

STUDY OF TRANSFER OF ALCOHOL (methanol, ethanol, isopropanol) DURING NANOFILTRATION IN WATER/ALCOHOL MIXTURES

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Supplementary informations

Supplementary 1 : viscosity of water/alcohol mixtures at 20°C

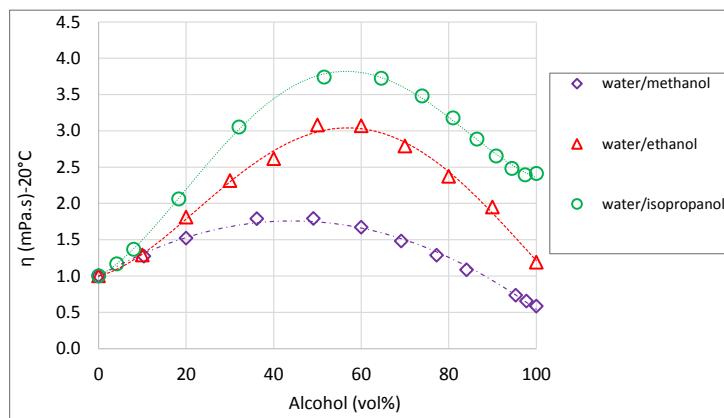


Fig. S1-1 : Viscosity of water/alcohol mixtures according to [35-37]. ○: water/isopropanol –
△: water/ethanol, ▲: water/methanol

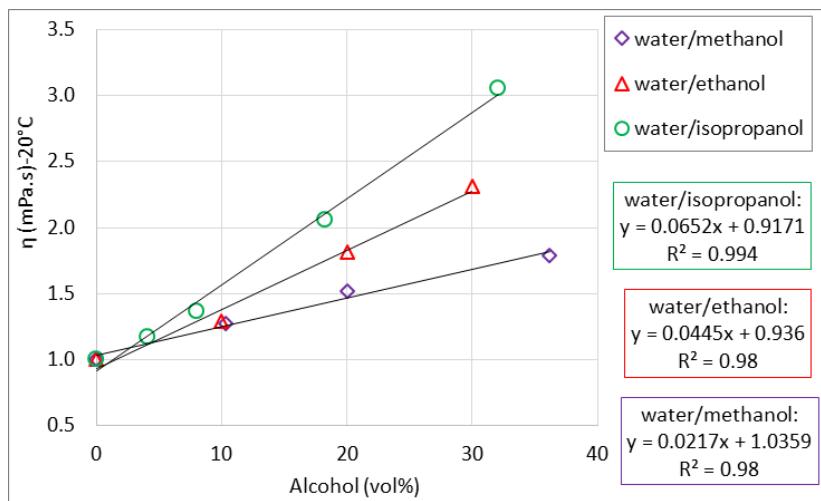


Fig. S1-2 : Viscosity of water/alcohol mixtures at 20°C according to [35-37].

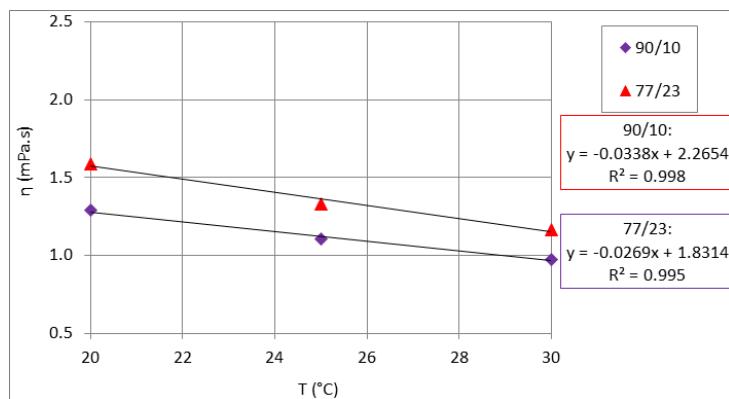


Fig. S1-3: Viscosity of water/methanol mixtures versus temperature according to [35].

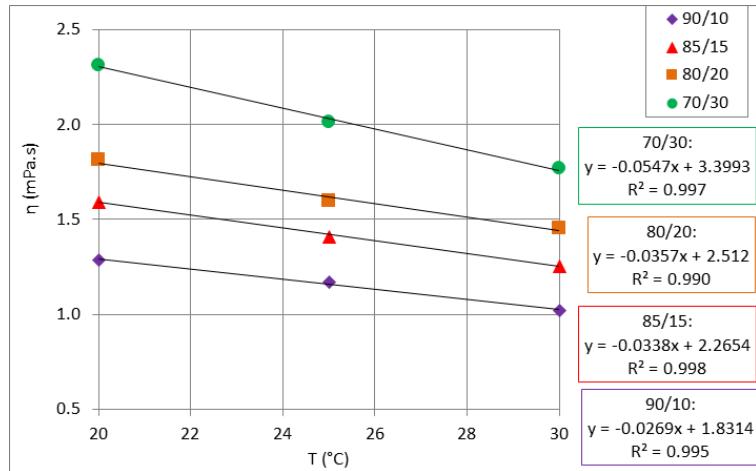


Fig. S1-4 : Viscosity of water/ethanol mixtures versus temperature according to [37].

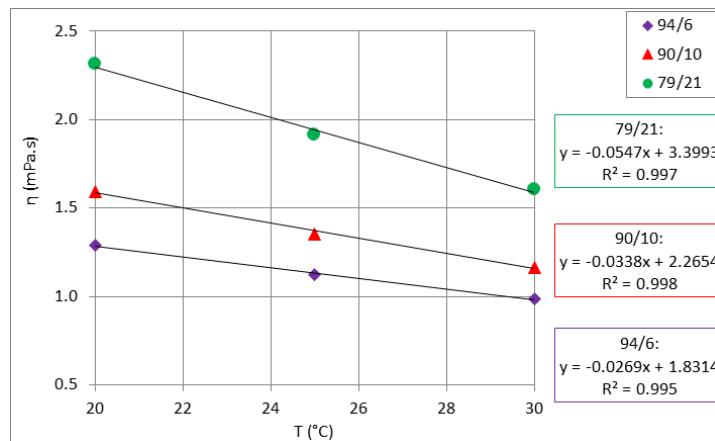


Fig. S1-5: Viscosity of water/isopropanol mixtures versus temperature according to [36].

Supplementary 2 : dielectric constant of water/ethanol at 20°C

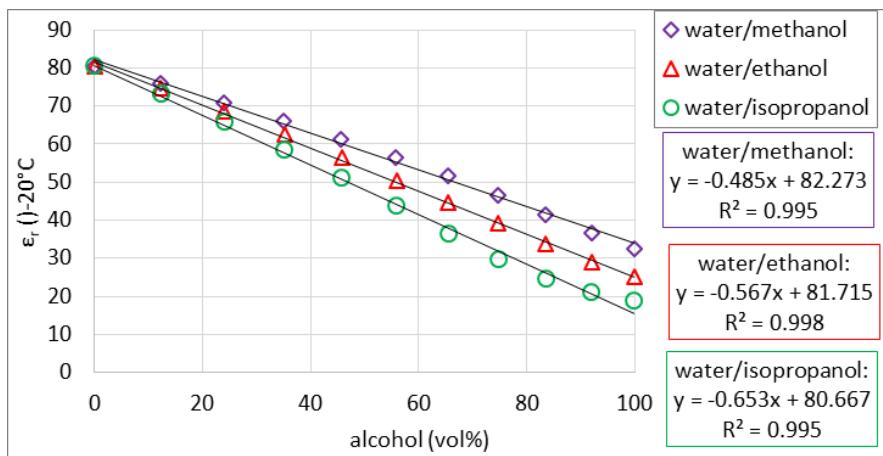
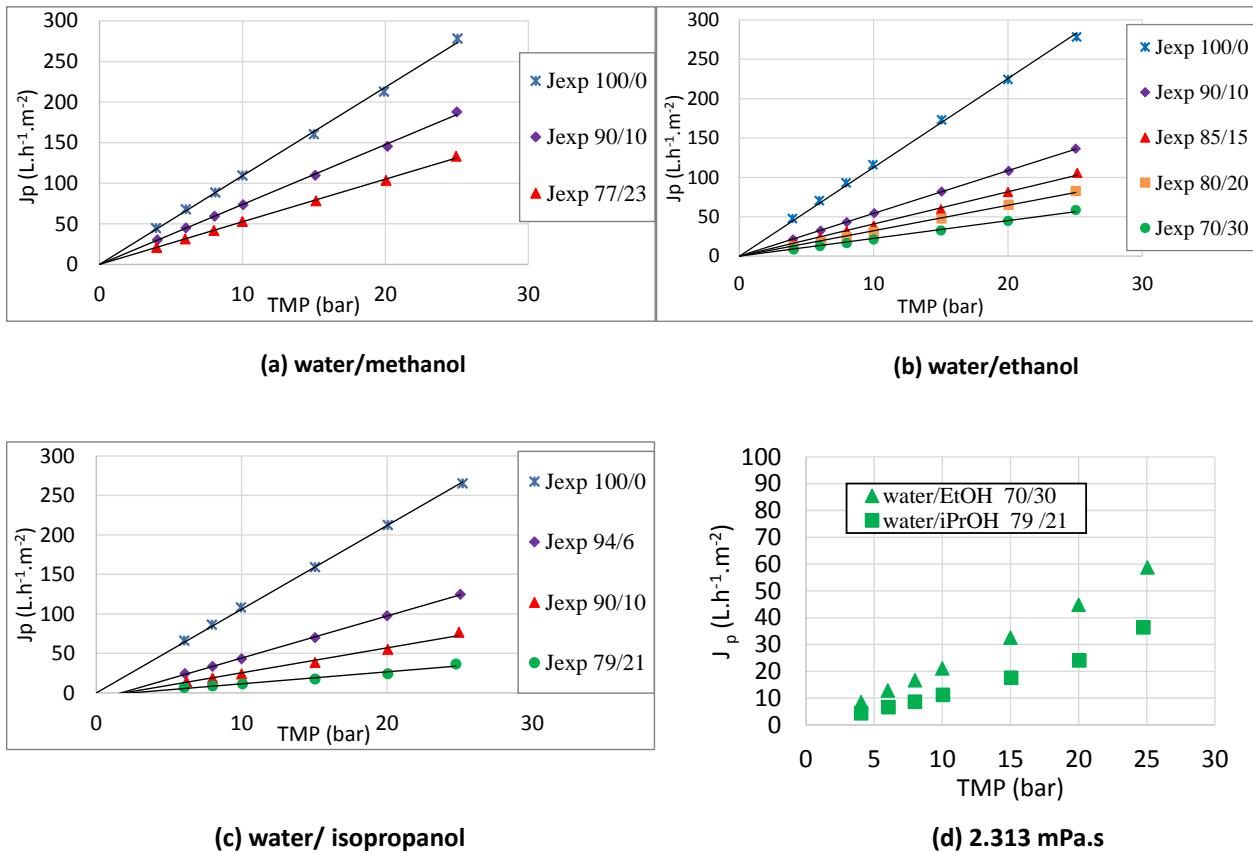
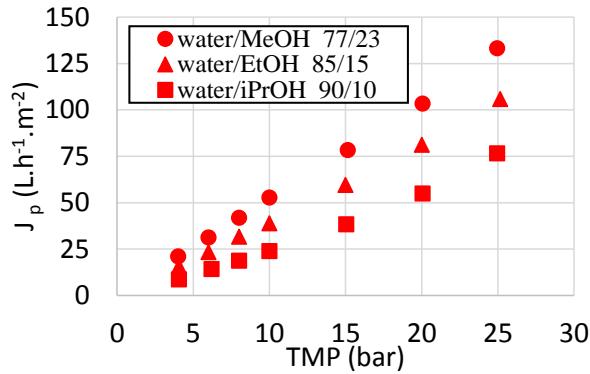


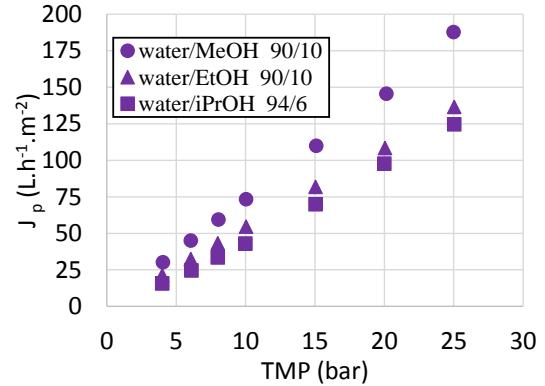
Fig. S2-1 : Dielectric constant of water/alcohol mixtures at 20°C according to [54].

Supplementary 3 : Experimental flux (J_p) of water/alcohol mixtures





(e) 1.593 mPa.s



(f) 1.289 mPa.s

Fig. S3-1: Experimental flux (J_p) of water/alcohol mixtures during NF in standard conditions

Supplementary 4 : mass transfer coefficient from correlations relating the Sherwood, Reynolds and Schmidt numbers

The thickness of the polarization layer (further called $\delta_{S\&M}$) can be also estimated from the Sherwood & Michel relation using the Chilton & Colburn analogy (eq. S4-1) and based on the Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) dimensionless numbers [S4-1, S4-2].

$$Sh = 0.023 \times Re^{0.875} \times Sc^{0.25} \quad (\text{eq.S4-1})$$

$$Sh = \frac{k_{S\&M} \cdot d_H}{D} = \frac{d_H}{\delta_{S\&M}} \quad (\text{eq. S4-2})$$

$$Re = \frac{\rho \times v \times d_H}{\eta} \quad (\text{eq.S4-3})$$

$$Sc = \frac{\eta}{\rho \times D} \quad (\text{eq. S4-4})$$

With:

$k_{S\&M} = \frac{D}{\delta_{S\&M}}$: value of the mass transfer coefficient calculated according to eq. S4-2 that will be compared to k_{SD-F} and k_{SK-F} in the following.

ρ : the density of the solvent mixture (**Erreur ! Source du renvoi introuvable.**)

v : the cross-flow velocity in the liquid channel calculated from d_H

d_H : the hydraulic diameter of the liquid channel taking into account the presence of the retentate spacer (**Table S4-1**) was calculated by the following equation [**S4-1**]:

$$d_H = \frac{4 \times \varepsilon}{\frac{2}{h_{SP}} + (1 - \varepsilon) \times S_{VSP}} \quad (\text{eq. 1})$$

Table S4-1: Property of 47 mil retentate spacer

spacer thickness h_{SP} (mm)	1.2
filament thickness d_F (mm)	0.7
mesh length (mm)	3.0
porosity ε	0.75
specific surface of the spacer S_{VSP} (mm ⁻¹)	5.71

The mass transfer coefficients were determined for S& M for sake of comparison.

Table S4-2 depicts the calculated dimensionless numbers and the mass transfer coefficient and polarisation layer thickness deduced from the Sherwood & Michel relation. The Reynolds number decreased when the alcohol content increased. It means that the turbulence was decreased when the alcohol content increased, in good accordance with viscosity increase. In empty and smooth channels, the flux is laminar for Reynolds numbers up to 2000 [**S4-3**]. However, in the narrow channels, the flux becomes unstable at much smaller Reynolds numbers (order of one hundred) [**S4-4**, **S4-5**, **S4-6**, **S4-7**]. Therefore, in this study, the turbulent regime has been established, even without accounting the local turbulences due to the added retentate spacer. So, it can be guessed that the effect of concentration polarization could be more noticeable for a filtration with more alcohol content. This is in good accordance with the increase of the polarization layer thickness (**Table S4-2**).

Table S4-2: Re, Sc, Sh and parameters of the S&M model

water/alcohol v/v		Re	Sc	Sh	$k_{S\&M}$ ($10^{-5} \cdot m.s^{-1}$)	$\delta_{S\&M}$ (μm)
water/	90/10	377	20.10^5	155	10	6
	methanol	77/23	300	31.10^5	141	8
water/	90/10	344	26.10^5	153	8	6
	85/15	293	38.10^5	146	7	7
ethanol	80/20	254	50.10^5	138	5	7
	70/30	200	81.10^5	126	4	8
water/ isopropanol	94/6	371	31.10^5	171	7	6
	90/10	298	48.10^5	157	6	6
	79/21	201	103.10^5	135	3	7

The mass transfer coefficient in the polarisation layer deduced from the 3 calculations, $k_{S\&M}$, k_{SD-F} and k_{SK-F} , exhibited the same trends with respect to the alcohol content: k decreased with alcohol increase. All the 3 values were of the same order, but generally k_{SD-F} and $k_{S\&M}$ were closer than k_{SK-F} and $k_{S\&M}$ (**Fig. S4-1**). Accordingly, the three calculation methods gave values of the polarization layer thickness in the same order of magnitude but those obtained from SK-F were lower than the two others (**Fig. S4-1**).

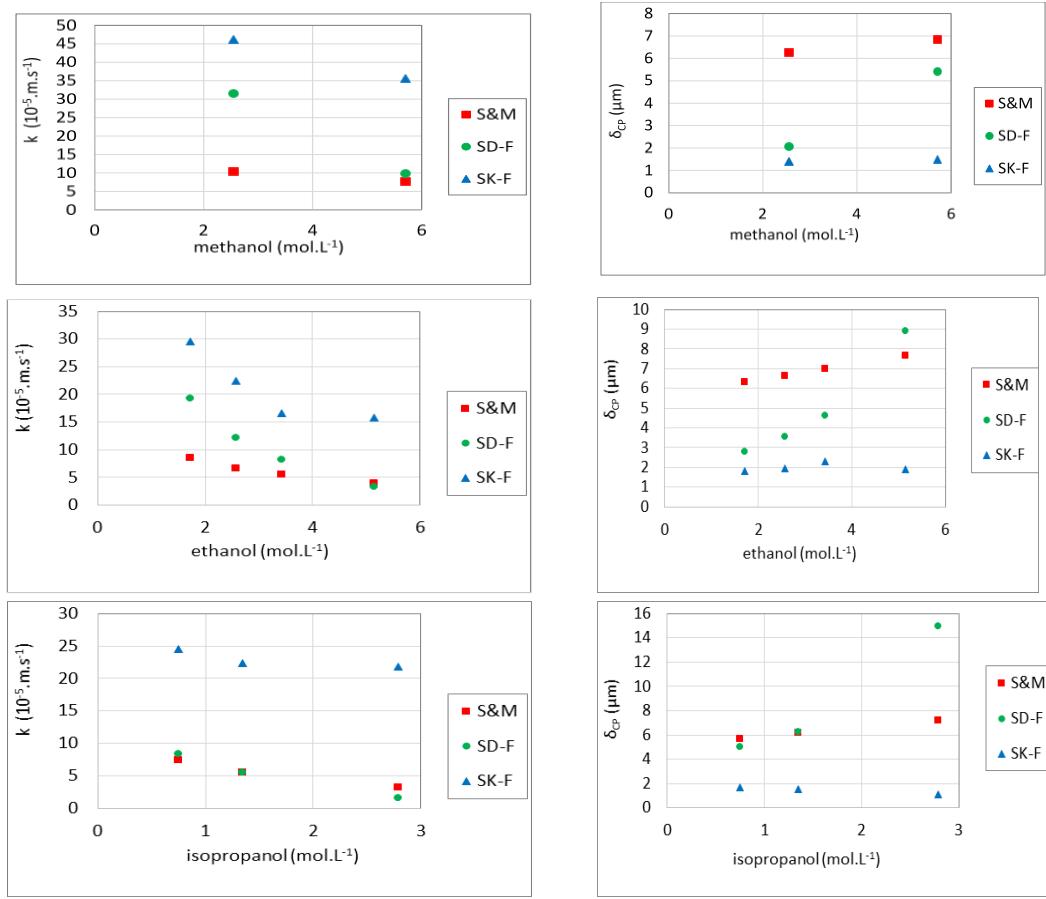


Fig. S4-1: Mass transfer coefficients of alcohol in the polarization layer (k) and thickness of the polarization layer δ_{CP} during NF of water/alcohol mixtures as calculated according three different approaches: from analogy using dimensionless numbers (S&M), combination of solution diffusion and film (SD-F) and combination of Spiegler & Kedem and film (SK-F).

Supplementary 5 : concentration polarisation by SD-F model

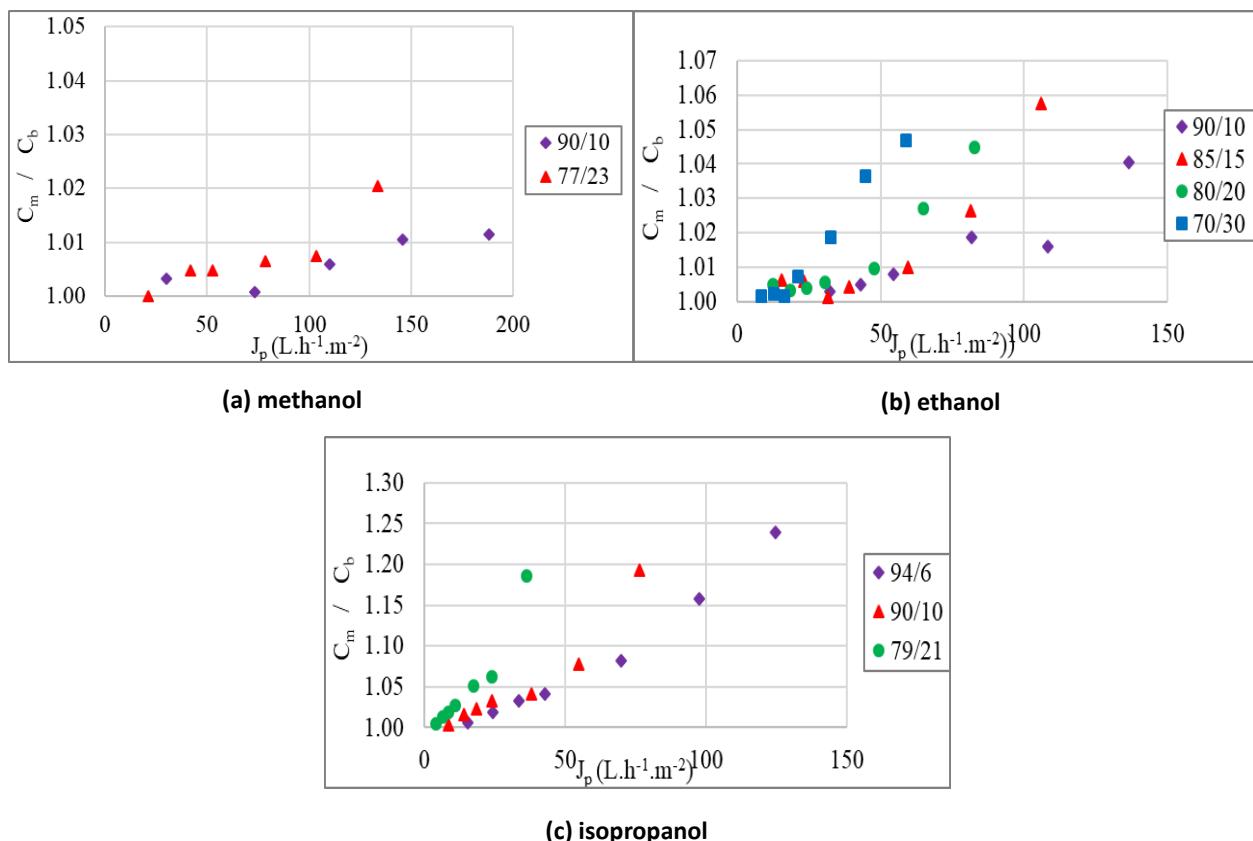


Fig. S5-1: C_m/C_b polarization coefficient during NF of water/alcohol mixtures as calculated according to combination of Solution Diffusion and film (SD-F).

Supplementary 6 : pore radius value depending on the alcohol radii selected for the calculation

Table S6-1: Several solute radii (in nm) according to [40]

Alcohol	r_s, Stokes	r_s, Vm	$r_s, \text{theoretical}$
MeOH	0.26	0.26	0.21
EtOH	0.31	0.29	0.26
i-PrOH	0.40	0.31	0.29

1- Solute radius = Stokes radius (in water)

Table S6-2 summarizes the obtained values when using the Stokes radii of alcohols deduced from diffusion experiments in water given in **Table 2** when fitting σ_{SHP} and $\sigma_{\text{SK-F}}$.

Table S6-2: Estimation of apparent pore radius from single alcohol rejection according to SK-F + SHP and using alcohol Stokes radius (in water)

water/alcohol v/v	$r_p, \text{SK-F + SHP}$ (nm)
water/methanol	90/10 0.45
	77/23 0.49
water/ethanol	90/10 0.46
	85/15 0.54
	80/20 0.61
water/ isopropanol	70/30 1.12
	94/6 0.57
	90/10 0.66
	79/21 0.72

2- Comparison of pore radius according to assumption on solute radius

The following Figures were obtained from values in **Table 10**.

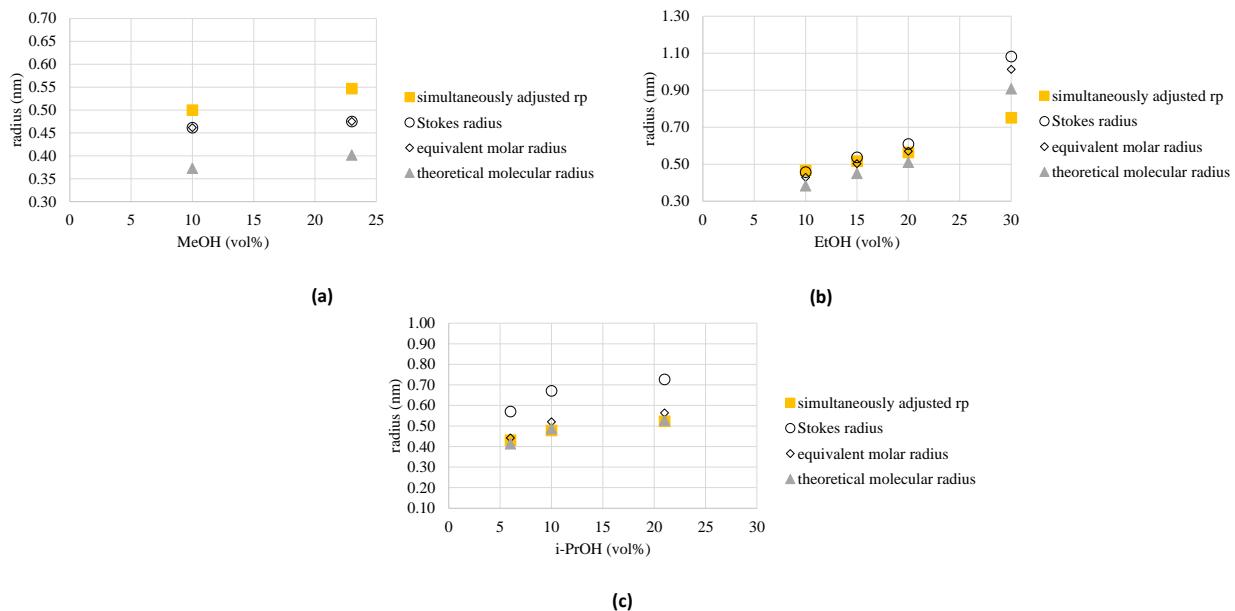


Fig. S6-1: Pore radii according to various assumptions on solute radii

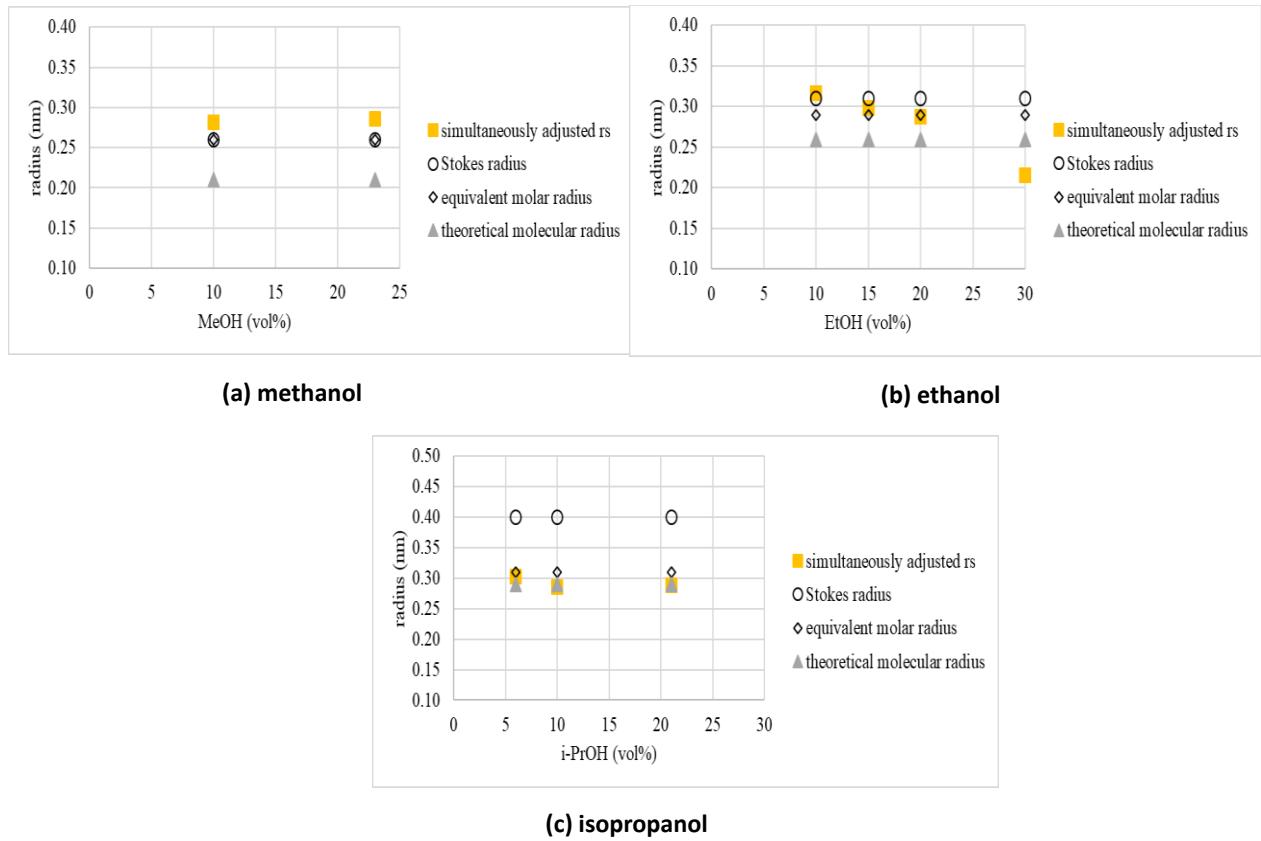


Fig. S6-2: Alcohol radii according to various assumptions

Supplementary 7: osmotic pressure detailed calculations for water/ethanol mixtures

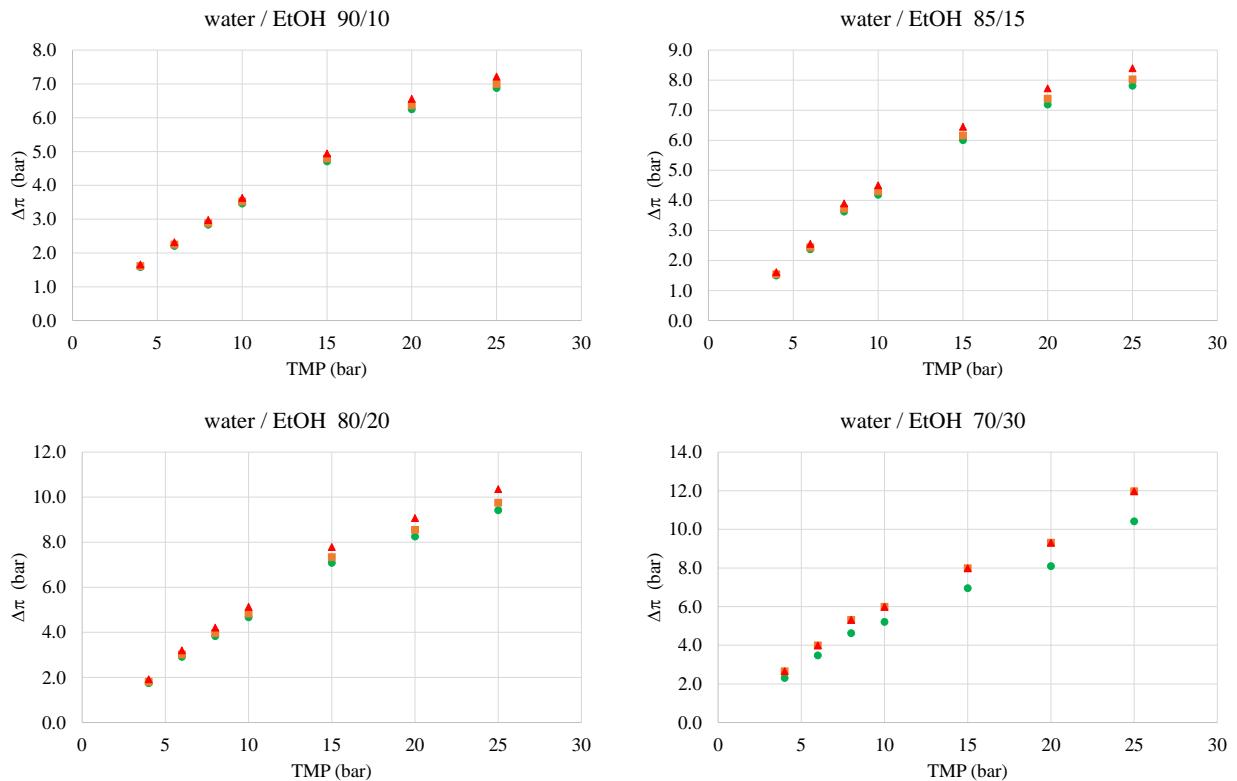


Fig. S7-1: Calculated $\Delta\pi_{\text{obs}}$, for the water/ethanol mixtures according to assumption on B' value (see **Table 4**)
●: van't Hoff - ■: $B' = 2.1 \times 10^{-5}$ - ▲: $B' = 5.82 \times 10^{-5}$

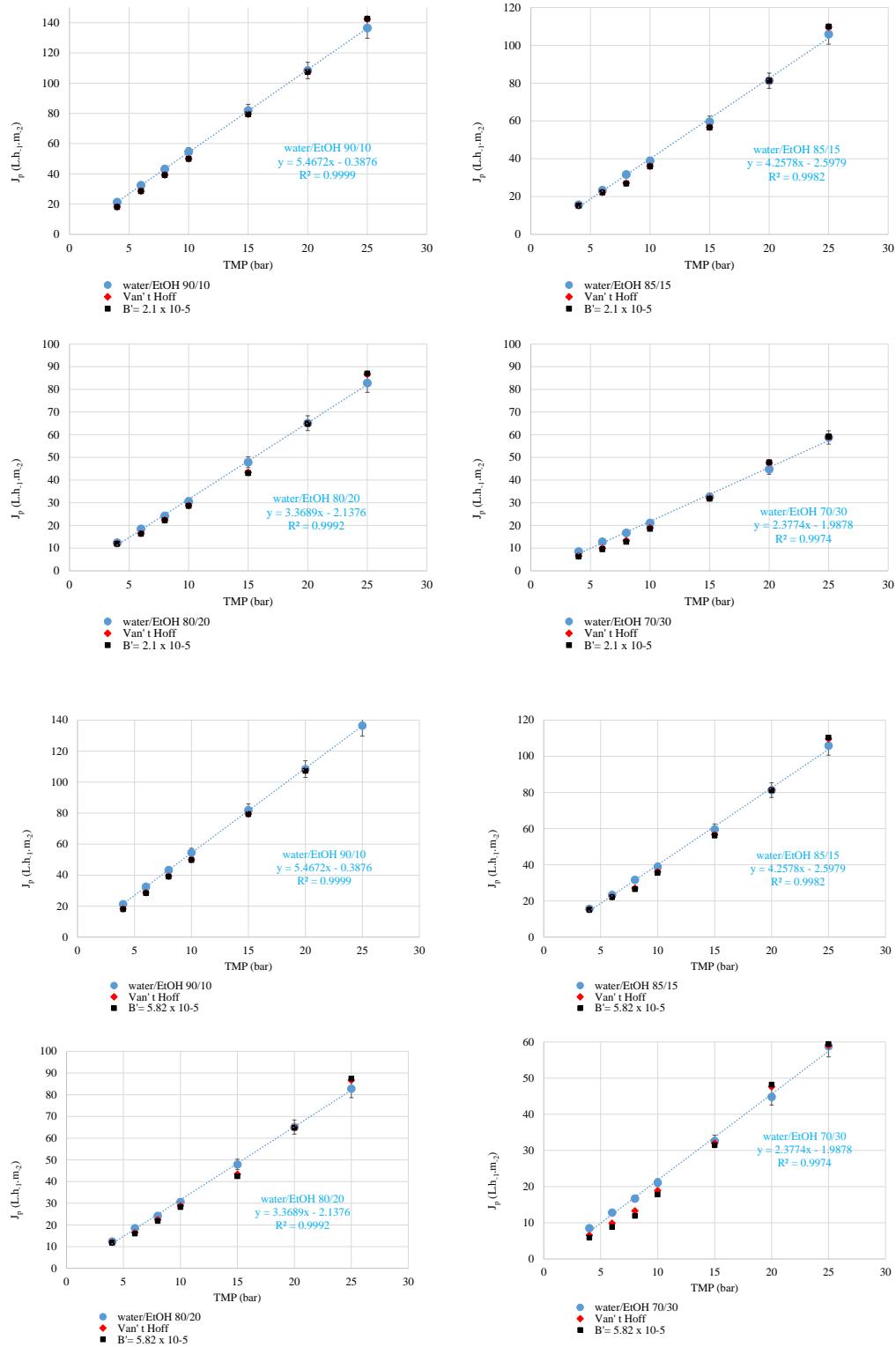


Fig. S7-2: Results of adjustment of experimental flux (J_p) in water/ethanol according to the best $L_{p,BGS}$ value calculated (eq. 17) with respect to assumption to calculate $\Delta\pi_{obs}$. ● experimental water/ethanol; ◆ van't Hoff assumption, ■: virial assumption. Equations on figures are those corresponding to the experimental data

Supplementary 8: osmotic pressure detailed calculations for water/methanol mixtures

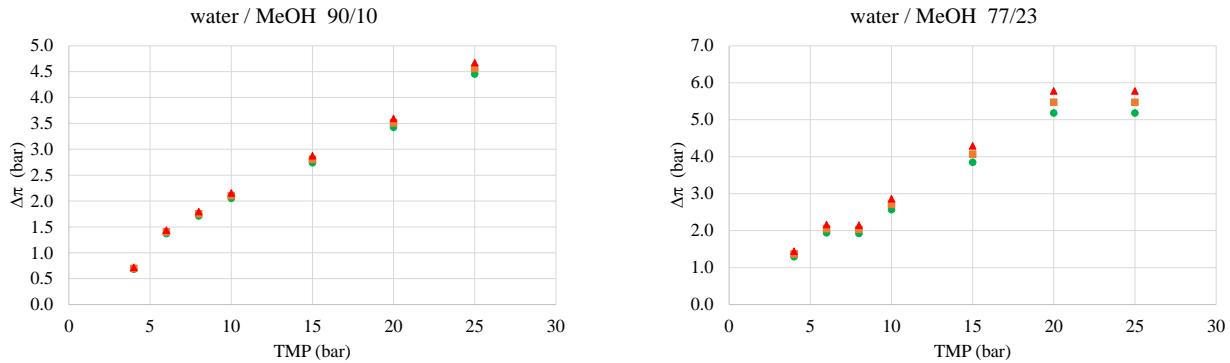


Fig. S8-1: Calculated $\Delta\pi_{\text{obs}}$, for the water/methanol mixtures according to assumption on B' value (see **Table 4**) ●: van't Hoff - ■: $B' = 2.0 \times 10^{-5}$ - ▲: $B' = 4.05 \times 10^{-5}$

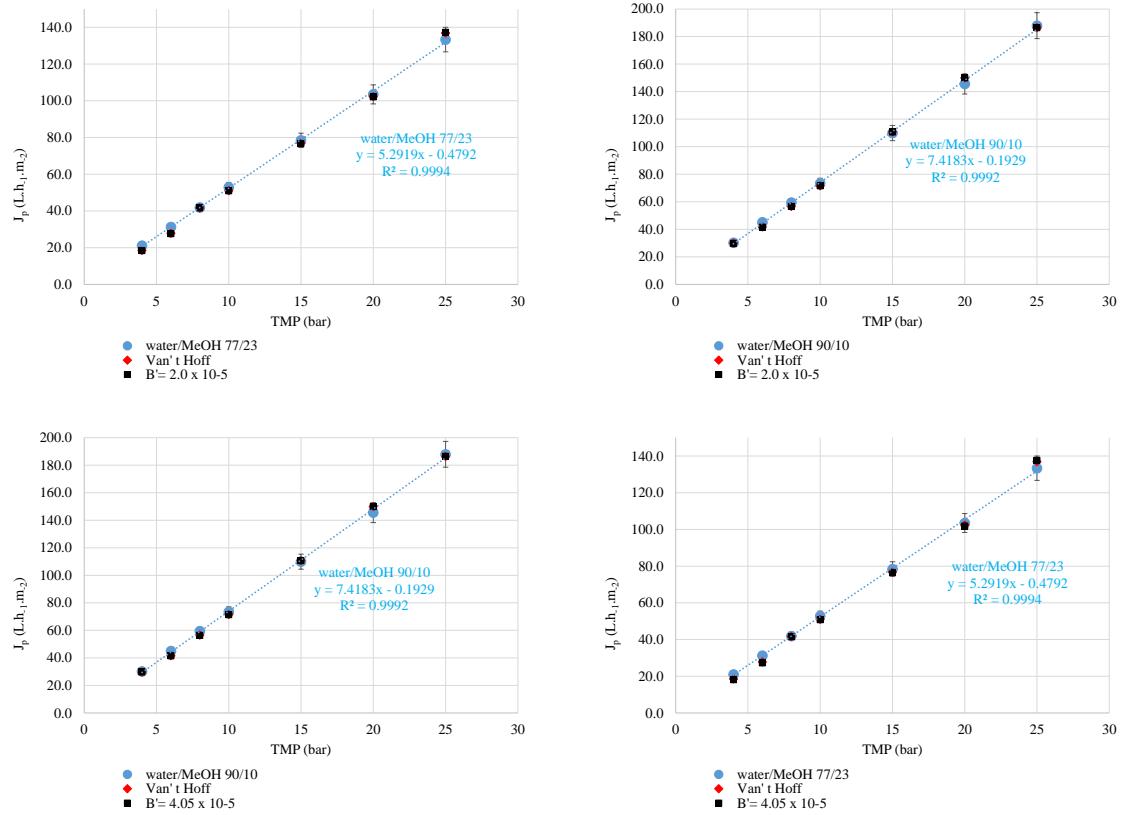


Fig. S8-2: Results of adjustment of experimental flux (J_p) in water/methanol according to the best L_p,BGS value calculated (eq. 17) with respect to assumption to calculate $\Delta\pi_{\text{obs}}$. ●: experimental water/methanol; ◆: van't Hoff assumption, ■: virial assumption ($B' = 4.05 \times 10^{-5}$). Equations on figures are those corresponding to the experimental data

Supplementary 9: osmotic pressure detailed calculations for water/isopropanol mixtures

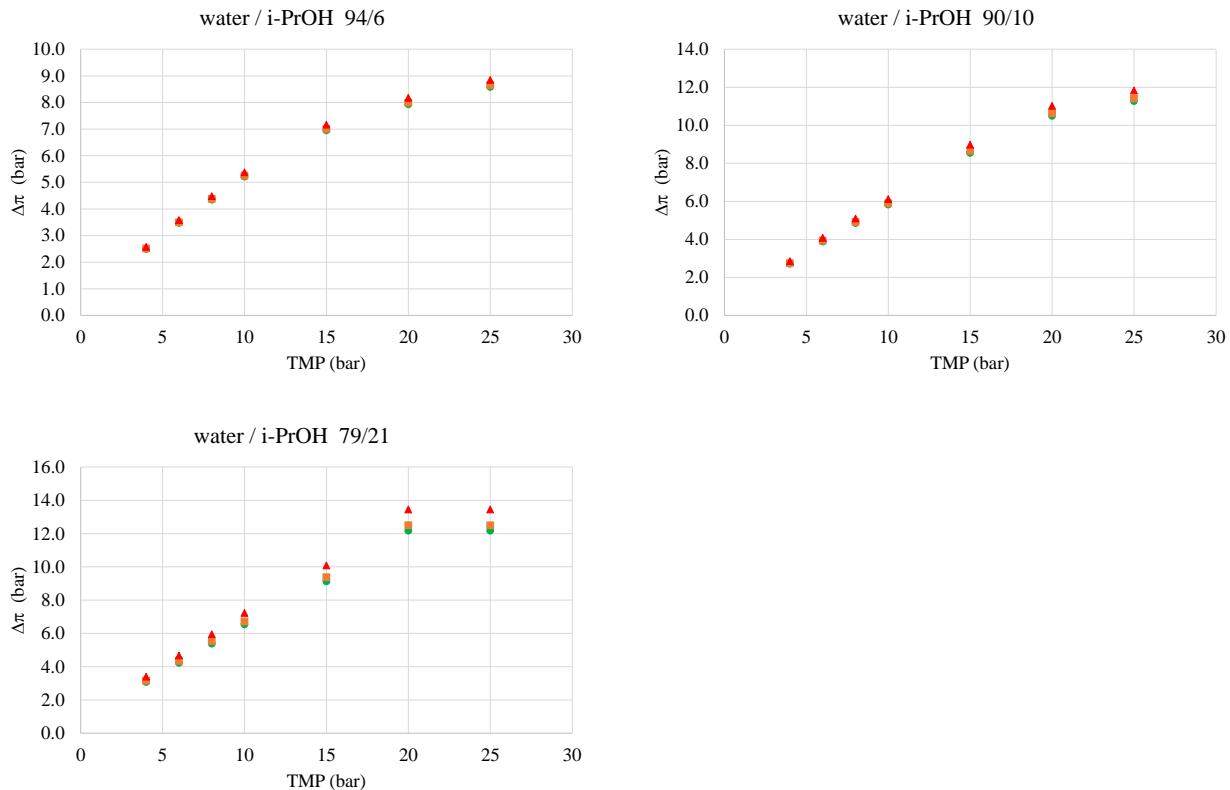


Fig. S9-1: Calculated $\Delta\pi_{\text{obs}}$, for the water/methanol mixtures according to assumption on B' value (see **Table 4**)

●: van't Hoff - ■: $B' = 2.0 \times 10^{-5}$ - ▲: $B' = 7.65 \times 10^{-5}$

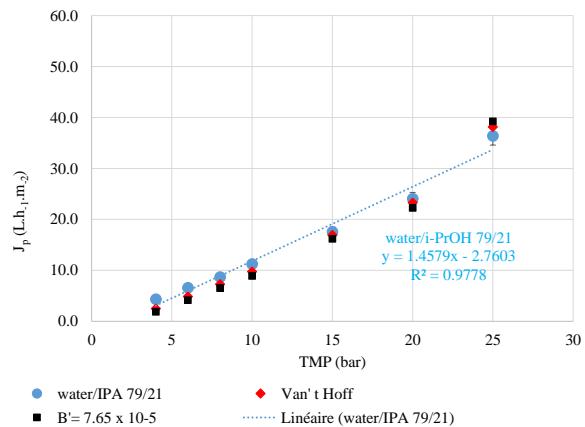
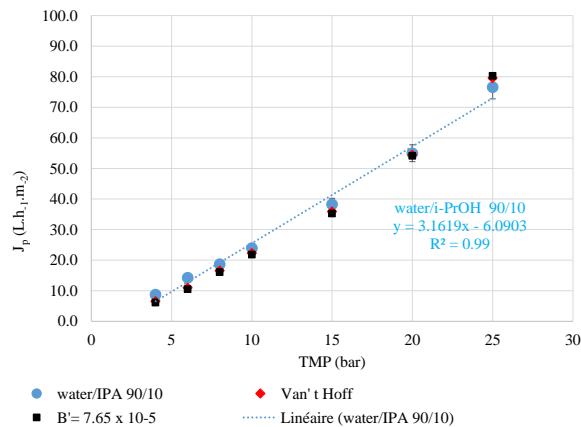
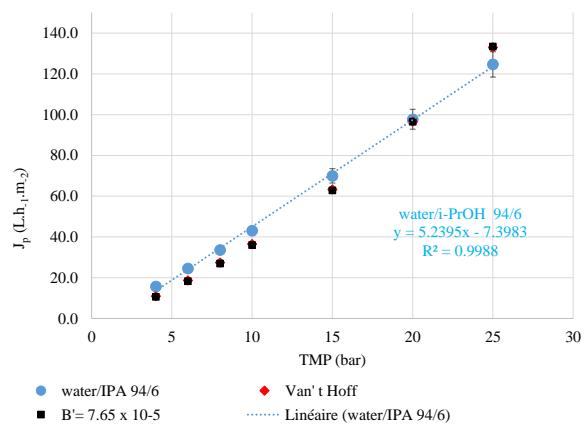
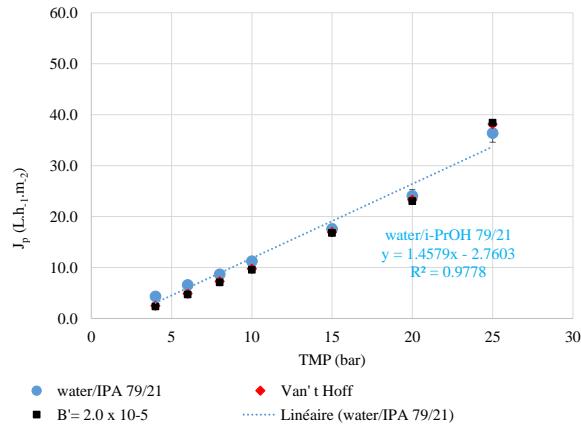
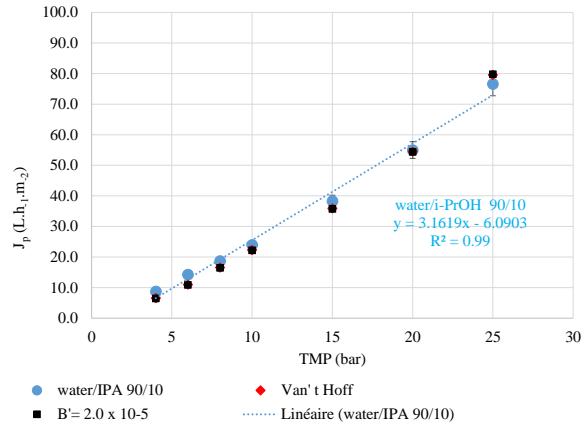
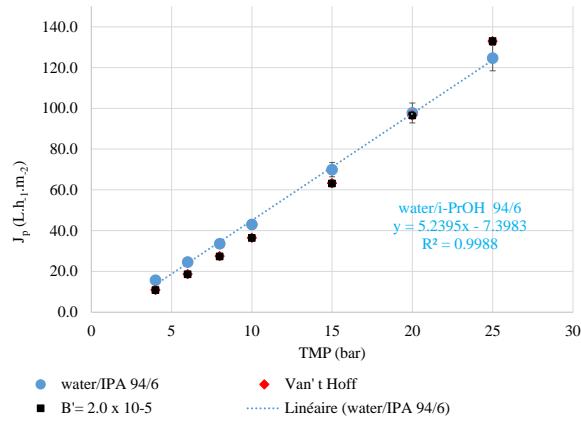


Fig. S9-2: Results of adjustment of experimental flux (J_p) in water/isopropanol according to the best $L_{p,BGS}$ value calculated (eq. 17) with respect to assumption to calculate $\Delta\pi_{obs}$. ● experimental water/methanol; ♦ van't Hoff assumption, ■: virial assumption ($B' = 7.65 \times 10^{-5}$). Equations on figures are those corresponding to the experimental data