Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2022

Organic solvent mixture separation using fluorine-incorporated thin film composite reverse osmosis membrane

Wataru Kushida^{a,b,1}, Ralph Rolly Gonzales^{a,1}, Takuji Shintani^{a,c}, Atsushi Matsuoka^{a,b}, Keizo Nakagawa^{a,c}, Tomohisa Yoshioka^{a,c}, Hideto Matsuyama^{a,b*}

^aResearch Center for Membrane and Film Technology, Kobe University, Japan

^bDepartment of Chemical Science and Engineering, Kobe University, Japan

^cGraduate School of Science, Technology and Innovation, Kobe University, Japan

*Corresponding author; Email: <u>matuyama@kobe-u.ac.jp</u>

¹These authors contributed equally.

Supplementary Information

1. Experimental

1.1. Materials

Polyketone (PK, Mw = 200000 g mol⁻¹), provided by Asahi Kasei Corporation (Japan), was used for the membrane support. Resorcinol, methanol, acetone, and hexane (Fujifilm Wako Pure Chemical Co., Ltd., Osaka, Japan) were used for PK support preparation. 5-Trifluoromethyl-1,3phenylenediamine (TFMPD, pKa=3.66), 1,3,5-benzenetricarbonyl trichloride (TMC), 10camphorsulfonic acid (CSA) (Tokyo Chemical Industry, Japan), 1,3-phenylenediamine (MPD, pKa=4.88), sodium dodecyl sulfate (SDS), and triethylamine (TEA) (Fujifilm Wako Pure Chemical Co., Ltd.) were used in the interfacial polymerisation (IP) polyamide formation reaction.

Sodium chloride (NaCl, Fujifilm Wako Pure Chemical Co., Ltd.) was dissolved in Milli-Q water (Merck Millipore Co., Germany) for evaluation of the membrane salt rejection in aqueous condition. Organic solvent separation performance of the membrane was evaluated using polar protic solvents (methanol, ethanol, 1-propanol, butanol and pentanol) and non-polar solvents (hexane, heptane, octane, nonane, decane, hexadecane, isooctane, toluene, 1,3,5-triisopropylbenzene, 1,3 -diisopropylbenzene, 1,4-diisopropylbenzene, o-xylene, m-xylene, p-xylene, cumene, naphthalene), all purchased from Wako Pure Chemicals (Japan).

1.2. Membrane characterisation

The membrane morphology (surface and cross-section) was observed using a field emission scanning electron microscope (FE-SEM; JSF-7500, JEOL, Tokyo, Japan). The membrane surface chemical composition was analysed using X-ray photoelectron spectroscopy (XPS, JPS-9010MC, JEOL). Prior to FE-SEM imaging and XPS characterisation, the samples were freeze-dried using a vacuum freeze dryer (FDU-1200; Tokyo Rikaikai, Japan). For FE-SEM imaging, the freeze-dried samples were sputter-coated using an osmium coater (Meiwa Forsys Co., Ltd., Japan) at 8 Pa and 10 mA for 10 s. The samples were then observed at an acceleration voltage of 5 kV and an emission current of 10 A. Membrane surface hydrophilicity was evaluated by measuring the water contact angle using a contact angle goniometer (DM-300, Kyowa Surface Science, Japan). Surface roughness of the membranes was observed using atomic force microscopy (AFM, SPI3800N, Hitachi, Ltd., Japan). The pore size of the membranes was evaluated by positron annihilation lifetime spectroscopy (PALS, Toray Research, Japan). The membrane samples were analysed at 1.5 kEv by utilisation of an intense pulsed-positron beam generated from an electron linear accelerator. The functional groups on the membrane surfaces were analysed using attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet iS5, Thermo Fisher Scientific Inc., USA). The surface zeta potential of the membrane samples was measured with an electrokinetic analyser for solid surface analysis (SurPASS[™] 3, Anton Paar GmbH, Austria). All measurements were conducted using 1 mM KCl solution as background solution at 25°C.

1.3. Membrane performance evaluation

Reverse osmosis (RO) filtration tests were performed using a cross-flow system with a membrane cell whose effective area is 8.04 cm². The feed solution was supplied at a constant rate of 9.9 mL min⁻¹. Pressure of 1 to 3 MPa were applied during operation. To mitigate the effect of concentration polarisation, magnetic diffusion conditions were supplied with magnetic stirring at 200 rpm was conducted in the cell. The flux (*J*, L m⁻² h⁻¹) was calculated according to:

$$J = \frac{M}{A \times t \times \rho} \tag{S1}$$

where *M*, *A*, *t*, and ρ are the mass (g) of accumulated permeate, effective membrane area (m²), filtration time (h), and permeate density (g L⁻¹), respectively. The solute rejection, on the other hand, was calculated from the concentrations of the feed (*C*_{*f*}) and permeate (*C*_{*p*}):

$$R = \left(1 - \left(\frac{C_p}{C_f}\right)\right) \times 100 \tag{S2}$$

For NaCl rejection calculation, the conductivity of the feed and permeate was measured to obtain the respective NaCl concentrations. Meanwhile, for the organic solvent separation test, the composition of the permeate and feed samples was determined using gas chromatography.

The pure solvent permeance of organic solvents was measured using applied pressure of 1 MPa in the following order: alcohols, aliphatic hydrocarbons, and aromatic hydrocarbons, and increasing carbon chain length for each. OSRO separation tests were conducted at 3 MPa using solvent mixtures containing 95 wt% toluene and 5 wt% other organic solvents. The rejection of solute organic solvent was determined by gas chromatography (GC-8A, Shimadzu Corp., Japan) with a flame ionisation detector (FID) and a porous silica column (Shinwasorb-U 60-80, Shinwa Chemical Industries Ltd., Japan).

Finally, the long-term stability of the membranes was evaluated using a feed solution containing 5 wt% 1,3,5- triisopropylbenzene (TPB) in toluene, and OSRO operation was performed for over 20 d at an applied pressure of 3 MPa.

2. Results and Discussion

2.1. Interfacial polymerisation reaction

The mechanism of the interfacial polymerisation reactions of MPD and TFMPD with TMC are shown in **Figure S1**.

(a)



Figure S1. The reaction mechanism of the diamine monomers during interfacial polymerization: (a) MPD + TMC (PA) and (b) TFMPD + TMC (F-PA).

2.2. Diamine monomer diffusivity

Spectrophotometry was used to evaluate the diffusivity of the diamine monomer into the organic phase. 1.3 wt% of aqueous solutions of MPD and TFMPD with 6.3 wt% methanol were prepared. 500 μ L of aqueous diamine solution was added in a quartz cuvette, followed by 3 mL of hexane, and the absorbance of the hexane phase was measured continuously over 200 s. The measurement wavelength was performed at the maximum absorption wavelength of 295 nm.



Figure S2. Diamine monomer absorbance in the organic phase over time.

2.3. Membrane surface chemical composition



Figure S3. The influence of MPD and TFMPD ratio in the aqueous amine monomer solution on the surface F/N ratio.

2.4. Molecular dynamics simulation

The pore volumes were calculated for PA and F-PA membranes, respectively, using the BIOVIA simulation software Materials Studio. The densities of PA and F-PA membranes were determined to be 1.349 g/cm² and 1.485 g/cm², respectively, by performing 300 ps NPT-MD simulations at 0.1 Gpa and 298 K for the PA and F-PA-100 membrane models, respectively. Then, the NVT-MD simulation was carried out for 1.0 ns at 298 K for each membrane to measure the pore volume in the stabilised state. The pore volume was calculated by considering the pores as the range where a sphere with a diameter of 3.0 Å, equivalent to a water molecule, can exist.

2.5. Surface free energy

	Surface free energy (mN m ⁻¹)				
Solvents	γ_L^d	γ_L^p	$\gamma^{total}_{\ L}$	$\gamma_L^p / \gamma_L^{total}$	
Water	21.8	51.0	72.8	0.70	
Diiodomethane	49.5	1.3	50.8	0.03	

Table S1. Surface free energies of the solvents used in this study.¹

Extended Fowkes equation is given by:

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_s^d \gamma_L^d} + 2\sqrt{\gamma_s^p \gamma_L^p}$$
(S3)

where γ_L and γ_S are the surface free energies of the solvent and film, respectively, and the superscripts d and p denote the respective dispersion force and polarity components.

2.6. Pure organic solvent permeance

The obtained permeance of alcohol was calculated by Eq. (S4):

$$P = K \frac{\delta_p}{\eta d^2} \tag{S4}$$

where δ_p is the polar contribution of the Hansen solubility parameter (HSP) value of the organic solvent [Pa^{0.5}], η is the solvent viscosity [Pa s], *d* is the molecular diameter of the solvent [m], and *K* is a constant specific to the membrane [m³ Pa^{-0.5}].² The parameters described above showed excellent correlation to the results of PA (R²=0.9723). However, the R² values of F-PA-50 and F-PA were low (R²=0.6500, 0.5153), suggesting that the alcohol permeance of hydrophobic PA membrane could not be determined by Eq. (S4) (**Figure S4**).



Figure S4. Plot of alcohol permeances against HSP, viscosity and molar diameter.

Next, permeance of aliphatic solvents was determined. However, the polar term of HSP value of aliphatic compounds is zero, so the permeability could not be evaluated using Eq. (S4). Therefore, we used the HSP value difference (R_a) between the polyamide active layer and that of the organic solvent instead of δ_p to calculate the permeance according to Eq. (S5).

$$P = K \frac{1}{R_a \eta d^2}$$
(S5)

The difference can be calculated by:

$$R_a = \left(4\left(\Delta\delta_{D,m} - \Delta\delta_{D,s}\right)^2 + \left(\Delta\delta_{P,m} - \Delta\delta_{P,s}\right)^2 + \left(\Delta\delta_{H,m} - \Delta\delta_{H,s}\right)^2\right)^{0.5}$$
(S6)

where δ_D and δ_H are the solubility contributions from the dispersion force factor and the hydrogen-bonding force factor.³ The HSP value of the polyamide active layer were calculated by Hansen Solubility Parameter in Practice (HSPiP, USA) software. The HSPIP software can evaluate the Hansen solubility parameter of a polymer based on its solubility in any chosen solvent. 5 g of the polymer was added to 50 mL of a solvent having a known HSP value, and the mixture was stirred for 12 hours to confirm its solubility. 12 kinds of solvents were used

(acetonitrile, acetone, tetrahydrofuran, N-methylpyrrolidone, dimethyl sulfoxide, N,Ndimethylformamide, N,N-dimethylethanamide, cyclohexane, hexane, toluene, methanol, water). Isophthalic acid dichloride (IPC) was used instead of trimesoylchloride (TMC) because 3D crosslinked polyamide could hardly be dissolved in solvents. The HSP values of MPD-IPC, TFMPD-IPC-50 and TFMPD-IPC could be calculated (δ_d =17.9, δ_p =13.9, δ_H =7.8), (δ_D =17.9, δ_P =13.9, δ_H =7.8) and (δ_D =17.9, δ_P =13.9, δ_H =7.8). The literature HSP value of MPD-IPC is (δ_d =8.0, δ_p =11.9, δ_H =7.9) suggesting that our calculation method was highly accurate. The permeance of the alcohol and aliphatic solvents were determined from Eq. (S5), and the results showed good correlation (**Figure 6**).

2.7. OSRO performance results

The OSRO performance of the F-PA membrane using different feed solutions containing 95% toluene and 5% solute are shown in **Table S2**,

Table S2. OSRO performance (mixture permeance and rejection) of F-PA membrane. (Feed: Toluene/solute
(95:5 wt/wt))

Solute	Molecular weight [g/mol]	Mixture permeance [LMH/bar]	Rejection [%]
1,3,5-Triisopropylbenzene	204.4	0.14±0.03	93.9±1.02
1,3-Diisopropylbenzene	162.3	0.15±0.03	64.9±1.79
1,4-Diisopropylbenzene	162.3	0.13±0.03	61.8±4.37
Isopropylbenzene	120.2	0.12±0.11	24.3±1.90
Naphthalene	128.0	0.19±0.13	8.10±1.26
p-Xylene	106.2	0.08±0.03	4.90±1.51
n-Butylcyclohexane	140.3	0.15±0.09	62.5±5.95
Methylcyclohexane	98.2	0.12±0.05	39.3±4.14
Isooctane	114.2	0.08±0.04	59.6±4.64

2.8. Organic substance rejection mechanism of F-PA

$$\left(1 + \frac{C_{aromatic}}{C_{total}}\right)$$

The plot of solute rejection against *Mw* (Figure S6) exhibits good correlation, similar to a previous study which employed spirobifluorene aryl diamine (SBAD-1).⁴ In polyamide membranes without clear pores, solvent permeation is based on the dissolution-diffusion mechanism; thus, both solubility and diffusivity of the organic compounds could have influenced the solute rejection in mixed systems.



Figure S5. Dependence of rejection on aromaticity and molecular weight, where the effect of



aromaticity (sorption) and molecular weight (diffusion) are represented by

References

- 1. D. K. Owens and R. C. Wendt, *Journal of Applied Polymer Science*, 1969, **13**, 1741-1747.
- 2. S. Karan, Z. Jiang and A. G. Livingston, *Science*, 2015, **348**, 1347.
- 3. C. M. Hansen, *Hansen solubility parameters : a user's handbook*, CRC Press, Boca Raton, 2007.
- K. A. Thompson, R. Mathias, D. Kim, J. Kim, N. Rangnekar, J. R. Johnson, S. J. Hoy, I. Bechis,
 A. Tarzia, K. E. Jelfs, B. A. McCool, A. G. Livingston, R. P. Lively and M. G. Finn, *Science*, 2020, **369**, 310.