Supporting Information for:

Insights into Hydrophobic Molecule Release from Polyelectrolyte Multilayer Films Using *In Situ* and *Ex Situ* Techniques

Yongjin Shin [1], Weng Hou Cheung [2], Tracey T.M. Ho [1], Kristen E. Bremmell *[2], David A. Beattie [1]*

[1] Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095

[2] School of Pharmacy and Medical Sciences, University of South Australia, City East Campus, North Terrace, Adelaide, SA 5000

* Corresponding authors: Kristen.Bremmell@unisa.edu.au; David.Beattie@unisa.edu.au

PDADMAC/PSS PEM Growth:

The adsorption of the PDADMAC/PSS multilayer assembly was observed to follow a non-linear growth pattern with increasing bilayer number (Figure 2 and 4 in the main manuscript). The two techniques used to follow the adsorption provide direct evidence of this nonlinear growth through the Sauerbrey mass (QCM sensor, determined after rinsing stage for each bilayer) and the FTIR peak area of vibrational modes (which is proportional to adsorbed mass, determined after rinsing stage for each bilayer). The two forms of data are presented in Figure S.1. Both techniques used exactly the same PEM formation conditions. It can be seen that the mass growth and absorbance growth (proportional to mass) can be fitted with simple exponential growth expressions (fitted in Origin 8.5.1). Differences in the fitting parameter, $t1$, are attributed to the fact that QCM detects adsorbed polymer plus hydration water; FTIR absorbance is proportional to the adsorbed polymer mass only. This implies that there is an alteration in the hydration content of the multilayer with increasing bilayer number.
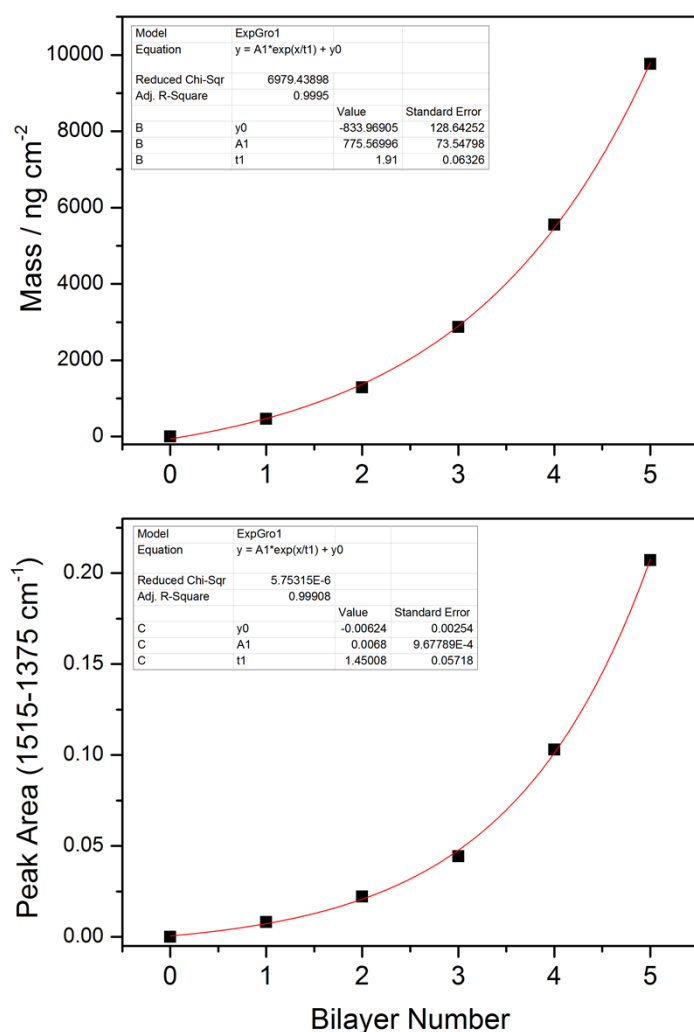
Figure S.1: Top – Sauerbrey mass of the PDADMAC/PSS multilayer as a function of bilayer number (QCM 7th overtone frequency change). Bottom – peak area of the region between 1515 and 1375 cm^{-1} for the *in situ* FTIR spectra of the PDADMAC/PSS multilayer as a function of bilayer number.

Incorporation of Curcumin in PDADMAC/PSS PEM

UV Visible Spectroscopy: The incorporation of curcumin into the 5-bilayer PDADMAC/PSS multilayers was studied with UV-visible spectroscopy. A sample UV-visible absorbance spectrum (measured in transmittance) is shown in Figure S.2, along with a picture of two of the quartz plates with curcumin incorporated (and one blank PEM-coated plate). The UV-visible spectrum of curcumin is dominated by a peak at approx. 440 nm, which is slightly altered in position and band shape from that of curcumin in water:ethanol solution [1], due to interaction with the PEM (potential π-π interactions between the molecule and the aromatic ring on the PSS).
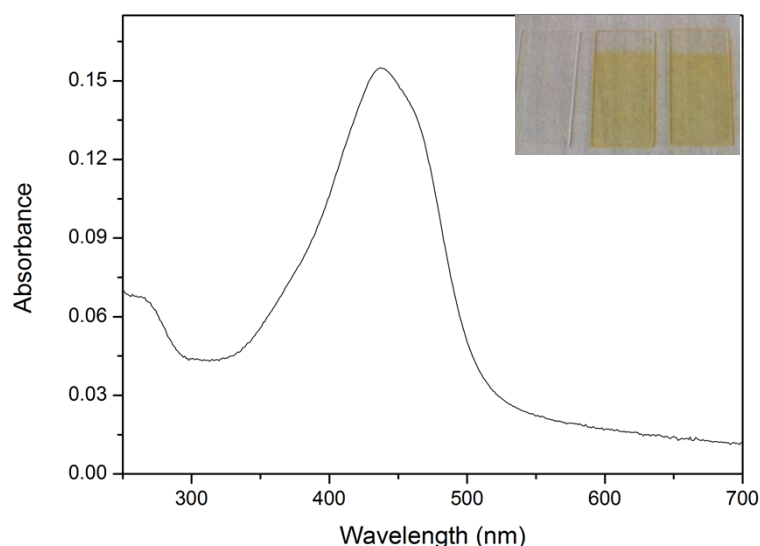
Figure S.2: UV-visible spectrum of incorporation of curcumin into a 5-bilayer multilayer of PDADMAC/PSS deposited on a quartz plate. Samples were exposed to 0.001% solutions (by weight) of curcumin in 90:10 water:ethanol solution for 12 hours. Picture inset shows two slides with incorporated curcumin, and one slide with just a PEM coating.

Ionic Strength Dependence of Curcumin Release

In addition to the low and high ionic strength NaCl solutions used to follow the release of curcumin from the PDADMAC/PSS PEMs (and detailed in the manuscript for both UV-visible and FTIR spectroscopy), an intermediate ionic strength was investigated using a release solution of 0.1 M NaCl. This ionic strength was only investigated using UV-visible spectroscopy to monitor the release as a function of immersion time. As expected, the release of curcumin from the PEM using 0.1M NaCl was intermediate in extent when compared to low salt (0.001M NaCl) and high salt (1 M NaCl) (see Figure S.3).
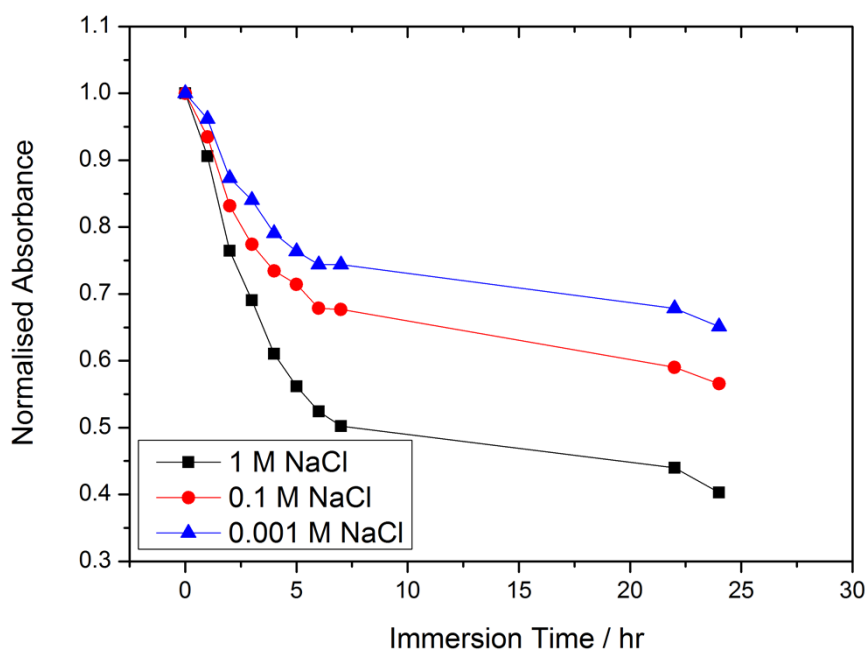
Figure S.3: Unloading of curcumin versus immersion time from UV visible spectroscopy data, including a long timescale immersion in the middle of the dataset (blue triangles – 0.001M NaCl release solution; red circles – 0.1M NaCl release solution; black squares – 1M NaCl release solution).

References

1.   P. Kittitheeranun, N. Sanchavanakit, W. Sajomsang and S. T. Dubas, *Langmuir*, 2010, 10, 6869-6873.