Appendix – Supporting information

The diffusion system follows the Fick's laws, and at steady state, the flux can be considered constant within the membrane. This hypothesis is supported by the small thickness of the membrane. The number of particles N which passes through an unit area in an unit time, or flux, J can expressed, at the steady state as:

$$J = -D\frac{dC}{dx} = \frac{D}{L}(C_1 - C_2) \tag{1}$$

The number of molecules in the system is constant, so:

$$V_1 C_1 + V_2 C_2 + V_m C_m = constant \tag{2}$$

where V_m was the volume of membrane and C_m the GP concentration within the membrane itself. Considering a small variation of the elements of equation 2 it resulted equal to zero:

$$d(V_1 C_1) + d(V_2 C_2) + d(V_m C_m) = 0 \tag{3}$$

The membrane volume is negligible respect to V_1 and V_2, and in addition V_1, V_2 and V_m did not vary during the experiment, thus eq. 4 can be assumed:

$$V_1 dC_1 = -V_2 dC_2 \tag{4}$$

integrating equation 10:

$$\int_{C_1}^{C_{11}} V_1 \, dC_1 = -\int_0^{C_2} V_2 \, dC_2 \tag{5}$$

where C_1 was the starting concentration of GP solution and C_{11} the final concentration in the LC. The concentration in the DC at the beginning of the experiment is zero, while final concentration is

C2. Solving equation 5:

$$V_1 C_{11} - V_1 C_1 = -V_2 C_2 \tag{6}$$

The equations that describe mass balance of GP in the two chambers are:

$$\begin{cases} V_1 \dfrac{d}{dt}(C_1) = -J_1 A \\ V_2 \dfrac{d}{dt}(C_2) = -J_2 A \end{cases} \tag{7}$$

where J_1 and J_2 are the fluxes from the LC and from the DC respectively. Applying the approximation of quasi steady state,

$$J_2 = -J_1 = J \tag{8}$$

Generally this approximation is valid if the characteristic time for the system to reach the equilibrium (τ_{eq}) was bigger that the characteristic time for the flux to reach the steady state (τ_{ss}). The τ_{eq} can be deduced from equation 7:

$$\tau_{eq} = \frac{C_1 V_1}{J_1 A} = \frac{L(A \cdot h)}{DA} = \frac{Lh}{D} \tag{9}$$

where h is the length of the chamber (obtained by dividing the volume by the diffusion surface A), while the τ_{ss}, as each diffusion phenomenon, is:

$$\tau_{ss} = \frac{L^2}{D} \tag{10}$$

By comparing equation 9 and 10,

$$\tau_{ss} \ll \tau_{eq} \Rightarrow \frac{L}{h} \ll 1 \tag{11}$$

From equation 7,

$$J \cdot A = \frac{D \cdot A}{L} \cdot (C_1 - C_2) = -V_1 \cdot \frac{dC_1}{dt} = V_2 \cdot \frac{dC_2}{dt} \tag{12}$$

the molecules flow from V_1 per second or those coming in V_2 per second is thus obtained. From equation 6:

$$C_{11} = \frac{V_1 C_1 - V_2 C_2}{V_1} \tag{13}$$

and replacing it in equation 12:

$$\frac{D \cdot A}{L} \cdot \frac{V_1 C_1 - V_2 C_2}{V_1} - C_2 = V_2 \cdot \frac{dC_2}{dt} \tag{14}$$

$$\frac{V_1 C_1 - (V_1 + V_2) \cdot C_2}{V_1 V_2} \frac{DA}{L} dt = dC_2 \tag{15}$$

$$\frac{D \cdot A}{L} \cdot \frac{1}{V_1 V_2} dt = \frac{1}{V_1 C_1 - (V_1 + V_2) \cdot C_2} dC_2 \tag{16}$$

integrating eq. 22:

$$\int_0^t \frac{D \cdot A}{L} \cdot \frac{1}{V_1 V_2} dt = \int_0^{C_2} \frac{1}{V_1 C_1 - (V_1 + V_2) \cdot C_2} \tag{17}$$

$$\frac{D \cdot A}{L} \cdot \frac{1}{V_1 V_2} t = \frac{1}{-(V_1 + V_2)} [\ln(V_1 C_1 - (V_1 + V_2) \cdot C_2) - \ln(V_1 C_1)] \tag{18}$$

$$-\frac{D \cdot A}{L} \cdot \frac{V_1 + V_2}{V_1 V_2} t = \ln\left(\frac{V_1 C_1 - (V_1 + V_2) C_2}{V_1 C_1}\right) \tag{19}$$

$$e^{\frac{D \cdot A}{L} \cdot \frac{V_1 + V_2}{V_1 V_2} t} = 1 - \frac{(V_1 + V_2) C_2}{V_1 C_1} \tag{20}$$

from eq.20, C_2 can be deduced:

$$C_2 = \frac{V_1 C_1}{V_1 + V_2} \cdot \left(1 - e^{\frac{D \cdot A}{L} \cdot \frac{V_1 + V_2}{V_1 V_2} t}\right) \tag{21}$$