Supporting Information

1. Pore size distribution and effective pore radii

- Calculation of pore radii distribution uses following assumptions: (i) pores are straight and cylindrical, (ii) all of the pores have identical length and (iii) pores in the membrane may have different radii.

- Pore radii are distributed within interval $R_{min} < R < R_{max}$. The smallest pore radii is defined as $R_{min} = 2r_w$ while the biggest pore radii was $R_{max} = 100\ r_w$, where r_w was the radii of a single water molecule, 0.083 nm respectively. Initially a grid of pores with M intervals is defined within interval $R_{min} < R < R_{max}$. Then the pore radii in the grid may be defined as $R_i - \Delta/2 \leq R \leq R_i + \Delta/2$, where $i = 0, 1, 2, \dots M$, $\Delta = (R_{max}-R_{min})/M$ and $R_i = R_{min} + (i+1/2)\ \Delta$.

- Flux of the solution through the membrane is additive value meaning the total flux of the solution is the sum of the particular fluxes occurring through N_i pores of R_i radii. Using SFPF model particular flux $q_{p,i} \equiv q_p(R_i)$ through particular pore of pore radii R_i, may be calculated. Here $q_{p,i}$ has the dimension of kg m^{-2} s^{-1}. Since the molar fraction of organic solutes in the feed solution (at the entrance of the pore) was negligible, below 0.0004, and 1 kg of pure deionized water occupies 1 dm^3, $q_{p,i}$ may be expressed as particular volume flux through the particular pore of radius R_i, $J_{v\,p,i} = 0.001\ q_{p,i}$ [m^3 m^{-2} s^{-1}]. Then the total volume flux of the solution may be represented as:

$$J_{v,theor} = \sum_i N_i J_{v\,p,i} \qquad\qquad A(1),$$

where N_i is the total number of pores.

- Using SFPF model the rejection of solute $f_i \equiv f(R_i)$ by a particular pore may be calculated. Rejection is not an additive value but the product of rejection and particular volume flux $J_{v\,p,i}$ is:

$$J_{v,theor}f_{theor} = \sum_i N_i J_{v\,p,i} f_i \qquad\qquad A(2)$$

- The values of total J_v and f may be determined experimentally. Their values will depend on the sizes of the solutes, i.e. their Stokes radius. It means that the corresponding microvalues of $J_{v\,p,i}$ and f_i will depend <u>on the type of the solutes</u> used. Therefore, new functions are defined, $J_{v\,p,\,i,J} \equiv J_{v\,p,J}(R_i)$ i $f_{i,J} \equiv f_J(R_i)$.

  $J_{v\,p,\,i,J}$ and $f_{i,J}$ in A(4) were calculated using SFPF model developed by Sourirajan and Matsuura. Six ($N_S = 6$) different organic solutes were used in this study, namely:

trimethylene oxide, 1-3-dioxolane, 1,4-dioxane, 12-crown-4, 15-crown-5 and 18-crown-6. The algorithm was written in Fortran and may be described in steps.

1. Stokes radius was calculated from diffusivity of solute (D_{AW}) in water at infinite dilution using $r_{St} = k_B T/(6\pi\eta D_{AW})$ where T = 298 K, η = 0.001 Pa s and k_B is the Boltzmann constant. Diffusivities of solutes used in the procedure are summarized in (Emil Draževiç, Krešimir Košutiç, Vladimir Dananiç, *Mass transfer of differently sized organic solutes at spacer covered and permeable nanofiltration wall*, Chem. Eng. J., **2014**, 244, 152-159).

2. Parameter B_J is a measure of solute – membrane interaction and it was taken $B_J = 0$, i.e. it was assumed that there are no Van der Waals forces between these polar solutes and the pore wall.

3. A grid of pore radii was defined, as explained above

$$R \equiv R_i = R_{\min} + i\frac{R_{\max} - R_{\min}}{M} \quad i = 0,1,\dots, M \qquad \text{A(3)},$$

where M = 1000.

4. The procedure began with the solute having smallest Stokes radius using R_i to calculate each φ_i.

$$\varphi_i = \frac{R_S\,[m]}{R_i + r_w\,[m]} \qquad \text{A(4)}$$

φ_i was used to calculate $b\,(\varphi_i)$, frictional function for a grid of pores:

$$b(\varphi_i) \equiv K_c = \frac{(1-\varphi_i)^2 \left[2-(1-\varphi_i)^2\right]K_s}{2K_t} \qquad \text{A(5)}$$

$$K_t = \frac{9}{4}\pi^2\sqrt{2}\,(1-\varphi_i)^{-5/2}\left(1+\sum_{i=1}^{2} a_n (1-\varphi_i)^n\right) + \sum_{n=0}^{4} a_{n+3}\varphi_i^{\,n}$$

$$K_s = \frac{9}{4}\pi^2\sqrt{2}\,(1-\varphi_i)^{-5/2}\left(1+\sum_{n=1}^{2} b_n (1-\varphi_i)^n\right) + \sum_{n=0}^{4} b_{n+3}\varphi_i^{\,n} \;,$$

where a_1 = -1.2167, a_2 = 1.5336, a_3 = -22.5083, a_4 = -5.6117, a_5 = -0.3363, a_6 = -1.2160, a_7 = 1.6470, b_1= 0.1167, b_2 = -0.0442, b_3 = 4.018, b_4 = -3.9788, b_5 = -1.9215, b_6 = 4.392 and b_7 = 5.006.

5. Value of $C_{p,i}$ was assumed in order to calculate $C_{m,i}$ from:

$$C_m = C_p + (C_f - C_p)\exp(J_v / k) \qquad\qquad A(6)$$

where k was determined from Sherwood relation for non-permeable wall as explained in (Emil Draževic, Krešimir Košutić, Vladimir Dananić, *Mass transfer of differently sized organic solutes at spacer covered and permeable nanofiltration wall*, Chem. Eng. J., **2014**, 244, 152-159) and J_v is the experimental solution volume flux.

6. Using the data on operating pressure and C_m, dimensionless parameters $\beta_{1,i}$ and $\beta_{2,i}$ were calculated using following equations:

$$\beta_{1,i} = \eta / \left(X_{AW} R_i^2 C_m\right) \qquad\qquad A(7)$$

$$\beta_{2,i} = \Delta P / (R_g T C_m) \qquad\qquad A(8)$$

where $X_{AW} = R_g T / D_{AW}$ and R_g is the gas constant.

7. Data on $R_{S,J}$, $b_i(\varphi)$, $\beta_{1,i}$ and $\beta_{2,i}$ are loaded. Dimensionless radius $\rho = r/R_i$ and dimensionless concentration $C_A = C_p/C_m$ are used to calculate the solvent velocity profile in each pore R_i solving the equation:

$$\frac{d^2\alpha(\rho)}{d\rho^2} + \frac{1}{\rho}\frac{d\alpha(\rho)}{d\rho} + \frac{\beta_2}{\beta_1} - \frac{(b(\varphi_i)-1)\alpha(\rho)C_A(\rho)}{\beta_1} = 0 \qquad\qquad A(9)$$

Equation A(9) is solved with boundary conditions, $\rho = 0 \rightarrow d\alpha(\rho)/d(\rho) = 0$, and $\rho = 1 \rightarrow \alpha(\rho) = 0$.

**8.** $\alpha_i(\rho)$ from step 7. is used to calculate $f_{m,i}$ in the following equation.

$$f_{m,i} = 1 - \frac{\int_0^1 \left\{\exp(\alpha_i(\rho)) / \left[1 + b(\varphi_i)(\exp(\alpha_i(\rho))-1)\right]\right\}\alpha_i(\rho)\rho d\rho}{\int_0^1 \alpha_i(\rho)\rho d\rho} \qquad\qquad A(10)$$

9. C_p was then calculated from $f_m = 1 - C_p / C_m$ where f_m A(10). If C_p agrees with the assumed C_p from the Step 5. then the algorithm finishes, and if not, it returns to step 5. and repeats the procedure until this condition is satisfied.

10. Find the distribution $Y(R_i)$ for which S has the minimum value:

$$S = \sum_{J=1}^{N_s} \left(f_{J,\text{exp}} - \frac{\sum_{i=1}^{M} f_J(R_i) J_{vp,i,J}(R_i) Y(R_i)}{\sum_{i=1}^{M} J_{vp,i,J}(R_i) Y(R_i)} \right)^2 \qquad \text{(A11)}$$

A(11) has M fitting parameters. The $f_{(J)\text{exp}}$ is the measured rejection of marker J.

Minimum of A(11) is found using the gradient method under constraint $N(Ri) \geq 0$ and

$Y(R_i) > 0$, for each i. $Y(R_i)$ in A(11) is defined as $Y(R_i) = N_i/N_{\text{total}}/\Delta R_i$. The procedure

assumes no pore size distribution, it find most probable Y_i of pore radii R_i which give

the minimum of S for all solutes involved.
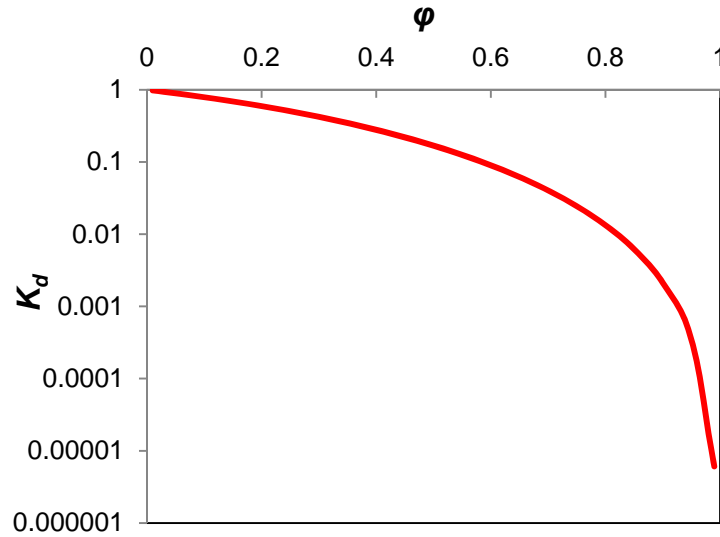
Figure S1. Diffusion hindrance, K_d, represented by Eq. (5). It is valid in range $0 < \varphi < 1$.
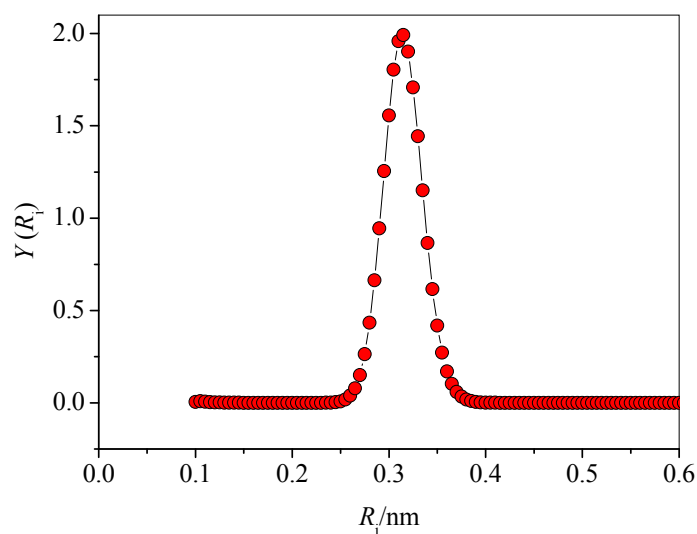
Figure S2. Log normal like pore size distribution of SWC4+ membrane calculated from rejection of 6 model solutes using above described numerical procedure.

Table S1. Bulk diffusion coefficients and Stokes radii of the organic solutes tested

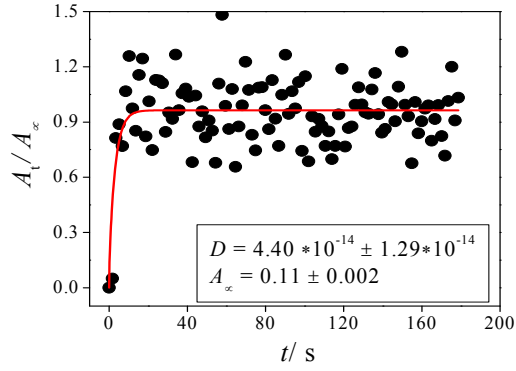| Organic solute	M/ g mol^{-1}	R_S/nm*	D_∞/ 10^{-10} m^{2}s^{-1}*	v/cm^{-1}**	Interval/cm^{-1}***
Ethylene glycol	62.07	0.198	11.02	1043	1000-1060
Glycerol	92.09	0.217	10.05	1044	1010-1080
1 - butanol	74.12	0.239	9.128	1070	1050-1090
1 - pentanol	88.15	0.261	8.359	1053	1040-1070
Benzyl alcohol	108.14	0.273	7.992	1006	960-1060

* Data on Stokes radii, R_S, and bulk diffusivities, D_∞, are taken From Ben-David *et al.*[45]
** IR band of specific solute used to estimate diffusion coefficient. *** Integration interval and baseline of band area.
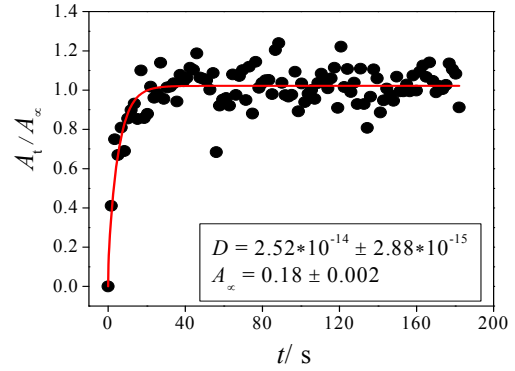
Table S2. The difference in experimental (*f*) and theoretical (*f*theor) values of rejection. Theoretical values were found using pore size distribution in Fig. S2.

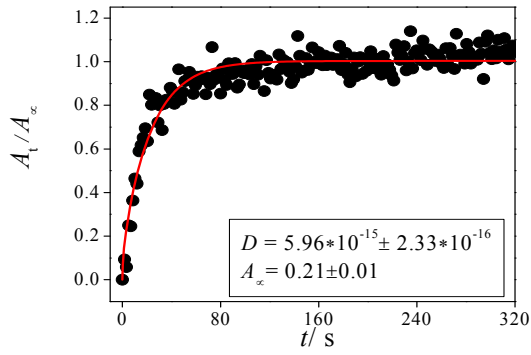| Organic solute	f	f_{theor}
trimethylene oxide	0.529	0.580
1,3−dioxolane	0.706	0.709
1,4−dioxane	0.951	0.785
12−crown−4	0.974	0.986
15−crown−5	0.974	0.986
18−crown−6	0.975	0.986

2. ATR-FTIR data and corresponding fitting examples

$D = 4.40 * 10^{-14} \pm 1.29 * 10^{-14}$
$A_{\infty} = 0.11 \pm 0.002$

A

$D = 2.52 * 10^{-14} \pm 2.88 * 10^{-15}$
$A_{\infty} = 0.18 \pm 0.002$

B

$D = 5.96 * 10^{-15} \pm 2.33 * 10^{-16}$
$A_{\infty} = 0.21 \pm 0.01$

C

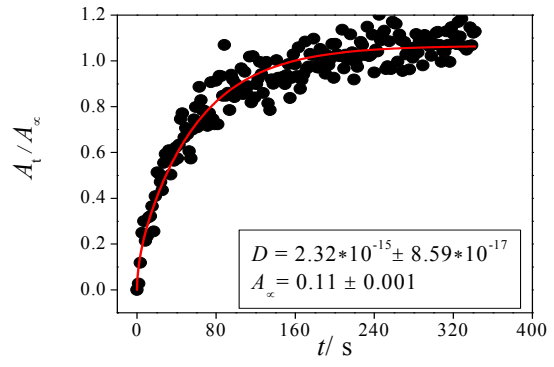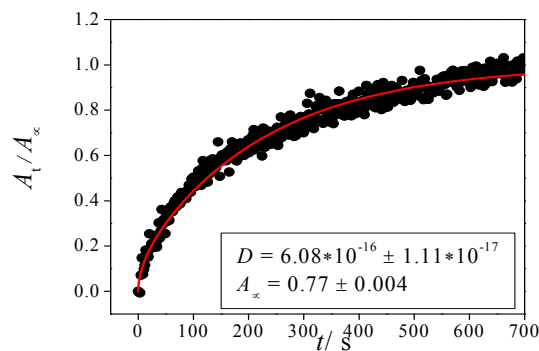$D = 2.32 * 10^{-15} \pm 8.59 * 10^{-17}$
$A_{\infty} = 0.11 \pm 0.001$

D

E

Figure S3. Experimental results on $A(t)$ and t used to estimate diffusion coefficients using hydrated stack of five SWC4+ layers. Red lines represent curve obtained from the two parameter fit of Eq. (2) to the experimental data. Black points represent different solutes i.e. surfaces under targeted bands; A) ethylene glycol; B) glycerol; C) 1 – butanol; D) 1 – pentanol; E) benzyl alcohol.
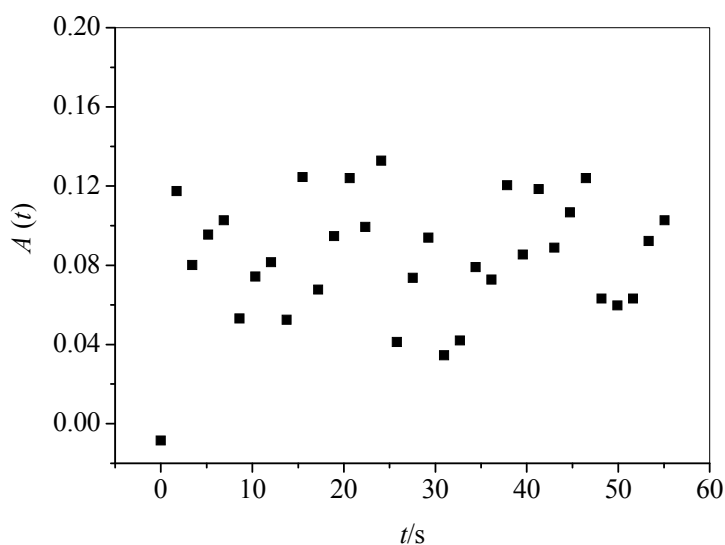
Figure S4. Band area of benzyl alcohol measured with a bare (without a film) crystal exposed to the same solution as with the film. The band area of benzyl alcohol with a polyamide film was about seven times higher (Figure S3E).