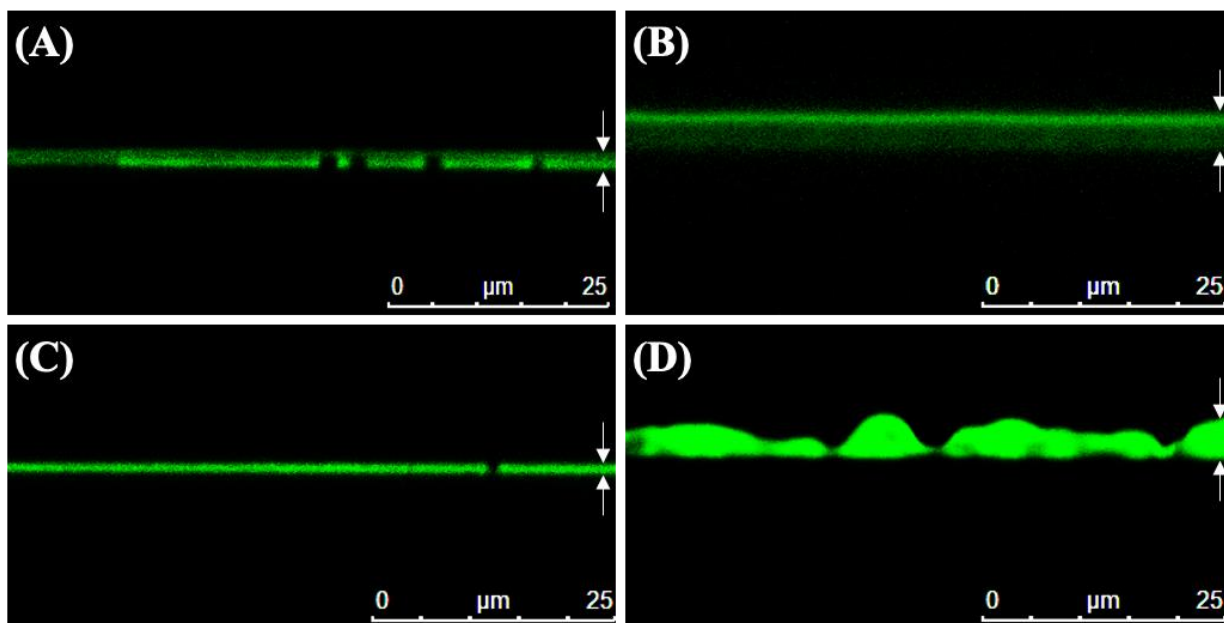


Figure S5. Confocal microscopy images of the axial position of PAA/PAH films with 40 bilayers loaded with CAL. Films assembled at (A) pH 4.5 and (B) pH 8.8 with postassembly drug loading, and at (C) pH 4.5 and (D) pH 8.8 with during-assembly drug loading. White arrows indicate the film interfaces.

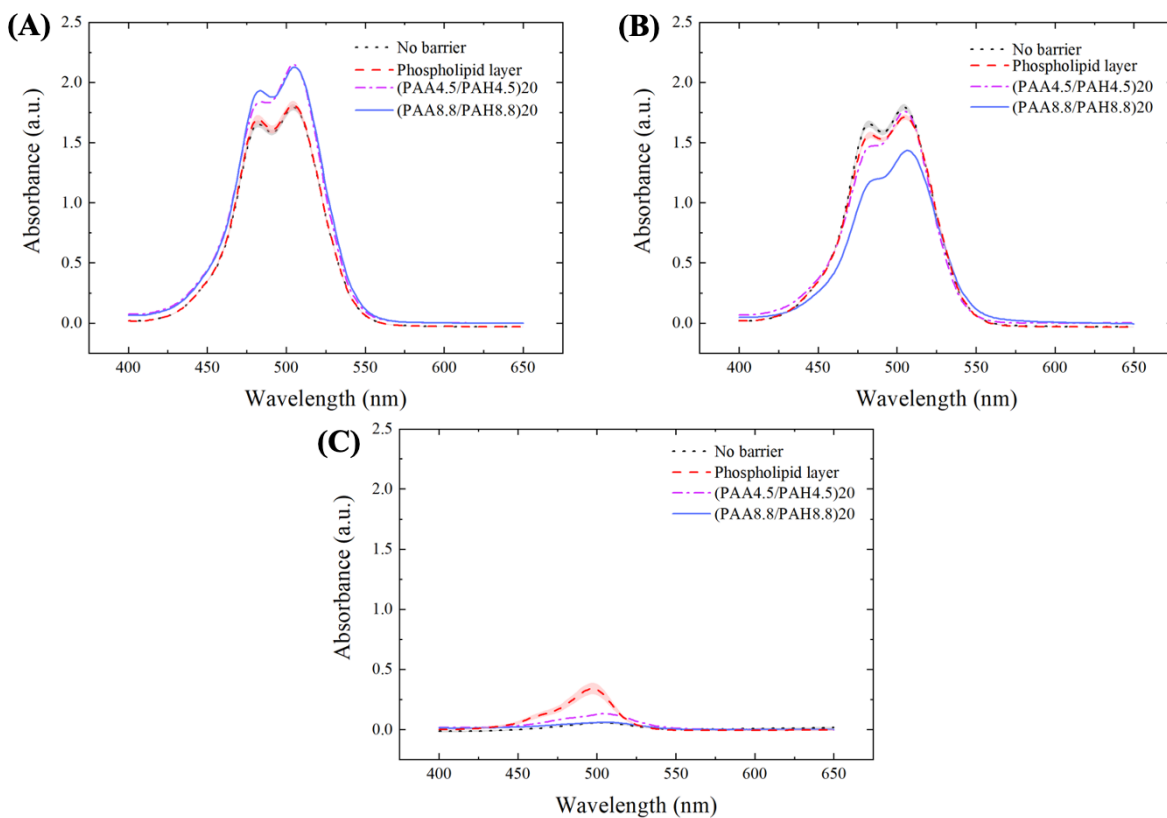


Figure S6. Absorbance spectra for PAA/PAH films loaded with CAL and capped with PEM or phospholipid films. Absorbance spectra for (PAA4.5/PAH4.5)40 films loaded with CAL (A) before and (B) after capping film deposition, and (C) 24 h after drug release indicate that nearly all drug was released from the films. Phospholipid-coated films are the only ones presenting a significant amount of CAL remaining after 24 h of release. Shaded areas represent standard error values.

REFERENCE

[1] Furry, J. Preparation, Properties and Applications of Calcein in a Highly Pure Form, 1985.