# Supported Liquid Membrane Using Ionic Liquid

Wonyoung Choi

Korea Univ. Chemical and Biological engineering
Thermodynamics & Properties Lab.

# Introduction

- 진행중인 실험목적
  - Ionic liquid 를 이용한 $CO_2$ 분리를 위해 여러 종류의 Ionic liquid(ILs)에 대한 $CO_2$와 $N_2$의 solubility 와 selectivity를 구하는데 목적이 있다.

- Liquid membrane
  - Gas separation 장치로 현재 활발히 연구 중
  - Liquid membrane의 특성을 알아보고 ILs 의 적합여부를 알아본다.

# Liquid membrane?

- Liquid membrane
  - Dissolution / desorption behavior of gases through the liquid
    - Pressure difference
  - Using the reversible reaction with liquid
    - Facilitated transport of gas species and solute
    - Concentration difference
  - Liquid is held in the membrane pores by capillary forces
    - Immobilized liquid membrane (ILM) or supported liquid membrane (SLM)

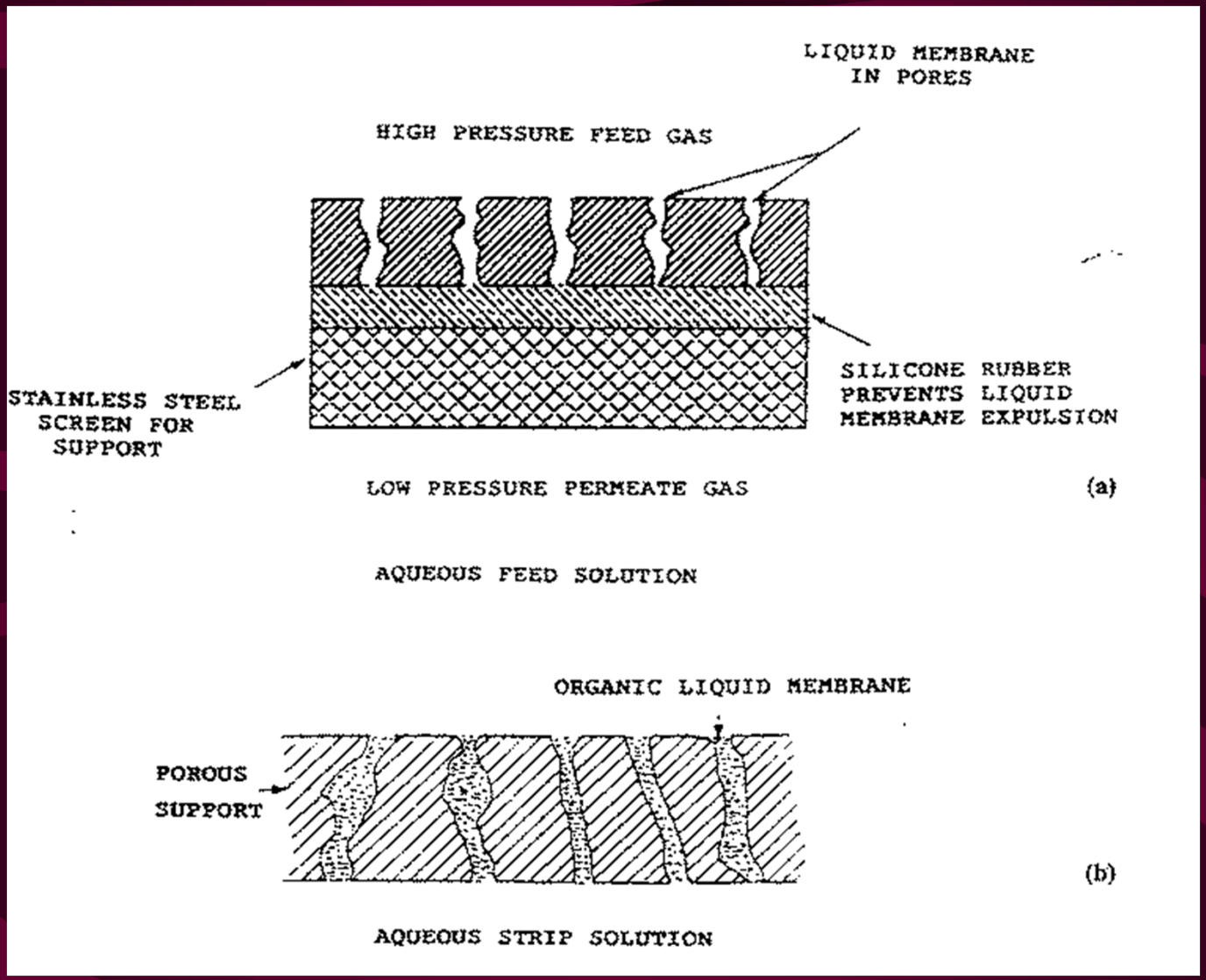


Figure 1. (a) for gas separation
(b) for liquid separation

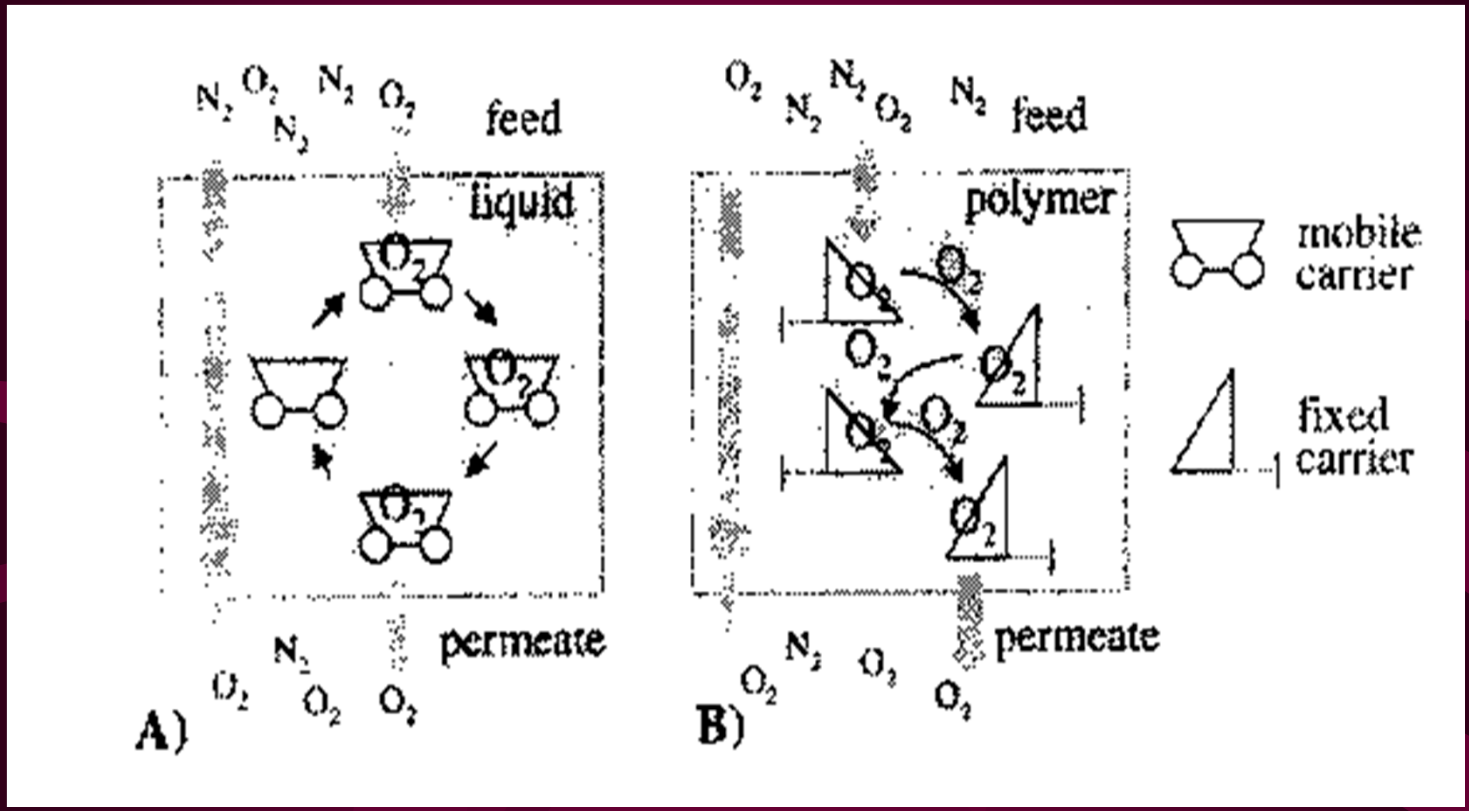


Figure 2. Scheme for facilitated of gaseous molecules by a carrier through a membrane
(A) liquid membrane with a mobile carrier
(B) solid membrane with a fixed carrier

# Characteristic of SLM ( I )

- Advantages
  - High separation (facilitated transport)
  - Low capital, operating, and energy costs
  - Fewer moving parts resulting in lower maintenance
  - Compact and modular hollow-fiber devices provide high mass transfer area

# Characteristic of SLM ( II )

- Limitations of SLM
  - Loss of extractant by solubility in mobile feed and strip solutions
    - *Volatilization of the solvent in the pores of the membrane*
  - Pressure differential across the membrane exceeding capillary forces holding the liquid
  - Progressive wetting of the support pores by surface-active carrier molecules

# Stabilization of SLM ( I )

- Hollow-fiber contained liquid membrane (HFCLM)
  - Microporous hydrophobic hollow fibers
  - A gas mixture flows on one side of the fiber while aqueous solution flows on the other side
  - Gas/liquid interface is immobilized at each gas-filled pore mouth on the liquid side of the fiber
  - Through the immobilized, both gas absorption and stripping can occur

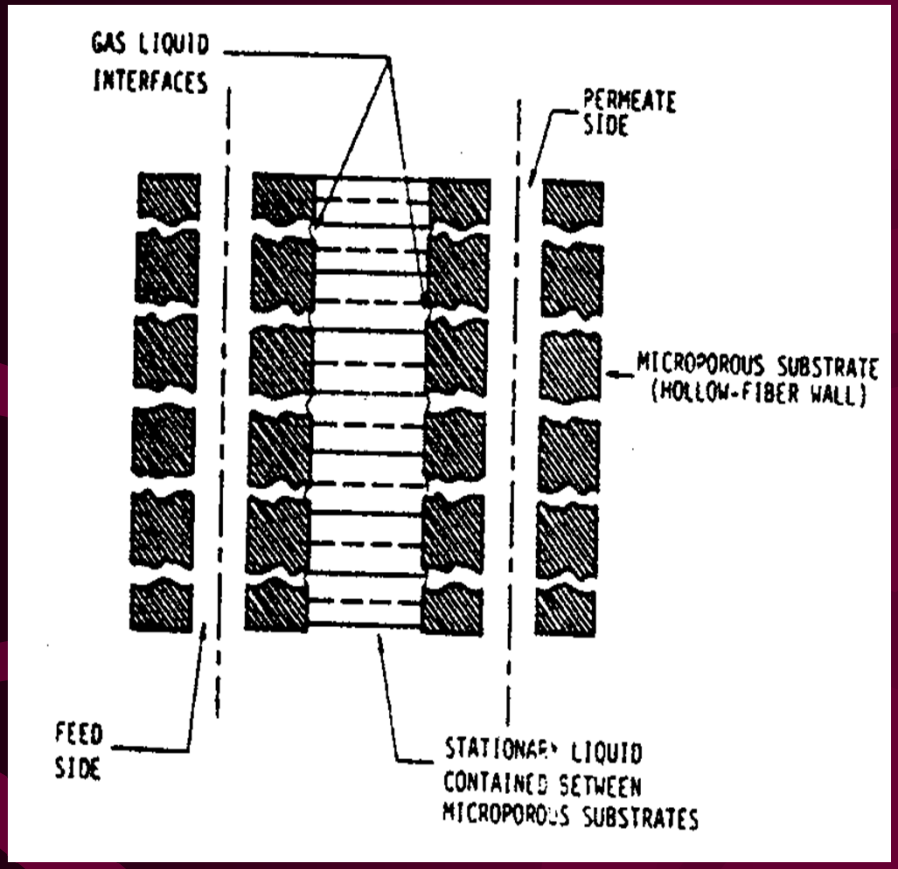


Figure 3. Aqueous liquid membrane between two hydrophobic microporous hollow fiber

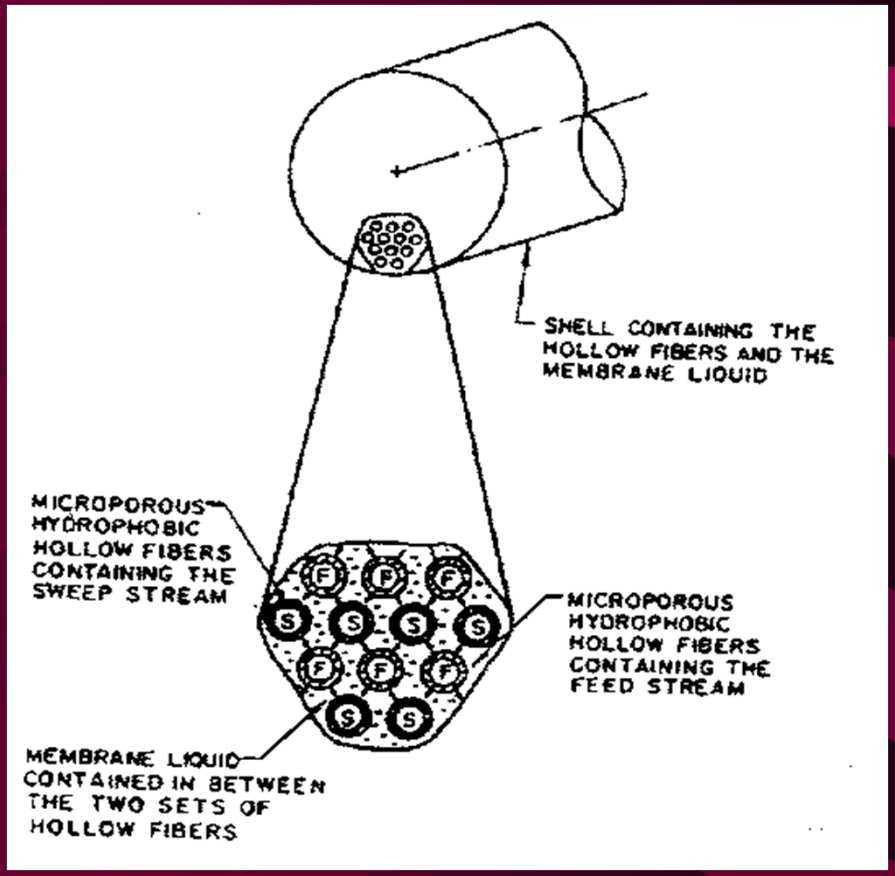


Figure 4. Configuration of the hollow-fiber contained liquid membrane in a permeator shell

# Stabilization of SLM ( I )

- Operation condition of the SLM
  - Pressure of the liquid solution should not exceed the bubble point or entry pressure
    - ▶ Exceeding the critical value, wetting the pore
  - The gas pressure must be lower than the liquid pressure
    - ▶ To prevent bubbling and maintain a stable gas/liquid interface

# Stabilization of SLM ( I )

- Advantages of the HFCLM permeator
  - Fiber wall defects lead only to a loss of membrane liquid through the fiber lumen.
    - Feed does no leak into the permeate gas
  - Gas humidification is unnecessary for a pure liquid
  - Membrane liquid replenishment is automatic and easy
  - The hollow-fiber porosity and the pore tortuosity do not influence the gas flux in general
  - High membrane surface area per unit permeator volume and low effective liquid membrane thickness

# Modes of Operation of a HFCLM Permeator

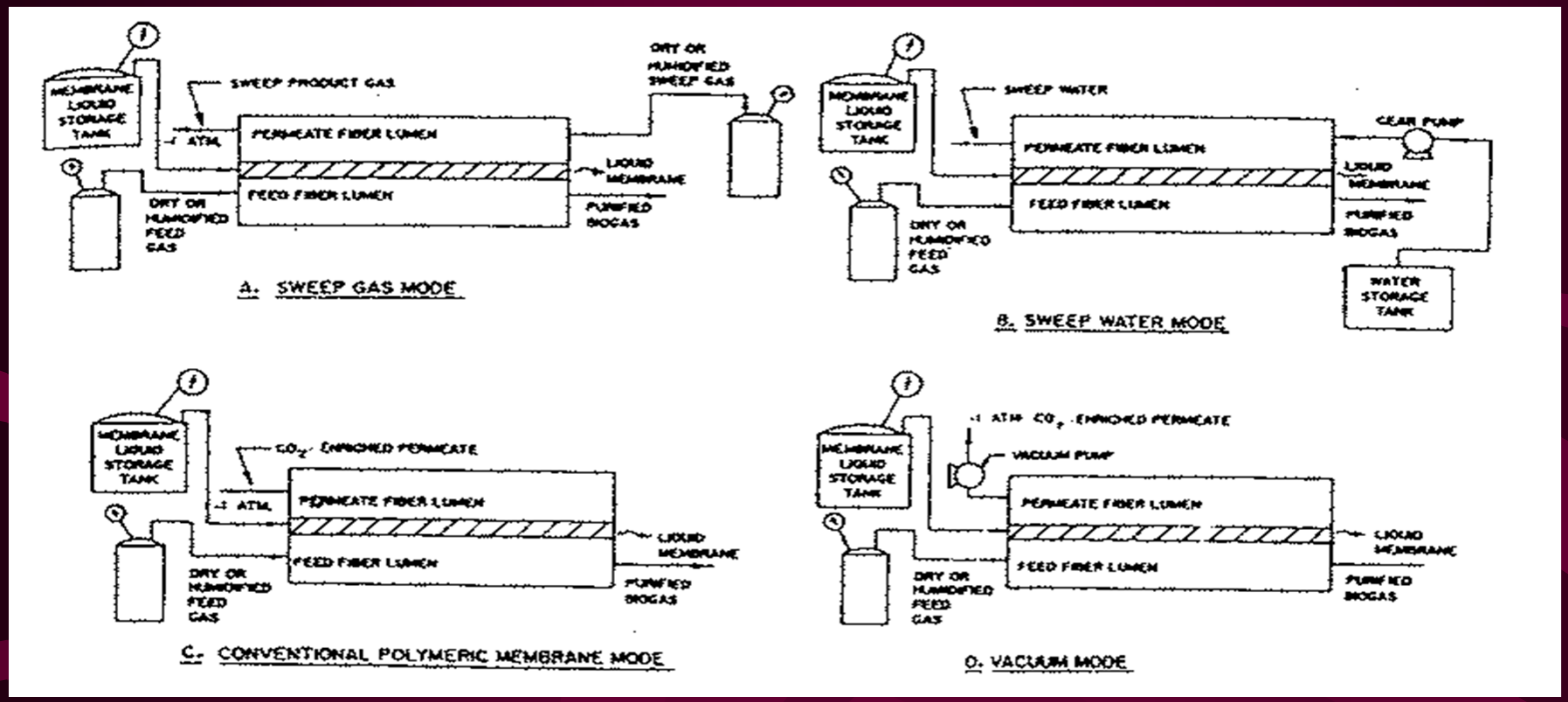


Figure 5. Four separation modes of purification of biogas using the HFCLM permeation

*Hydrophobic MHF* : non-wetting organic membrane liquid

*Hydrophobic MHF* : wetting organic membrane liquid

*Hydrophilic MHF* : organic or aqueous membrane liquid

# Stabilization of SLM ( II )

- Double-layer liquid membrane
  - The top layer is a conventional supported liquid membrane
    - Polytetrafluoroethylene(PTFE)
    - Hydorphilic and CO2 selective liquid
  - The bottom layer highly hydrophobic microporous membrane
  - This construction enable the liquid membrane pressure condition of over 200 kPa.

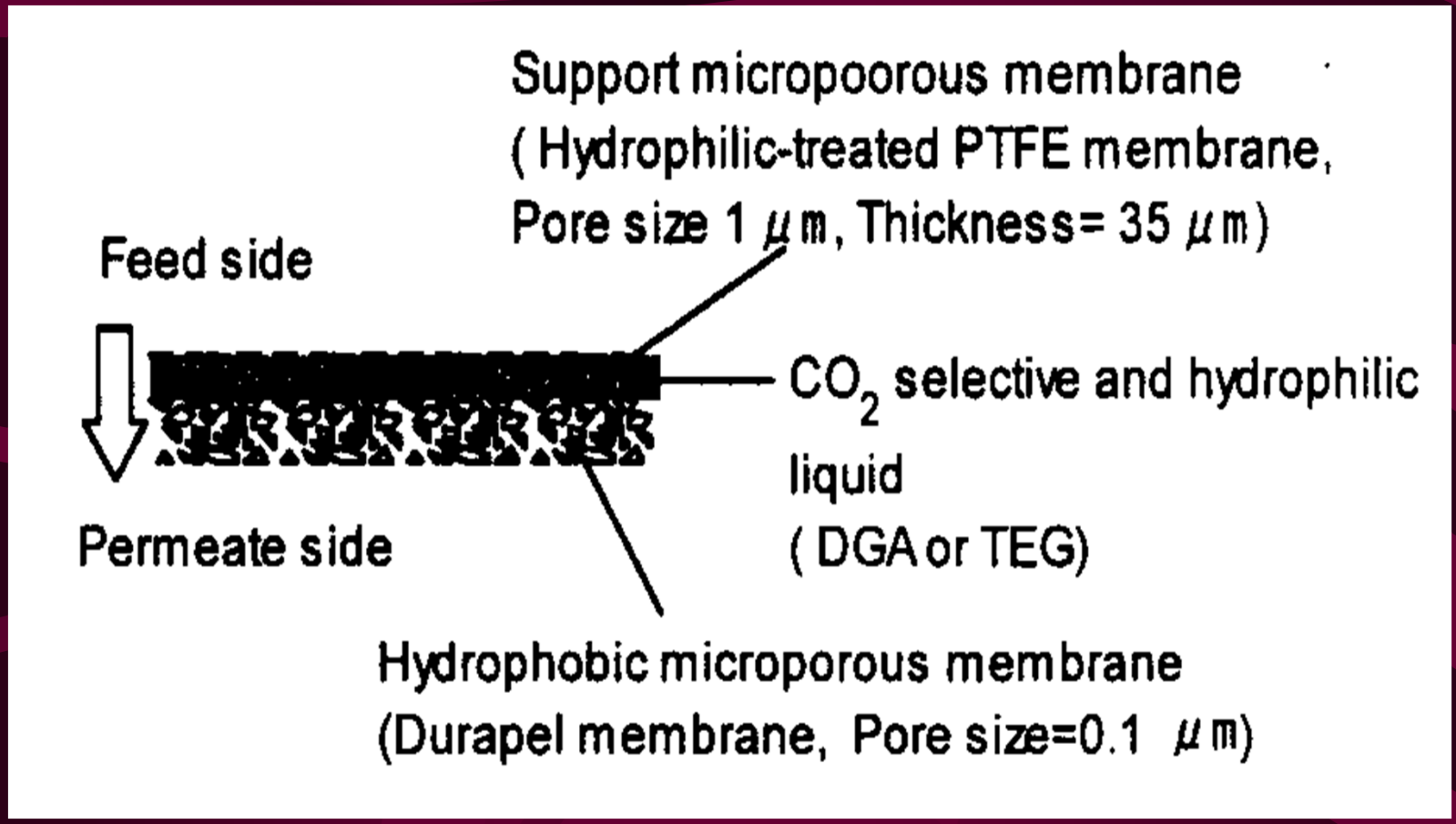


Figure 6. Supported liquid membrane placed on a hydrophobic microporous membrane

# Stabilization of SLM (III)

- SLM with convective flow of solution
  - Improvements of SLM
    - Loss of membrane solvent by evaporation
    - Unstable against the transmembrane pressure
    - Difficulty of preparing very thin membranes
  - Bulk flow liquid membrane
    - Membrane liquid is supplied to the feed side
    - And is forced to permeate through a membrane
    - The membrane liquid is not held stationary

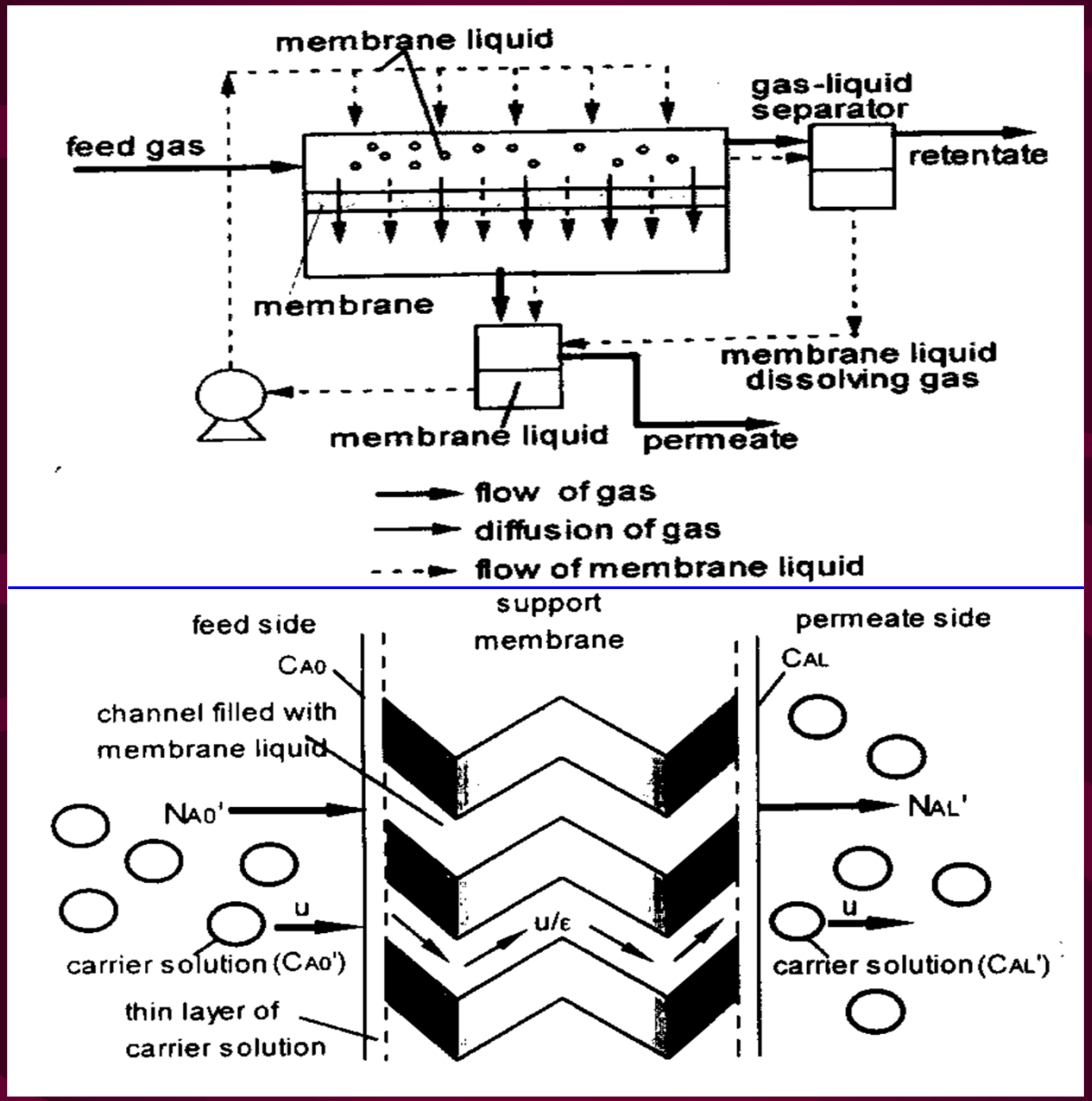


Figure 7. Concept of gas transport accompanied by convective flow of membrane liquid

# Stabilization of SLM (III)

- A hybrid of membrane separation and gas absorption
  - The feed side of the module has a function of a gas absorber
  - The Capillary and hollow fiber play the role of the packing in the packing tower
- Advantages of BFLM
  - Higher efficiency than conventional SLM
    - The permeation rate increases by molecular diffusion and also by convection
  - Easily replaced by a new membrane solution or can be regenerated
  - The membrane surface in each side is covered with a thin layer of the membrane

# Ionic liquid as a liquid membrane

- The characteristic of ILs
  - Negligible vapor pressure
    - Loss of solvent does not limitation of SML
  - (hydrophobic or hydrophilic) and hygroscopic
    - Using the hydrophobic or hydrophilic support membrane is useless
    - Feed gas contained water influence to the liquid
  - Solubility with CO2
    - It is possible to improve the solubility and selectivity by changing the alkyl group and anion
  - ILs as a solvent

| **Ionic liquid** (T = 40°C) | P (bar) | X $co_2$ |
|---|---|---|
| [bmim][$PF_6$] | 0.97 | 0.000 |
| | 15.17 | 0.231 |
| | 29.52 | 0.360 |
| | 43.58 | 0.445 |
| [$C_8$mim][$PF_6$] | 0.97 | 0.000 |
| | 17.93 | 0.234 |
| | 29.51 | 0.353 |
| | 42.06 | 0.452 |
| [bmim][$NO_3$] | 0.97 | 0.00 |
| | 15.47 | 0.196 |
| | 29.05 | 0.276 |
| | 42.63 | 0.342 |
| [$C_8$mim][$BF_4$] | 0.97 | 0.00 |
| | 17.26 | 0.197 |
| | 28.85 | 0.319 |
| | 44.15 | 0.417 |

# What have to do?

- 현재 많이 활용되고 있는 ionic liquid의 CO2 solubility, 다른 기체와의 selectivity등의 VLE Data 구축
- Gas separation 에 적합한 liquid를 Data 와 Model 을 통하여 선정
- ILs에서 gas diffusivity, 압력에 따른 surface-tension 등 liquid membrane 적용에 필요한 물성 값 측정