Interactions of Organics within Hydrated Selective Layer of Reverse Osmosis Desalination Membrane: a Combined Experimental and Computational Study

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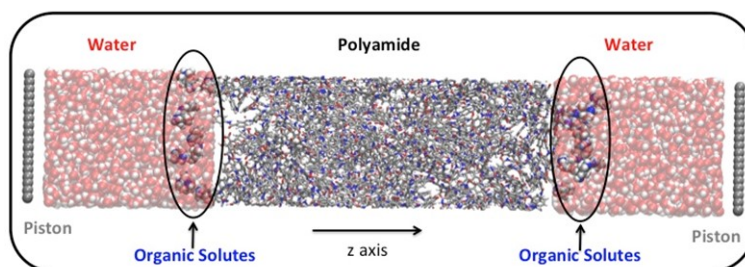e-mail: anthony.szymczyk@univ-rennes1.fr ; edrazevic@eng.au.dk

Supporting Information

Number of pages: 7

Number of equations: 7

Number of figures: 7

Computational details

Figure S1. Snapshot showing the system initial configuration.

NVT equilibration was carried during a short time in order to minimize the initial configuration. Our equilibration procedure is detailed below:

1) Simulation at 0K was performed in the NVT ensemble during 100 ps to minimize the system energy
2) Simulation at 298 K was further conducted in the NVT ensemble during 100 ps to avoid an energetic drift

This equilibration in the NVT ensemble did not induce cavities inside the water reservoirs because water molecules that entered the PA membrane were quickly replaced by other water molecules from the water reservoir (driving effect). It only led to a slight shift of the water reservoirs towards the PA membrane, thus inducing a thin empty slab between the reservoirs and the graphene walls, which was quickly removed during the first ps of the NEMD simulations (note that the z-position of the membrane atoms was fixed in NEMD simulations).
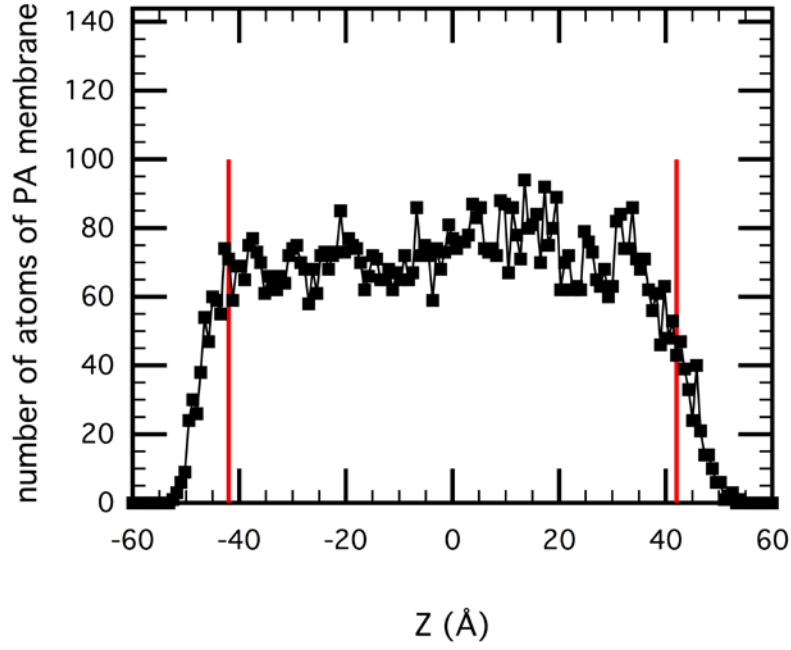
Figure S2. Axial profile of PA density. The red lines indicate the coordinates from which water molecules were considered to be in the membrane phase.

Equilibrium partitioning and diffusion measurements

The total equilibrium absorbance can be expressed as the sum of all contributions in parallel and perpendicular directions:

$$A_\infty = \left(A_\perp + \frac{1}{2} A_{\|x} + \frac{1}{2} A_{\|z} \right) \tag{S1}$$

where the different components are given by[1]

$$A_\perp = \frac{2x_1}{x_1^2 + x_3^2} \left\{ \left[\frac{n_w d_{p3}}{2} - Ln_w \frac{x_1^2 + x_2^2}{x_1^2 + x_3^2} \right] \varepsilon C + Ln_e \varepsilon^* C^* \right\} \tag{S2}$$

$$A_{\|x} = \frac{2x_1 x_3^2 / n_d^2}{x_1^2 n_w^4 / n_w^4 + x_3^2} \left\{ \left[\frac{n_w d_{p3}}{2} - Ln_v \frac{x_1^2 / n_w^4 + x_2^2 / n_e^4}{x_1^2 / n_w^4 + x_3^2 / n_w^4} \right] \varepsilon C + Ln_e \varepsilon^* C^* \right\} \tag{S3}$$

$$A_{\|z} = \frac{2x_1 \sin^2\theta}{x_1^2 n_w^4/n_w^4 + x_3^2} \left\{ \left[\frac{n_w d_{p3}}{2} - Ln_w \frac{x_1^2/n_w^4 + x_2^2/n_e^4}{x_1^2/n_w^4 + x_3^2/n_w^4} \right] \varepsilon C + Ln_e \frac{n_3^4}{n_2^4} \varepsilon^* C^* \right\} \tag{S4}$$

with $x_1 = n_d \cos\theta$, $x_2 = \sqrt{n_w \sin^2\theta - n_e^2}$, $x_3 = \sqrt{n_d^2 \sin^2\theta - n_w^2}$, $\theta = \pi/4$.

A(t) is the intensity at time *t*, *A(∞)* is the maximum intensity at infinite *t*, i.e., in equilibrium with solution, *L* is the thickness of the swollen (wet) film, here taken as 620 nm,[2] *D* is the average diffusivity of the solute in the film in the normal direction, *C* and *C** are the solute concentrations in the bulk solution and in the polyamide film, respectively, ε and ε^* are the solute molar extinction coefficients in the bulk solution and in the polyamide film, respectively, n_e is the effective refractive index of the swelled film, n_d is the refractive index of the ATR crystal (2.4), n_w is the refractive index of water (1.33), $\theta = \pi/4$ is the angle of incidence of the IR beam at the film-crystal interface, λ is the wavelength of the band, and d_{p3}, is the actual penetration depth given by the following equation:

$$d_{p3} = \frac{\lambda}{2\pi \sqrt{\sin^2\theta - \left(\frac{n_e}{n_d}\right)^2}} \tag{S5}$$

n_e was calculated (1.67) by solving the following equation while $\Phi = 0.14$ and $n_p = 1.70$:[2]

$$\Phi \frac{n_w - n_e}{n_w + 2n_e} + (1 - \Phi) \frac{n_p - n_e}{n_p + 2n_e} = 0 \tag{S6}$$

We assumed that $\varepsilon = \varepsilon^*$, and ε was evaluated from the linear fit of experimentally obtained *A* vs *C*, for a specific case, when $L = 0$, *i.e.* there was no film deposited on the crystal (Fig. S3, S4 and S5).

The solute concentration in the polyamide film C^* was estimated by fitting Equation (S1) to the equilibrium absorbance $A(\infty)$ value.

The equation used to evaluate diffusion coefficients is presented below[2]

$$\frac{A(t)-A(0)}{A(\infty)-A(0)}=1-\frac{8\gamma}{\pi\left[1-\exp(-2\gamma L)\right]}\sum_{N=0}^{\infty}\frac{\exp\left(\dfrac{-D(2N+1)^2\pi^2 t}{4L^2}\right)\left[\dfrac{(2N+1)\pi}{L}\exp(-2\gamma L)+(-1)^N(2\gamma)\right]}{(2N+1)\left[4\gamma^2+\left(\dfrac{(2N+1)\pi}{L}\right)^2\right]}$$

(S7)

where $\gamma = 1/d_{p3}$, t is the time in seconds, $A(0)$ is the absorbance at $t = 0$ (it was 0 in this study) and N, the number of terms, was set to 1000.
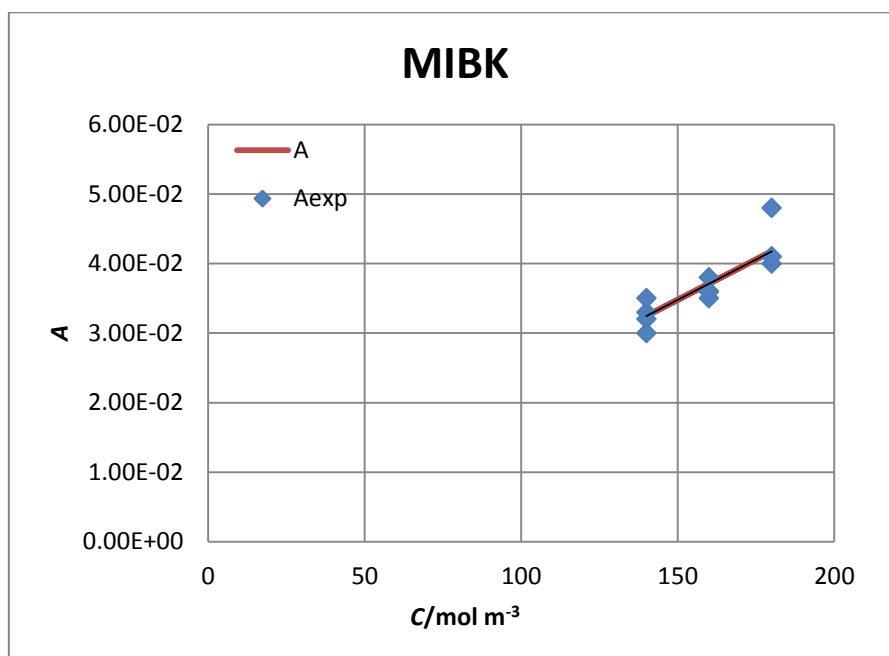
In Equation (S7) the two fitting parameters are the solute diffusion coefficient in the polyamide film, D, and the equilibrium absorbance $A(\infty)$.
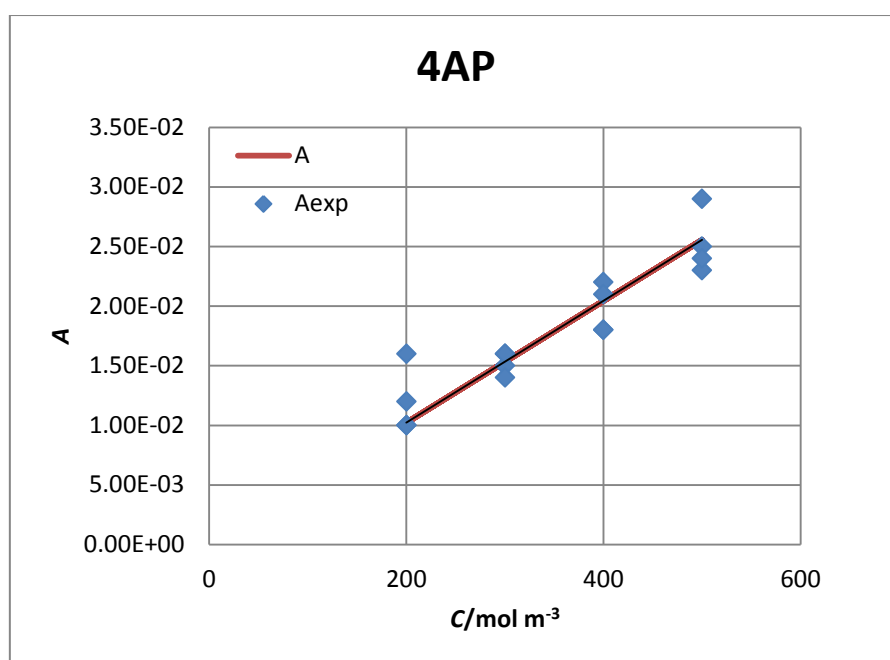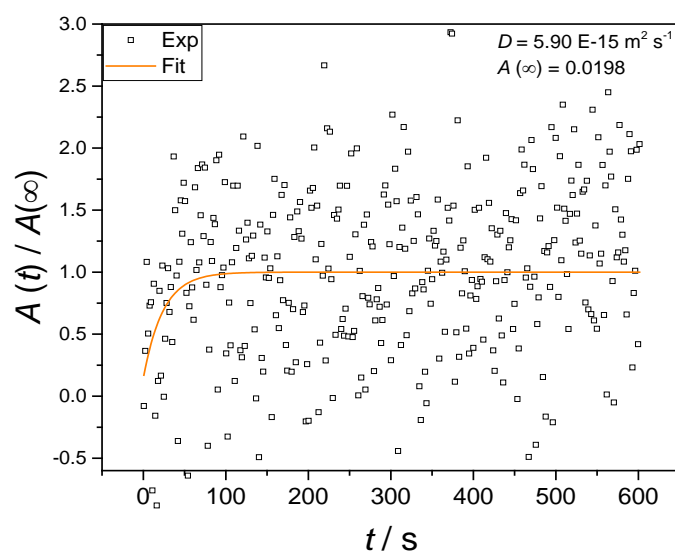

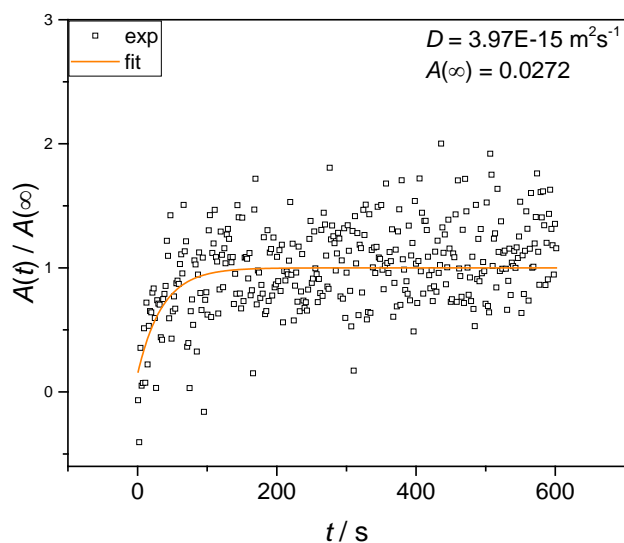**Figure S3.** Absorbance versus 4 aminopiperidine concentration, bare diamond, T=21 °C.
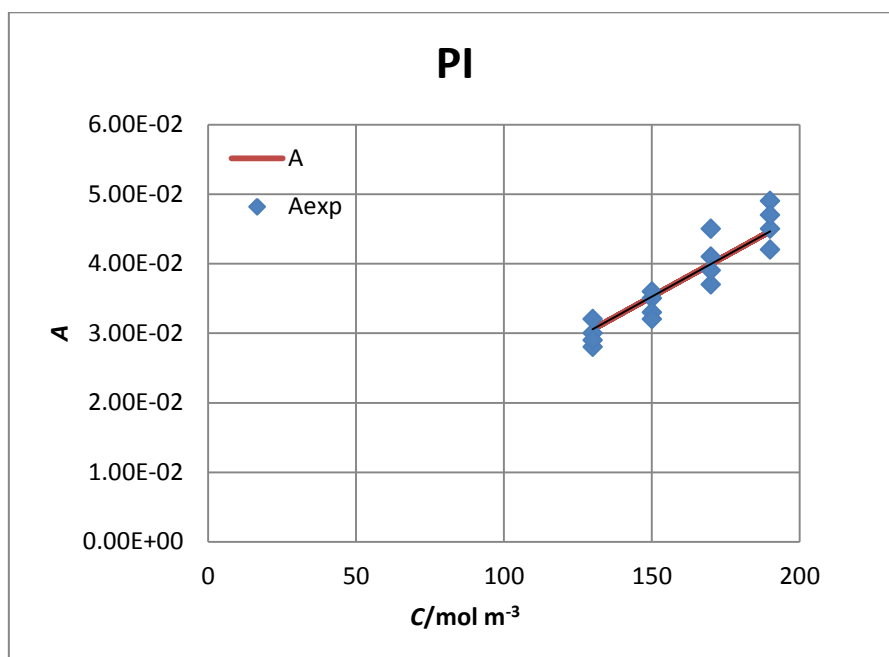
Figure S4. Absorbance versus pinacolone concentration, bare diamond, T=21 °C.

Figure S5. Absorbance versus methyl isobutyl ketone concentration, bare diamond, T=21 °C.

Figure S6. Diffusion of 4-aminopiperidine.

Figure S7. Diffusion of pinacolone.

References
(1) Freger, V.; Ben-David, A. Use of attenuated total reflection infrared spectroscopy for analysis of partitioning of solutes between thin films and solution. *Anal. Chem.* **2005**, *77*, 6019-6025.
(2) Dražević, E.; Košutić K.; Kolev, V.; Freger, V. Does hindered transport theory apply to desalination membranes? *Environ. Sci. Technol.* **2014**, 48, 11471-11478.