

Electronic Supplementary Information

Role of water in vapor permeation through graphene oxide membrane

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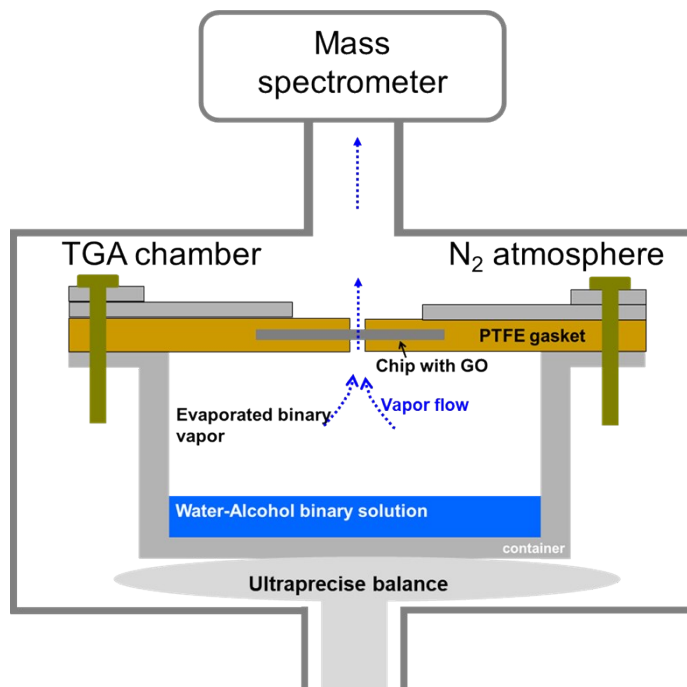
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Vapor permeation test with combined TGA-Mass spectrometer system

-Experimental setup

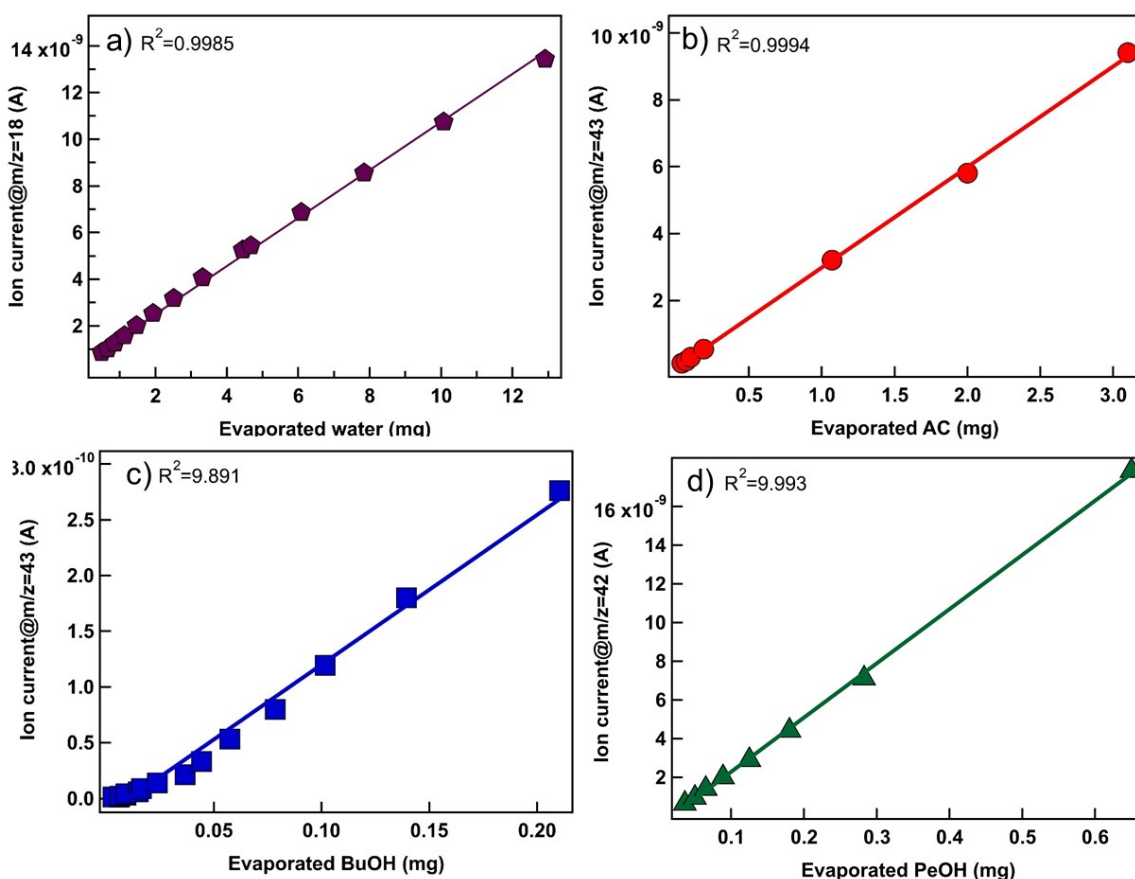
A small chamber for vapor permeation experiments were fabricated from stainless steel. First of all, mGO membrane was fabricated on AAO membrane (por size: $0.1\mu\text{m}$) through vacuum filtration and then transferred on the silicon chip with $60 \times 60 \mu\text{m}$ open window (refer to fig 1a). Mixture solutions with a 50:50 wt% component ratio was used in the experimental setup to generate the vapor mixture. The volume occupied by the mixture solutions in the sample holder (refer to figure S1) was always filled to the same volume. Therefore, the volume occupied by the vapor mixtures evaporated from the mixture solutions were also set to remain the same. the binary mixture solutions and the silicon chip with mGO membrane were loaded on top of the vessel. A PTFE film with a hole of dia. 300 μm on its center were used as seal gasket and then a stainless-steel gasket with a hole of dia. 1.2 mm in its center and stainless-steel lid were placed on the GO membranes. Finally, all were tightly locked with screw bolts (supplementary fig 1). Leak test was carried out for above the chamber setup without loading the GO membranes from room temperature to boiling point of AC. In the leak test, the silicon chip without open window was loaded instead of that with the open window. No weight loss and variation in mass number (m/z) for water, AC and BuOH and PeOH was detected in the leak test as shown in supplementary fig 3. Therefore, the weight loss detected when loading the GO membranes, came only from the permeate passing through the GO membranes.



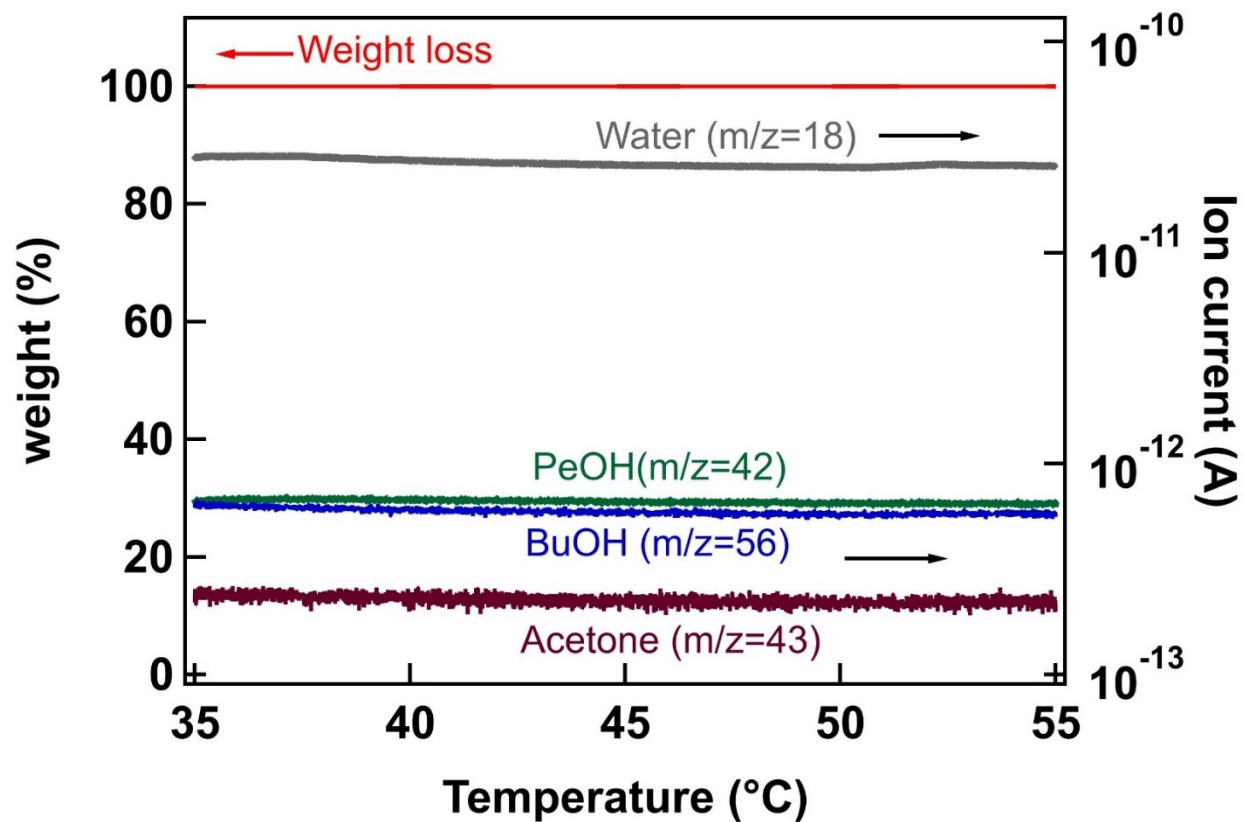
Supplementary Figure 1. A schematic diagram for the vapor permeation experiment with Thermogravimetric (TG)-Mass spectrometer combined system

- Vapor permeation experiments

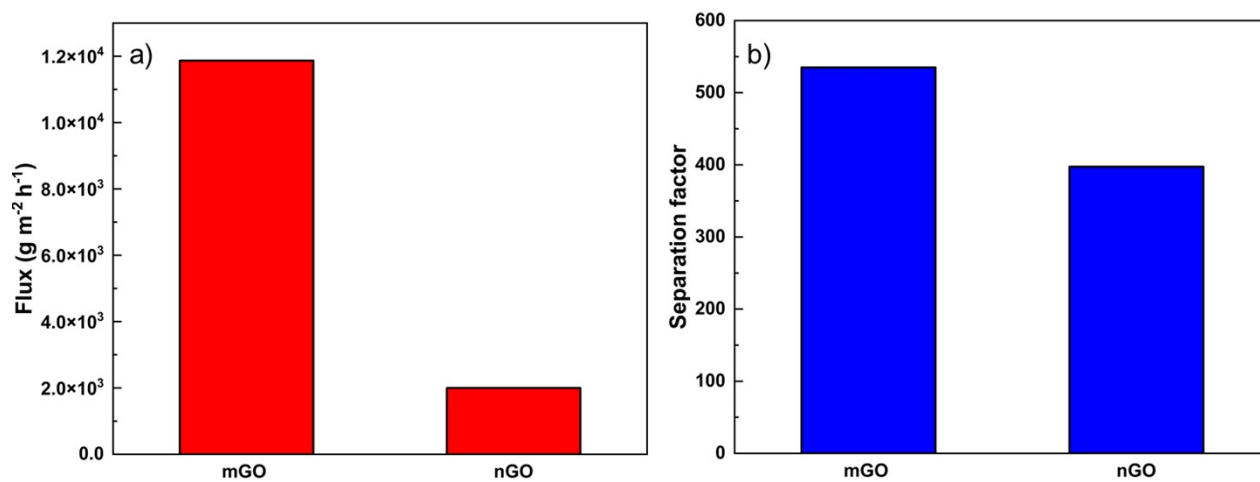
Vapor permeation experiments are accomplished with combined TGA-Mass Spectrometer (MS) system. All experiments were carried out under N_2 atmosphere. First, the calibration between TGA and MS was conducted via the pin hole method before vapor permeation experiments[1]. The calibration was carried out with the silicon chip with open window but without transferring the GO membrane. The calibration enables us to analyze the amount of each component in permeate with MS data. For calibration, pure solutions consisting of binary mixtures was loaded in the chamber as vapor source. In calibration, the evaporated weight of the components was controlled by limiting the evaporation area. Herein, the evaporated weight was controlled by limiting the hole size of the open window. The calibration was conducted without loading GO membranes. As an example, the calibration data for pure water, AC, BuOH and PeOH is shown in supplementary fig 2. The calibration data was obtained in the range from room temperature to around boiling point of each pure solutions. The mass numbers (from MS) according to the variation of weight losses (=evaporated amount, from TGA) for four pure solutions was measured. Finally, the amount of each component in permeate can be analyzed with each MS data for the pure solutions when the binary and quaternary vapors were measured.



Supplementary Figure 2. The calibration between TGA and MS for a) pure water, b) pure acetone, c) pure BuOH and d) pure PeOH.



Supplementary Figure 3. Leak test for the chamber. The mixture solutions including 20 wt. % AC were used as vapor source.



Supplementary Figure 4. (a) Flux and (b) separation factor of mGO and nGO for the separation of water-ethanol vapor mixture. Measurement temperature is 40°C

- Flux, separation factor and water contents in permeate

The flux was calculated as follows:

$$Flux = \frac{M_{permeate}}{A \times t} \quad (1)$$

Where $M_{permeate}$, A and t are the mass of permeate(g)(= weight loss from TGA), membrane area(m²) and measurement time (hr). The flux includes the water and alcohol and acetone flux.

The separation factor was calculated as follows:

$$Separation\ Factor = \frac{P_{water} \setminus P_{alcohol\ or\ AC}}{F_{water} \setminus F_{alcohol\ or\ AC}} \quad (2)$$

Where F_{water} , $F_{alcohol\ or\ AC}$, P_{water} and $P_{alcohol\ or\ AC}$ are the mass (g) of water vapor (F_{water}) and alcohol or acetone vapor ($F_{alcohol}$) in feed and in permeate (P_{water} and $P_{alcohol\ or\ AC}$). The mass of water and alcohol in permeate was calculated by the measured MS data through the calibration data for each component.

The water contents in permeate was calculated as follows:

$$Water\ contents\ in\ permeate(\%) = \frac{P_{water}}{P_{water} + P_{alcohol\ or\ AC}} \quad (3)$$

- Calculation of slip length and capillary pressure

The slip length was calculated using an indirect method[2]. The following equation was used[3]:

$$\emptyset = \frac{Q_{slip}}{Q_{non-slip}} \approx \frac{8\lambda}{\delta} \quad (4)$$

Where \emptyset , $Q(\lambda)$ and Q_{NS} are enhancement factor, the flow rates with slip and no-slip boundary conditions, respectively; λ is the slip length and δ is the pore size. Q_{slip} is matched with the experimentally observed flow rate when choosing the slip length. We used interlayer distance as the pore size. By assuming the water inside the interlayer space behaves as a classic liquid, We can use the Hagen-Poiseuille equation for $Q_{non-slip}$ as follows[3],

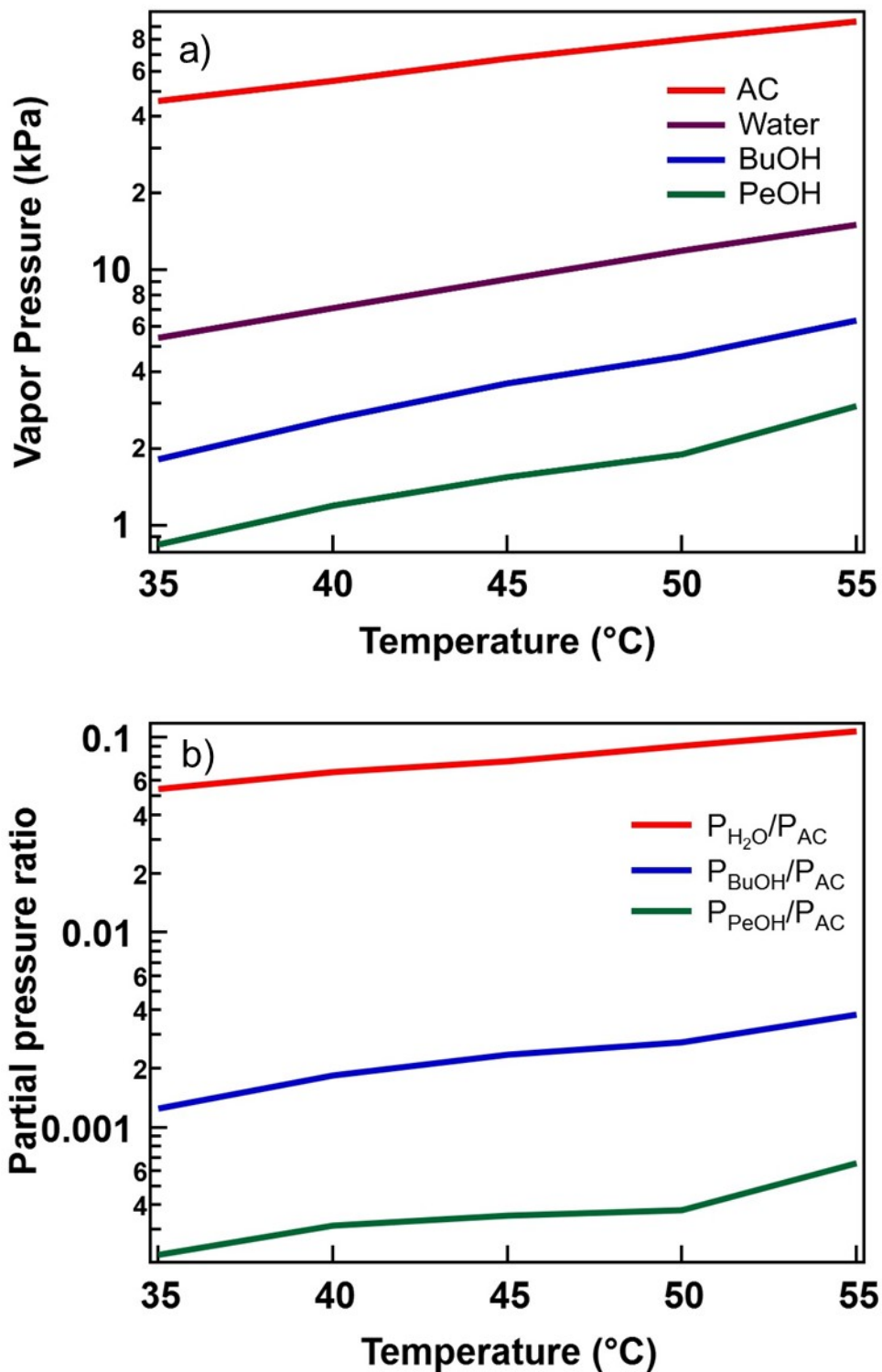
$$Q_{non-slip} \approx \delta^3 \left(\frac{1}{12\eta} \right) \left(\frac{1}{L} \right) \left(\frac{\Delta p}{l} \right) \rho \quad (5)$$

where Δp , ρ , η , L , l are pressure, bulk water density, water viscosity(mPa·s), channel width and channel length (=permeation length). The channel length(l) is calculated by $N \times L$. N and L are a number of turns and width of GO sheet where $N=h/d$, h and d are the thickness of GO membrane and interlayer distance, respectively. The interlayer distance of mGO and nGO membranes in wetted state was measured by XRD as shown in supplementary fig 6. For calculation of pressure

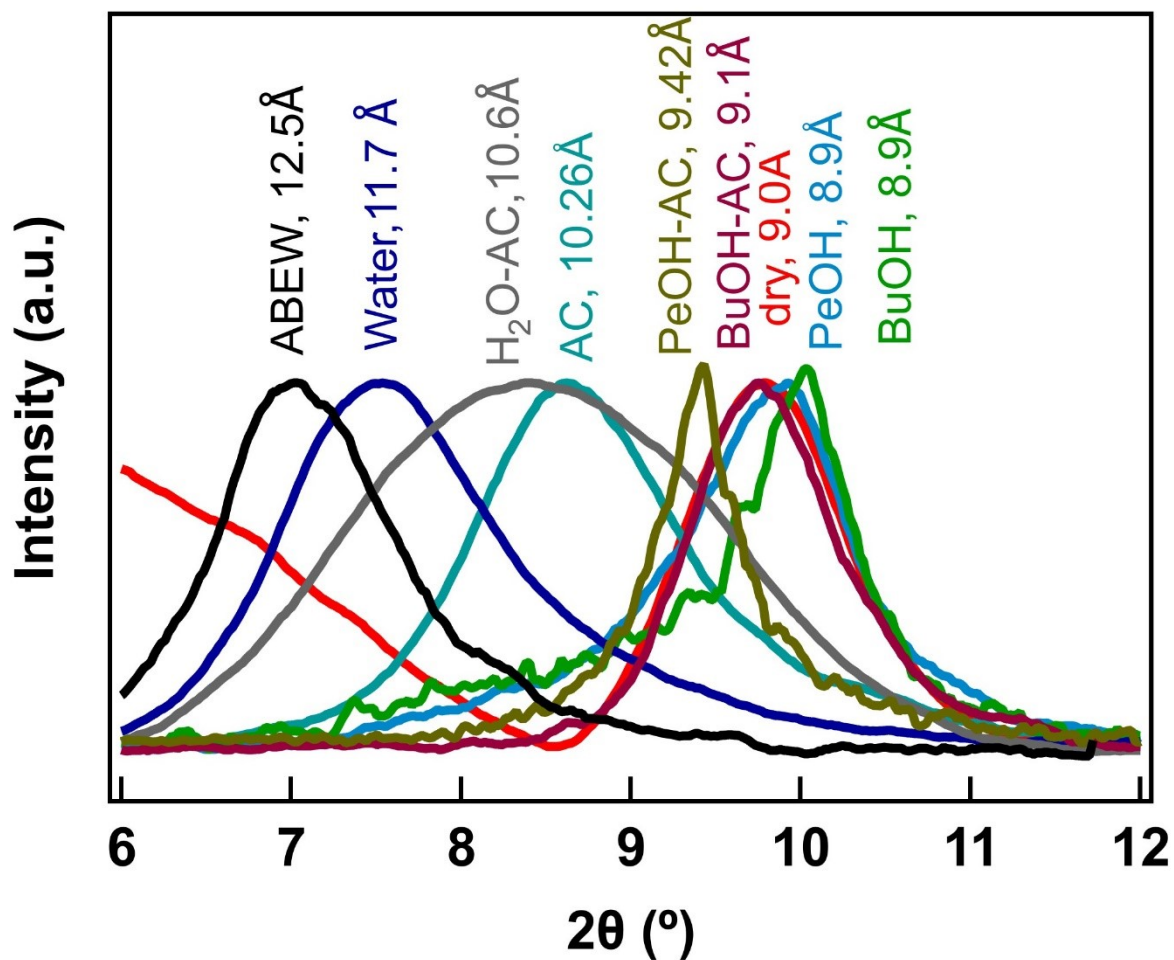
(Δp), We assume the capillary pressure is generated in interlayer space of GO membrane as reported by Nair et al[3]. So, the pressure(Δp) in eq. (5) can be replaced by the capillary pressure (P_c). the capillary pressure in GO membranes can be calculated using the Young-Laplace equation below[4]:

$$P_c = \frac{\gamma \cos \theta}{r} \quad (6)$$

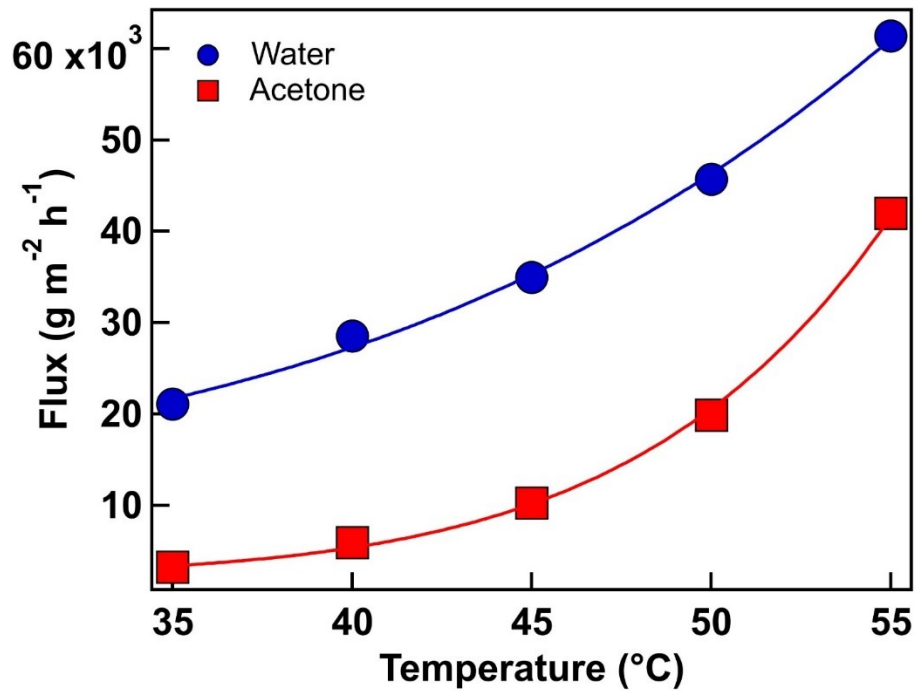
Where P_c is the capillary pressure, γ is the water-air interfacial tension, θ is the wetting angle and r is the half of the interlayer distance. We assume θ to be zero because water molecules evaporate from the GO surface on the permeate side. [4].



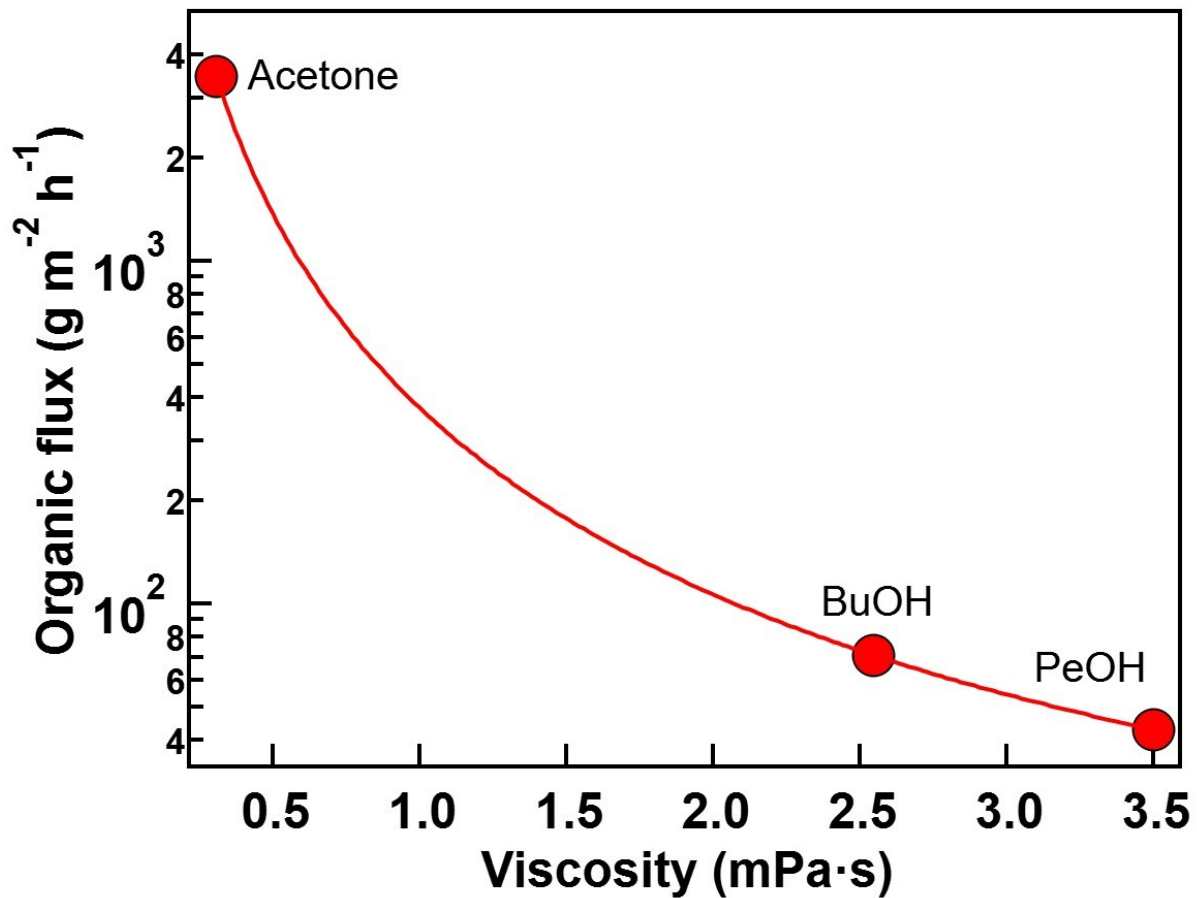
Supplementary Figure 5. a) Vapor pressure of water, AC, BuOH and PeOH and b) the ratio of partial pressure in the feed vapors according to the temperature.



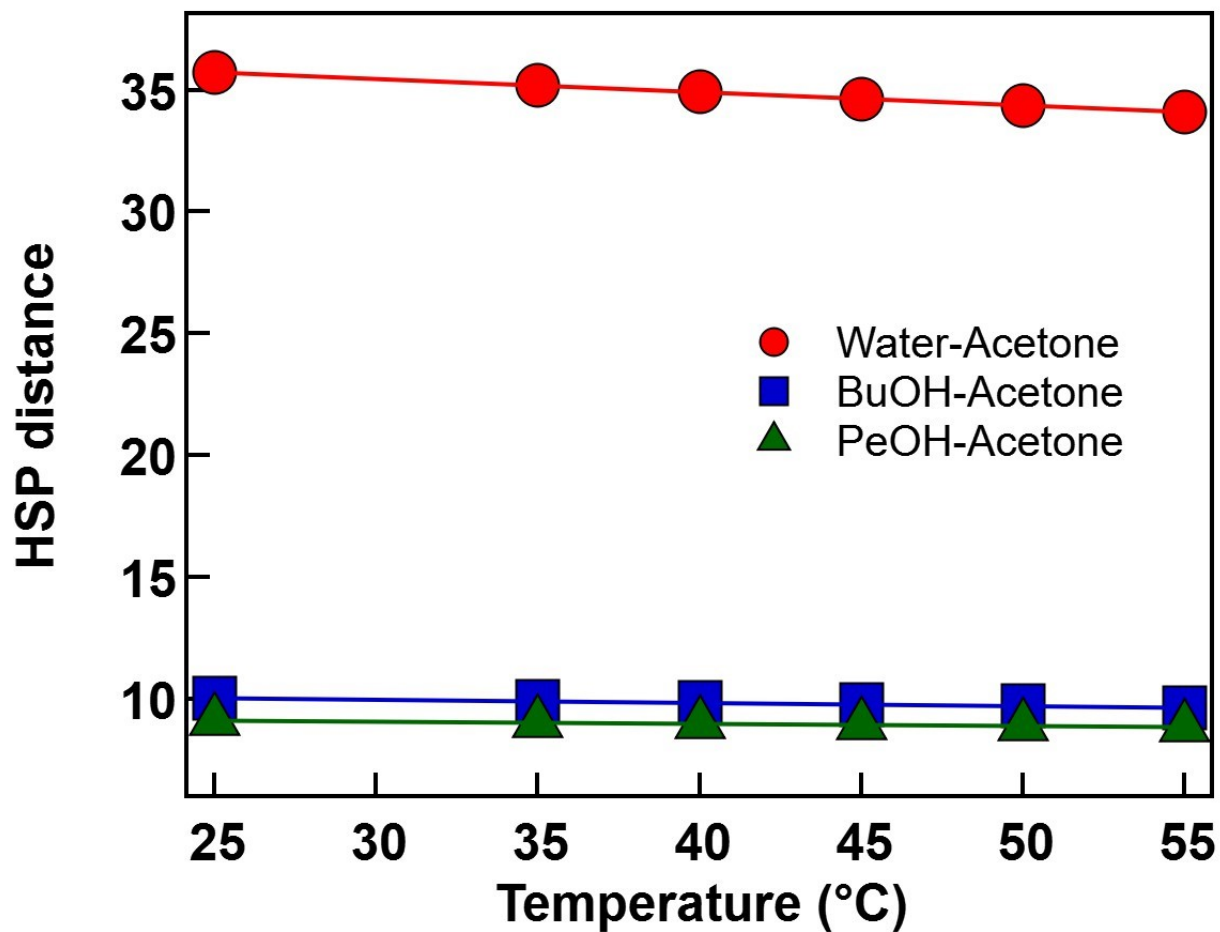
Supplementary Figure 6. XRD measurement for mGO membrane in the pure and mixture solutions. For this XRD measurement, mGO membranes were immersed into the pure and the mixture solutions including acetone for several hours. ABEW means acetone-butanol-ethanol-water quaternary mixture.



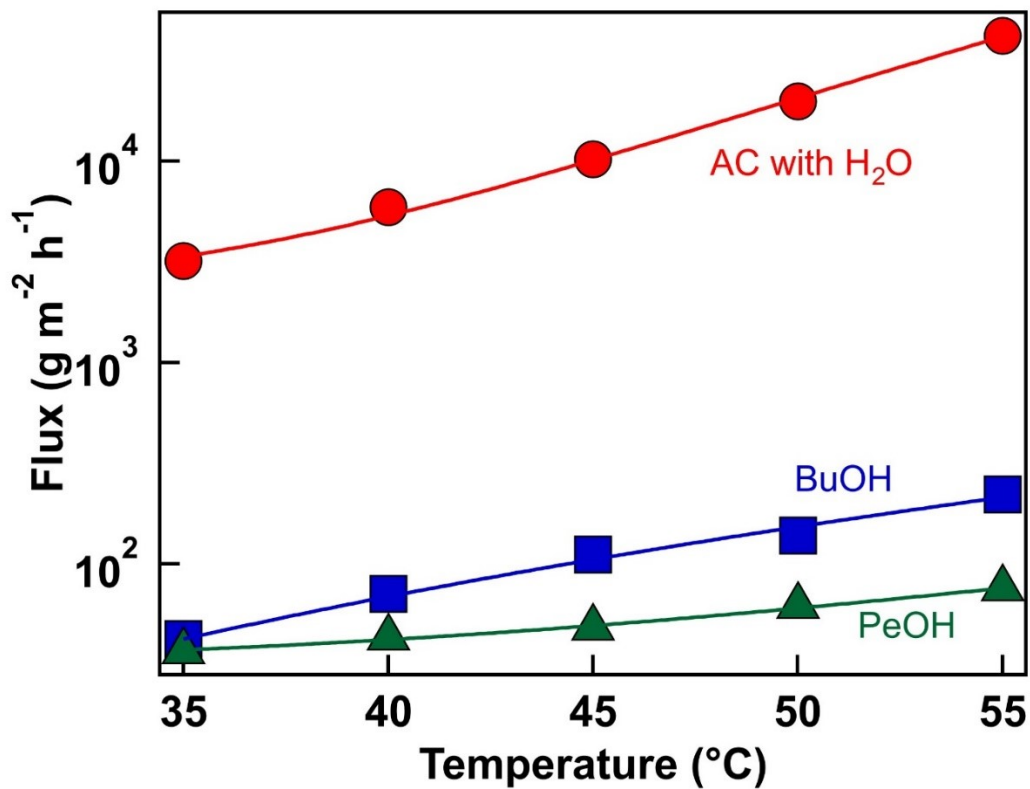
Supplementary Figure 7. Flux of water and acetone in water-AC binary vapor mixture according to the temperature.



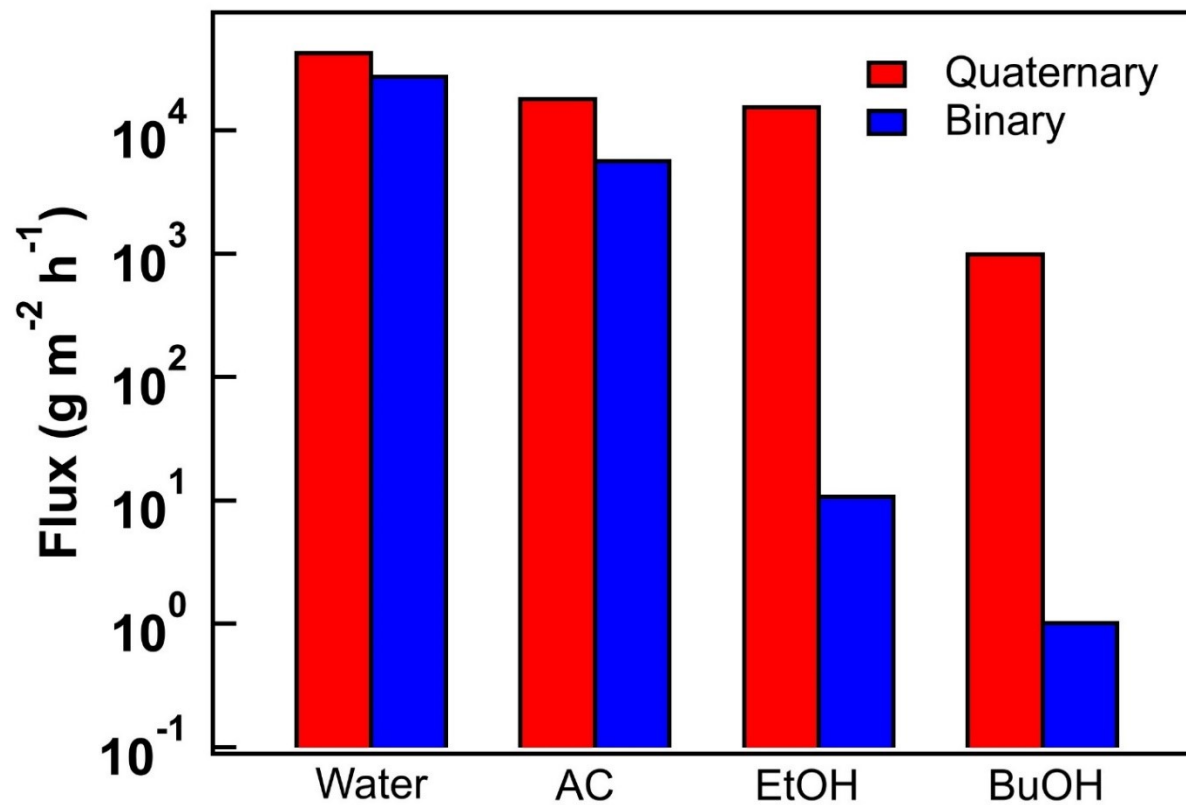
Supplementary Figure 8. Viscous flow of AC, BuOH and PeOH through mGO membrane. The flux of AC, BuOH and PeOH in the function of their viscosity



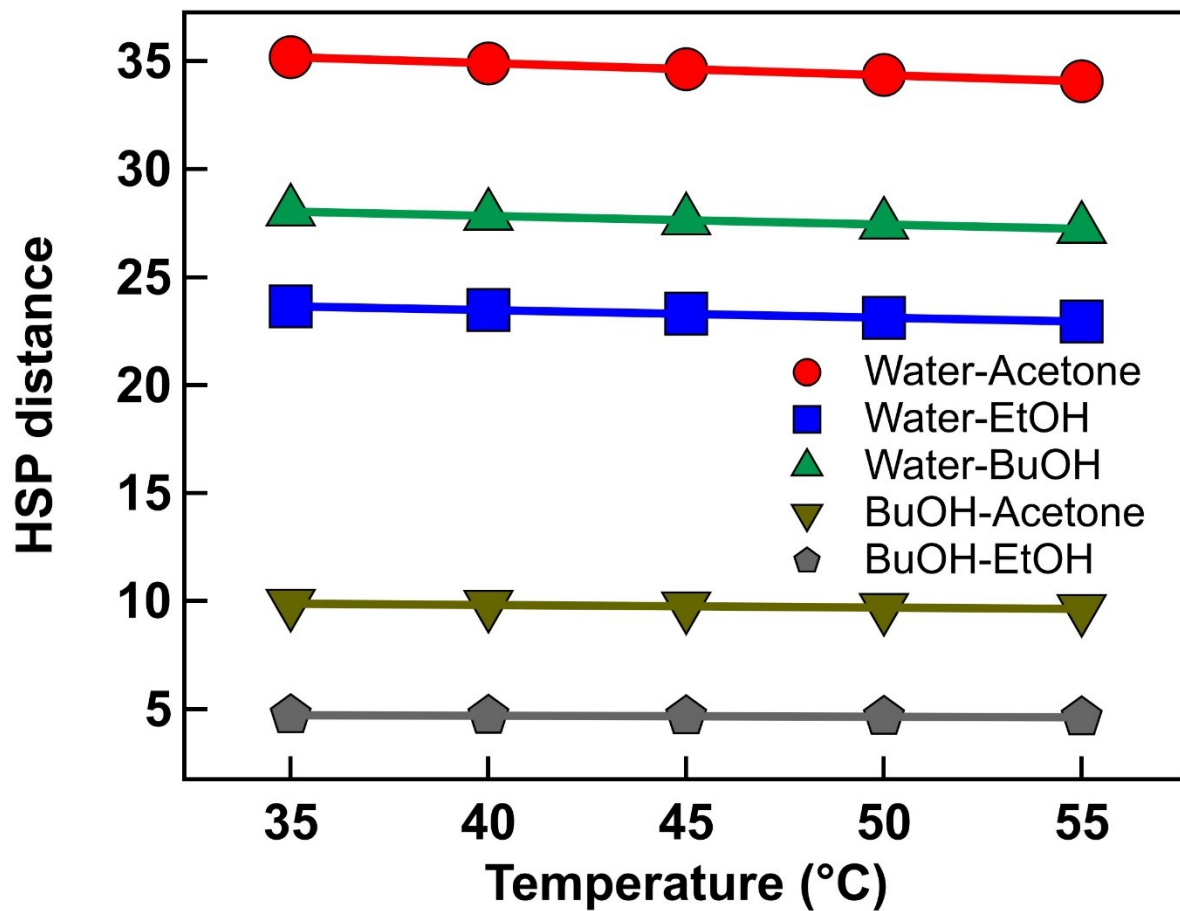
Supplementary Figure 9. Hansen Solubility Parameter (HSP) distance (R_a) between molecules consisting of the mixtures according to the temperature. The HSP distance according to the temperature was calculated with the formula provided by [5]



Supplementary Figure 10. Flux for the target molecules in the vapor mixtures according to the temperature. the target molecules mean the molecules which should be rejected by the GO membranes in the binary feed vapors (the target molecule: AC in AC-water, BuOH and PeOH in others).



Supplementary Figure 11. The flux of each vapor component in quaternary and binary vapor permeation. All the flux was measured at 40 °C. The flux for binary vapor mixture was measured with aqueous mixture (AC-water, EtOH-water and BuOH-water).



Supplementary Figure 12. Hansen Solubility Parameter (HSP) distance between water or BuOH and others according to the temperature. The HSP distance according to the temperature was calculated with the formula provided by[5]

Supplementary References

- [1] F. Eigenmann, M. Maciejewski, A. Baiker, Quantitative calibration of spectroscopic signals in combined TG-FTIR system, *Thermochimica acta* 440(1) (2006) 81-92.
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- [5] <https://hansen-solubility.com>.