

Recent Development of CO₂ Removal by Membrane Separation in DICP

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Outline

Brief introduction of our group

Novel cellulose membrane for CO₂ removal

Polyimide membrane for CO₂ removal

Membrane absorption for CO₂ removal

Part 1 Our Group

第一部分 课题组简介



Dalian Institute of Chemical Physics

One of the most important institutes of CAS

中科院大连化物所星海二站科研基地近期规划鸟瞰图



Laboratory of Environmental Engineering

环境工程研究室

Hydrogen generation 氢源制备

wastewater treatment 废水处理

micro CE technology 微化工技术

membrane separation 膜分离

Novel Membrane Technology Group

Group Leader: Prof. Yiming CAO 曹义鸣 研究员

Academic advisor: Prof. Quan YUAN 袁权 院士

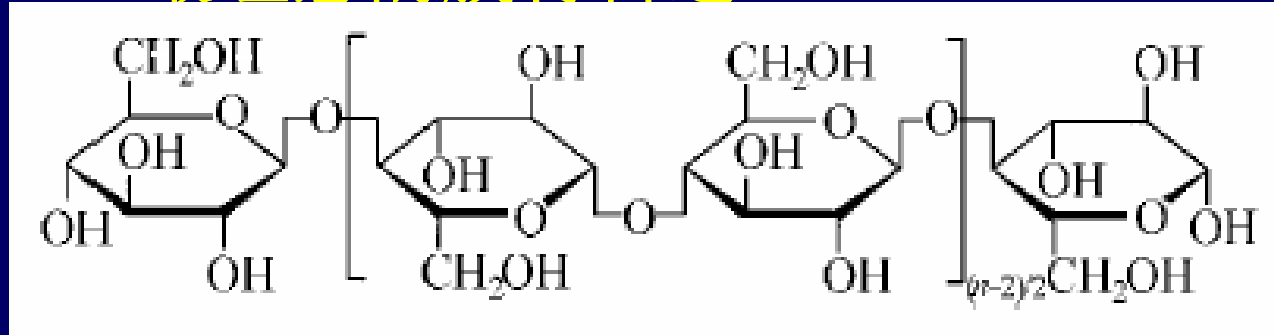
Staff: 8; Graduates: 9

Part 2 Novel Cellulose Membrane

第二部分 新型纤维素膜

Cellulose One of the most ideal membrane materials

纤维素 最理想的膜材料之一



Most abundant organic resource; 最丰富资源
Naturally degradable; 可自然降解
Biology compatible; 生物相容性好
Hydrophilic, foul resistance; 亲水, 耐污染
Acid, alkali and organic solvents resistance.

耐酸, 碱与

溶剂

Cellulose Hydroxyl groups, hydrogen bonding, cannot be dissolved by commonly used solvents

纤维素多羟基，多氢键，难溶于普通溶剂

Traditional methods of processing cellulose 传统利用

Modification 改性 cellulose acetate, cellulose nitrate

Regeneration 再生 cellphane, cuprophane

Problems of these chemical treatments including

化学处理带来的弊端包括

Inevitable cellulose degradations 纤维素降解

Severe environment problems 环境污染

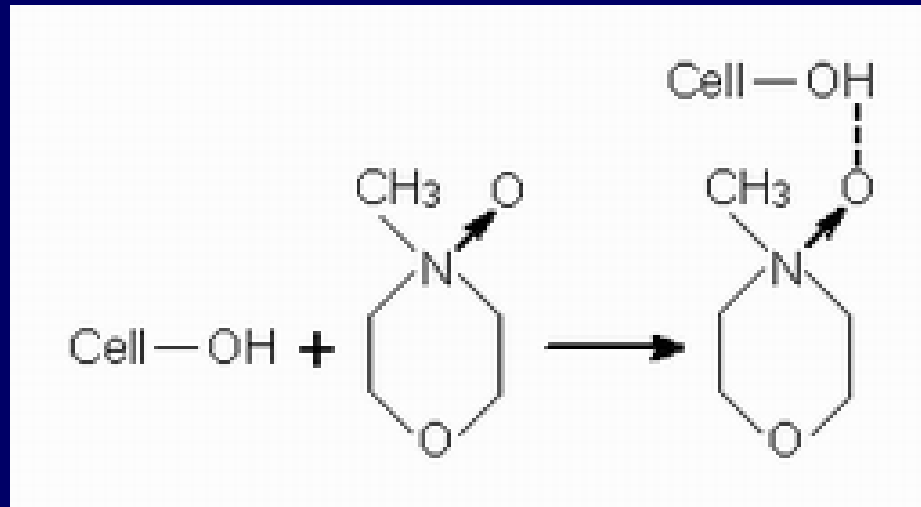
Demolishing the excellent characteristics of cellulose

纤维素自身优异性能被破坏

N-MethylMorpholine-N-Oxide

New solvent for cellulose

N—甲基吗啉—N—氧化物



NMMO can open the intrinsic hydrogen bonding of cellulose, and form new bonding with its hydroxyl groups, in this way cellulose is dissolved by NMMO.

NMMO可以与纤维素羟基形成新的氢键，使其溶解。

What are the advantages of this new dissolving method? NMMO溶解优点

Physical dissolution, protecting cellulose from degradation

物理溶解，可以很大程度避免纤维素降解

Friendly solvent, without environmental pollution

环境友好溶剂，没有环境污染问题

Simple dissolving process, and solvent is recyclable

溶解工艺简单，溶剂回收率高

This process has been successfully applied in textile industry to prepare Lyocell fiber, so what we want to ask is

NMMO溶解工艺已经成功应用于Lyocell纤维的纺制，我们希望知道的是

Can it be used for membrane preparation?

该工艺是否合适用于制膜？

Development of novel cellulose membrane preparation in our group

本课题组纤维素膜制备进展

Cellulose flat membrane for gas separation

纤维素平板膜—气体分离

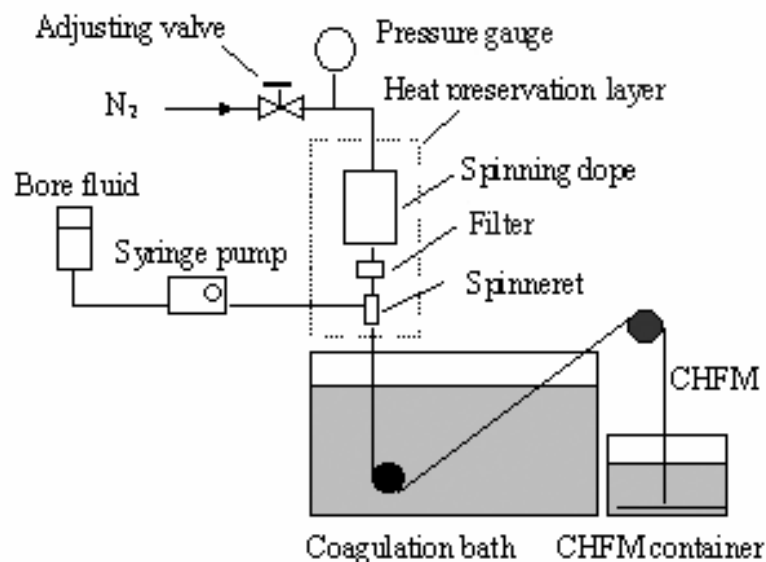
Chemical modification of cellulose membrane

纤维素膜的化学改性

Cellulose hollow fiber membrane for **gas separation** and oil/water separation

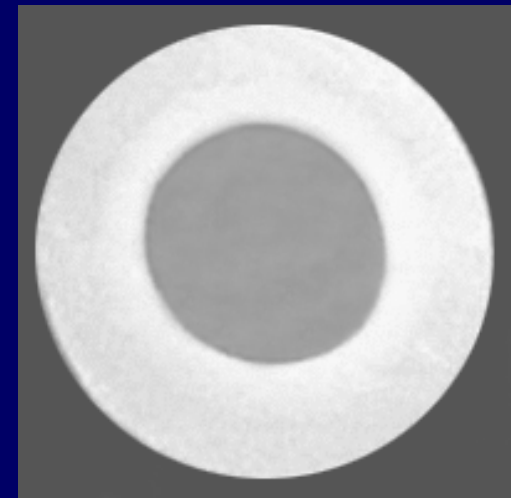
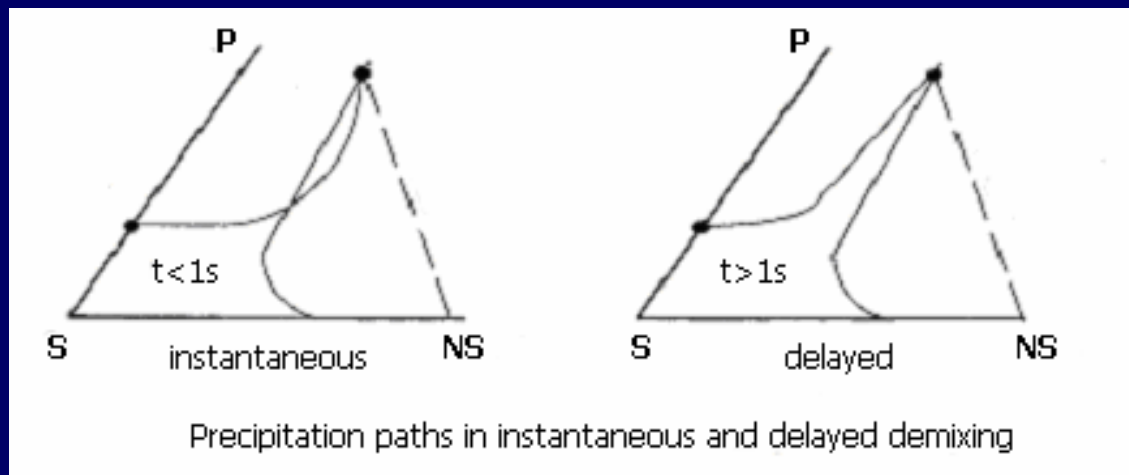
纤维素中空纤维膜—**气体分离**，油水分离

Spinning of cellulose hollow fiber membranes 纤维素中空纤维膜的制备



Dope composition	10wt% Cellulose
Spinning method	Wet spinning
Bore liquid (BL)	Deionized water
Flow rate of BL	0.10 cm ³ /min
T of BL	80 °C
Coagulant bath (CB)	Tap water
T of CB	20 °C
Spinneret	0.7mm/1.4mm
T of spinneret	80 °C
Spinning pressure	0.18MPa
Spinning rate	50 cm/min
Room temperature	25 °C

Morphology of wet cellulose hollow fiber membranes 湿态纤维素中空纤维膜的结构



Delayed phase separation 延迟相分离

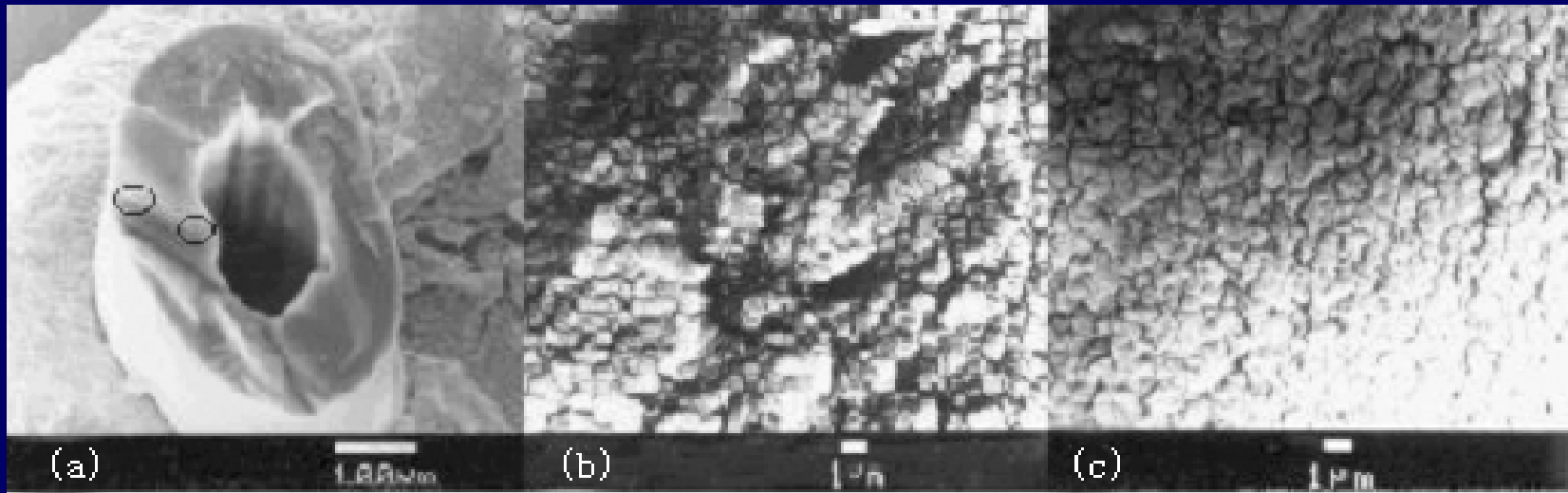
Hydrogen bonding between Cellulose and NMMO 氢键

Low coagulation temperature 凝胶浴温度低

Morphology of naturally dried cellulose hollow fiber membranes 自然干燥后膜的结构

Naturally drying method

25 °C, RH 50%



(a) Overall cross section (b) outer part (c) inner part

Tremendous shrinkage, Homogeneously dense structure, many tiny cellulose crystals 剧烈收缩，均质致密结构，由许多纤维素微晶组成

Gas permeability of dry cellulose hollow fiber membrane 干膜的气体渗透性能

Very poor and difficult to be measured, because Cellulose hollow fiber membrane prepared shows 非常差，难以测出，原因包括：

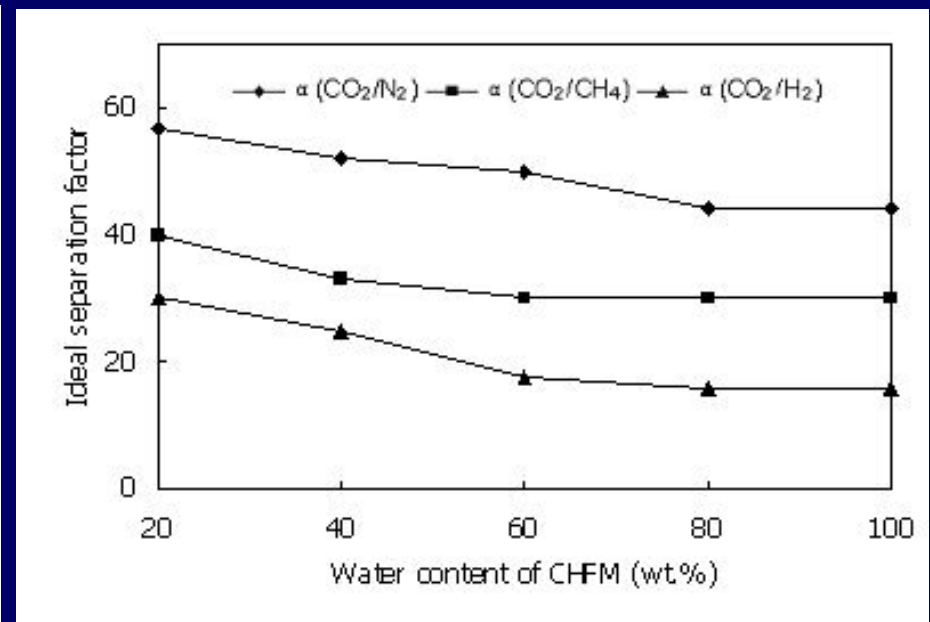
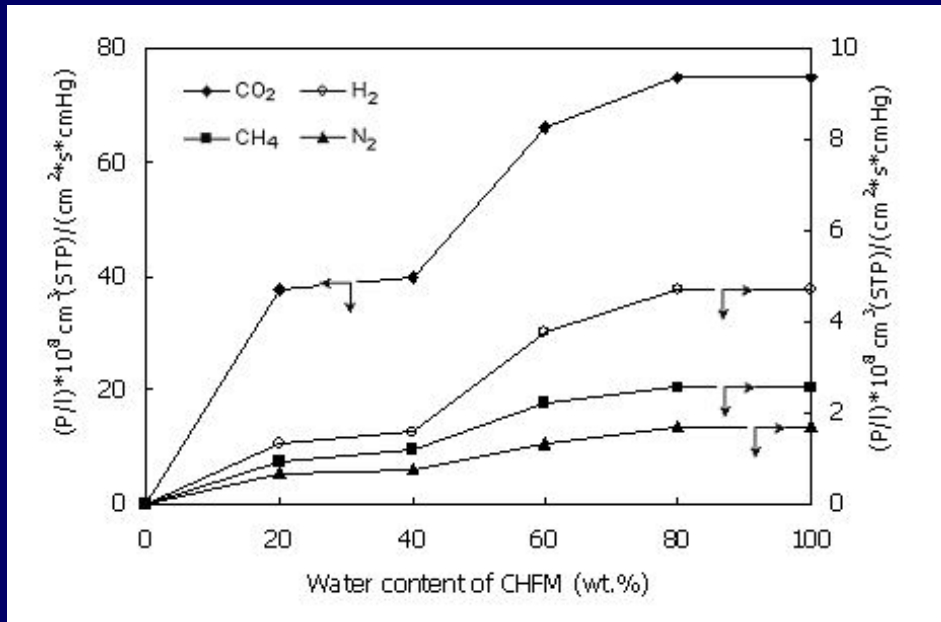
High degree of polymerization 聚合度较高

High degree of crystallinity 结晶度较高

Very dense membrane structure 致密结构

Gas permeability of water-swollen cellulose hollow fiber membrane 水溶胀后膜的性能

Influence of water content on its gas permeability 膜水含量对其气体渗透性能的影响



Test condition: 25°C, pressure difference 0.5MPa

Saturation value 0.75GPU, 1GPU=1×10⁻⁶cm³(STP)/(cm²*s*cmHg)

Gas permeation mechanism in water-swollen cellulose hollow fiber membrane

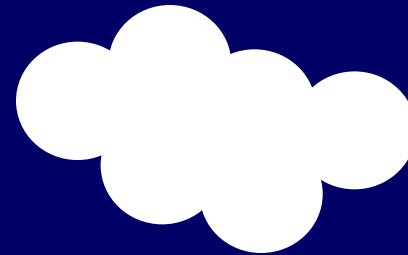
Cellulose membrane must be humidified, why?

纤维素膜被水溶胀后才表现出明显气体渗透性能

Dry cellulose HFM

Strong hydrogen bonding

Dense structure



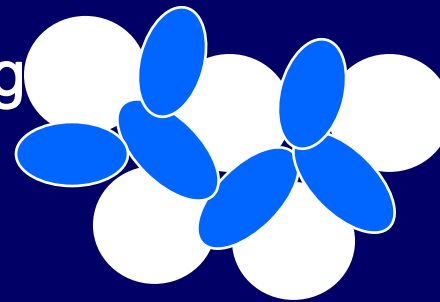
No space

Water swells cellulose

Forming new hydrogen bonding

Supplying permeation path

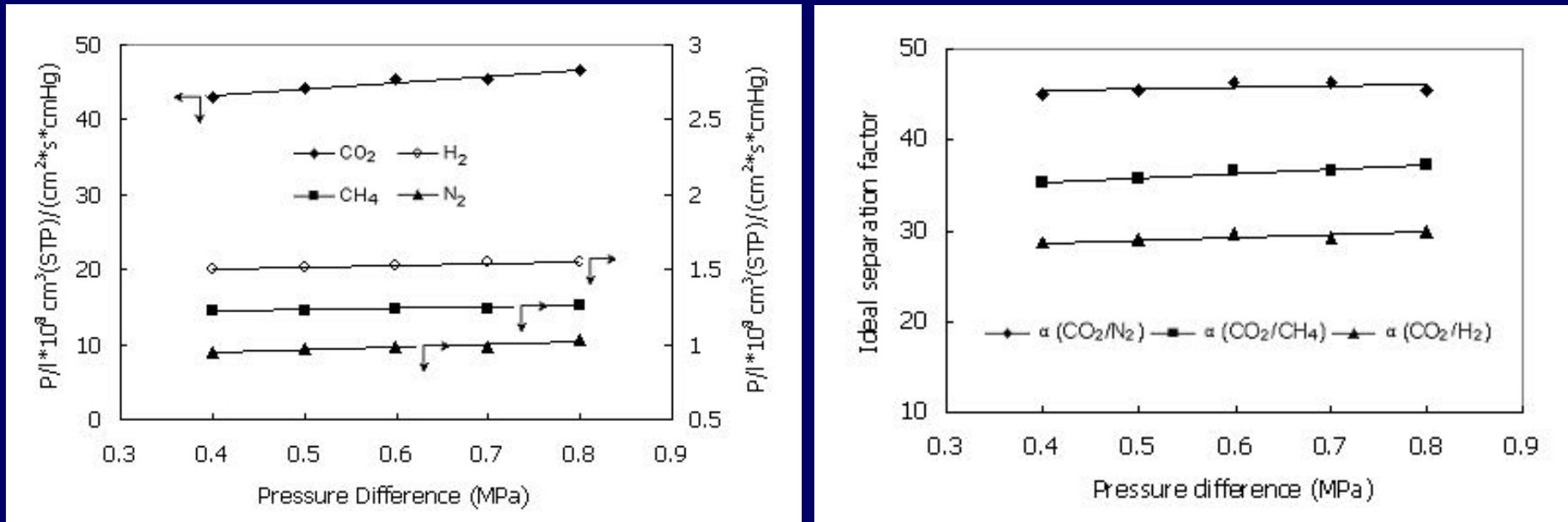
提供气体渗透“水通道”



Water paths

Gas permeation mechanism in water-swollen cellulose hollow fiber membrane

Influence of pressure difference 压力差对膜气体渗透性能的影响



Test condition: 25°C, with a wet gas flow of 60ml/min

What makes CO₂ permeate so fast in water-swollen cellulose hollow fiber membrane? CO₂渗透较快的原因

Gases permeate through water paths in cellulose hollow fiber membrane following solution-diffusion mechanism 气体通过水中溶解扩散渗透通过膜

Carbon dioxide has greater solubility coefficient in water than other gases CO₂水中溶解度较大

Water has an additional facilitated effect for carbon dioxide permeation: $\text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$ 水对CO₂有额外的反应促进渗透作用

Comparison between cellulose hollow fiber membrane and cellulose acetate membrane

纤维素中空膜与醋酸纤维素平板膜气体渗透性能比较

	P_{CO_2} barrer	P_{N_2} barrer	P_{CH_4} barrer	P_{H_2} barrer
CAFM	5.0	0.23	0.14	8.4
CHFM	112.5	2.55	3.83	7.07

	$\alpha(CO_2/N_2)$	$\alpha(CO_2/CH_4)$	$\alpha(CO_2/H_2)$
CAFM	22	35	0.60
CHFM	45	30	16

1barrer= $1 \times 10^{-10} \text{cm}^3(\text{STP}) \cdot \text{cm} / (\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$

Brief conclusion

Cellulose hollow fiber membrane prepared is suitable for acid gas, especially CO₂ separation.

纤维素中空纤维膜适合于酸性气体CO₂分离

Proper membrane drying method should be selected.

后续工作包括膜的干燥方法选择

Asymmetric membrane preparation is being studied.

以及非对称结构膜的制备

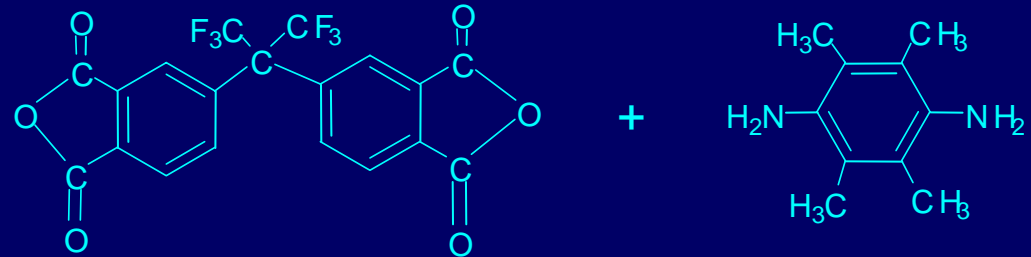
Journal of Applied Polymer Science, 2004, 91, 1873-1880.

Part 3 Polyimide Membrane

第三部分 聚酰亚胺膜

Chemical Structure of Polyimide

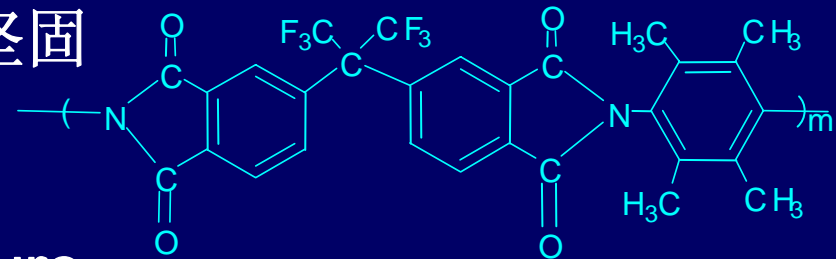
聚酰亚胺的化学结构



Dianhydride
moiety 二酐

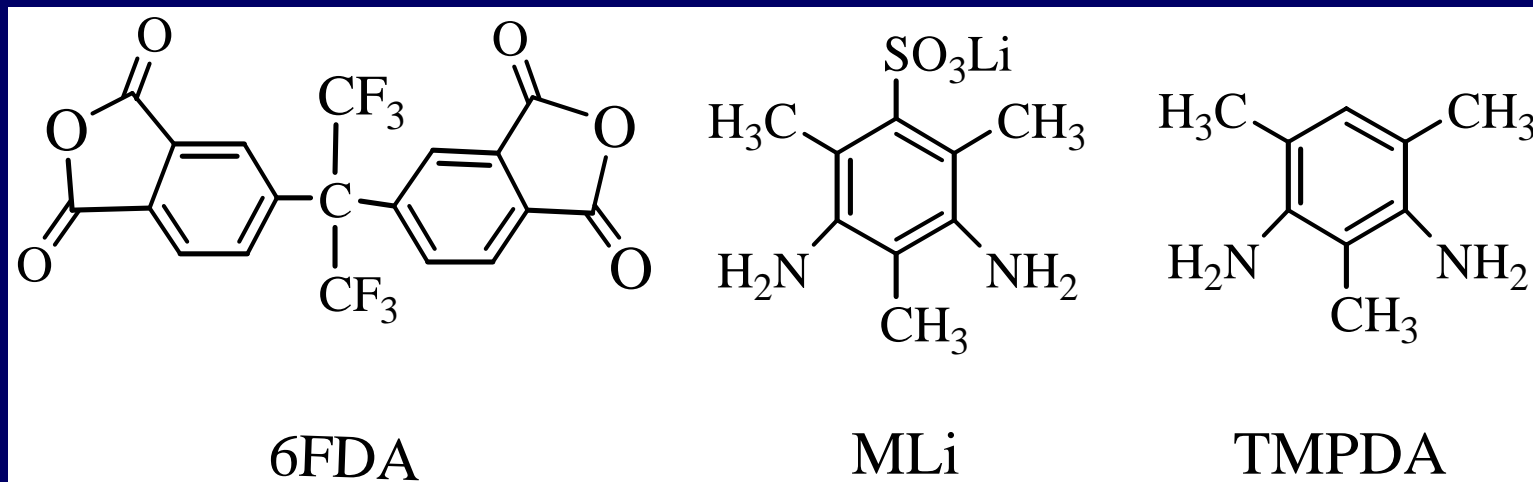
Diamine
moiety 二胺

- ✓ Stiff backbone chains 骨架链坚固
- ✓ Flexible side-group 侧链柔软
- ✓ High glass transition temperature
玻璃化转变温度高
- ✓ High fractional free volume 高自由体积



Polyimide

Preparation of 6FDA-MLi/TMPDA(50/50) polyimide 含磺酸Li盐基聚酰亚胺的制备



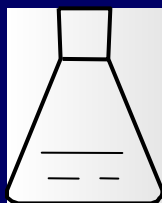
With the introduction of $-\text{SO}_3\text{Li}$: 磺酸Li盐基的引入可以
the solubility of CO_2 in material would increase, which lead
to an increase of the permeability of CO_2 and its separation
factor over CH_4 . 增加 CO_2 的溶解度，促进渗透与分离

Preparation of 6FDA-MLi/TMPDA(50/50) polyimide membrane 聚酰亚胺膜的制备

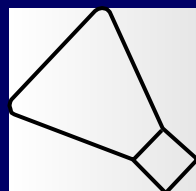
Filtration 过滤

Bubble eliminating

真空脱泡

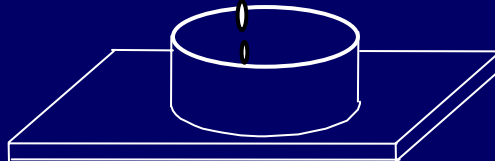


Polyimide dope
膜液



Solvent removing

溶剂挥发



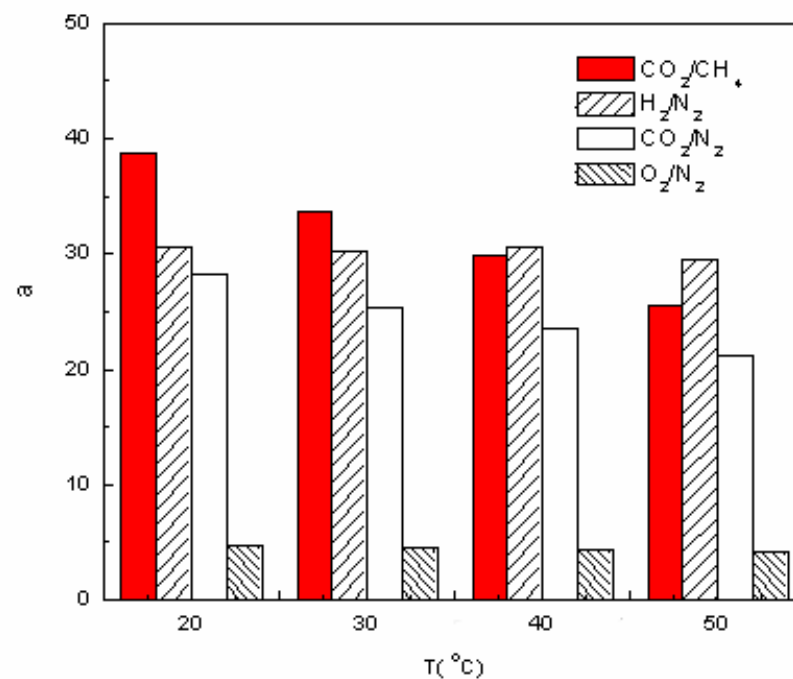
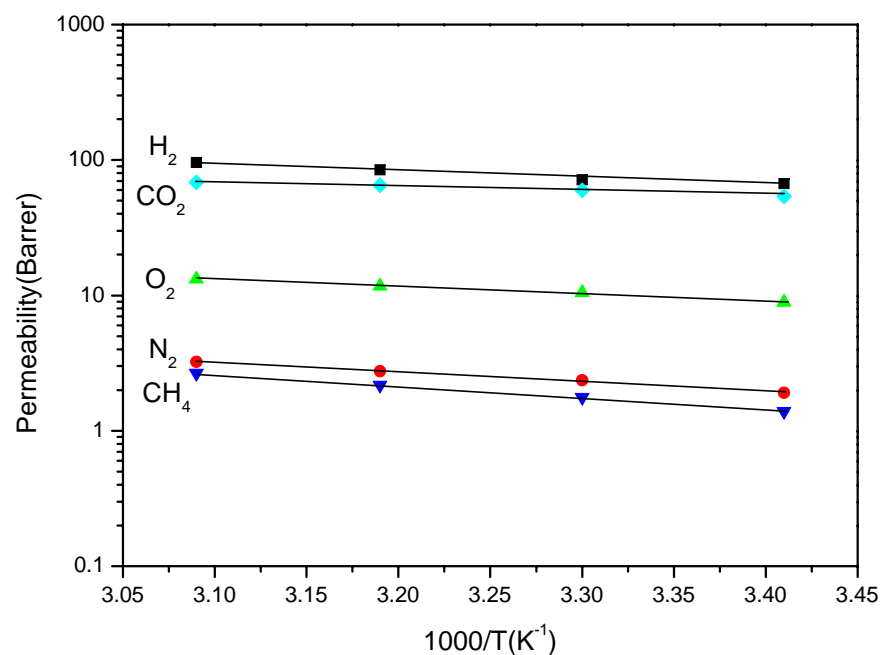
Casting 铸膜



Homogeneous membrane
均质膜

Gas permeability of 6FDA-MLi/TMPDA(50/50) polyimide membrane 聚酰亚胺膜的气体渗透性能

Influence of test temperature 温度影响



The relationship is in accord with Arrhenius' equation.

气体渗透系数与温度关系符合阿累尼乌斯公式。

Brief conclusion

Preliminary test results of 6FDA-MLi/TMPDA(50/50) polyimide membrane shows considerable CO₂ permeability and separation factor over CH₄.

30°C, 0.2MPa下所制备的含磺酸Li盐基聚酰亚胺CO₂渗透系数59.8barrer, 对CH₄分离系数33.8。

Continuing works such as polyimide synthesis and membrane preparation are being carried out.

后续工作包括合成与膜制备正在进行。

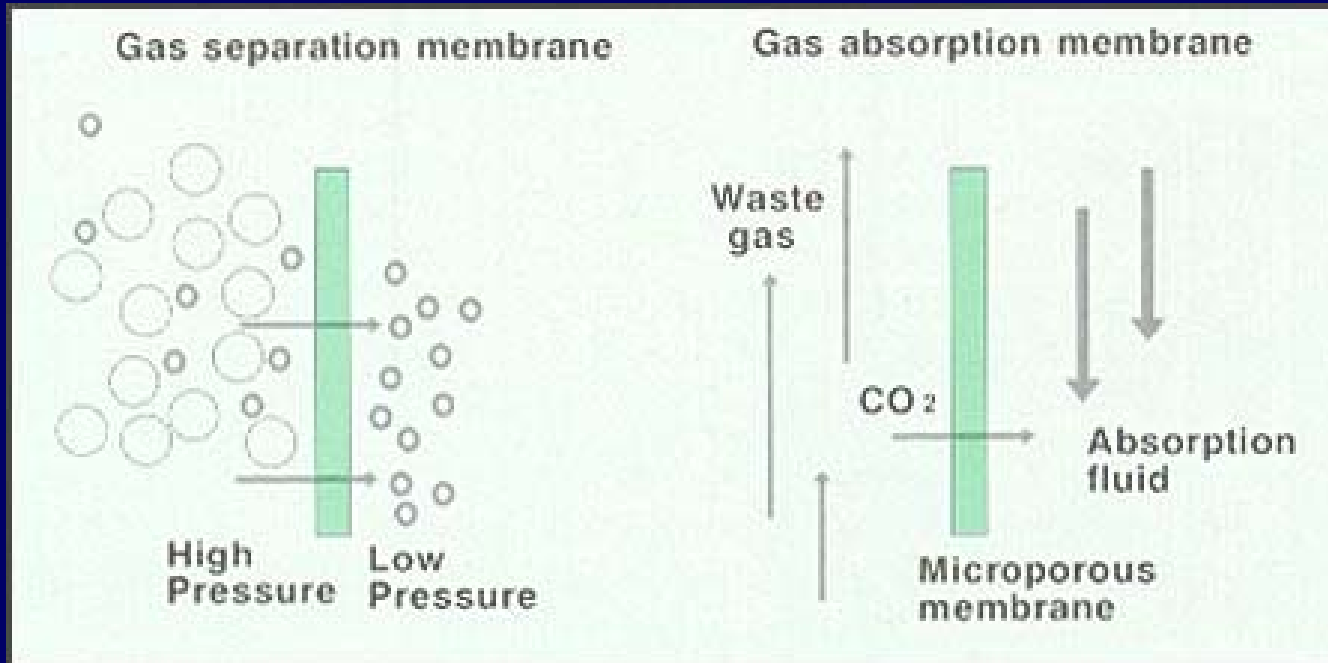
Part 4 Membrane absorption

第四部分 膜吸收

Definition of membrane absorption

膜吸收定义

The combination of membrane gas separation and liquid absorption. 膜气体分离与液体吸收相结合



Innovation points of membrane absorption developed in our group

本课题组膜吸收技术的特别之处在于

Dense hollow fiber membrane absorption process

致密中空纤维膜基吸收过程
Liquid phase and gas phase can be controlled separately

气液两相可单独控制

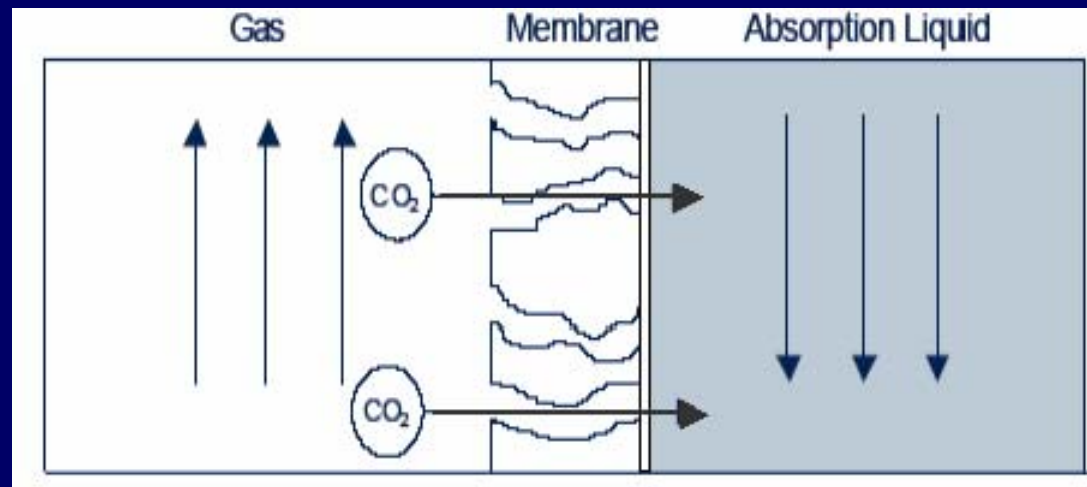
High loading density, high effective membrane area

高装填密度，膜组件比表面大

Phenomena such as bubbling, flooding and entrainment that are often happened in porous membrane can be avoided.

Module for membrane absorption

膜吸收组件示意图

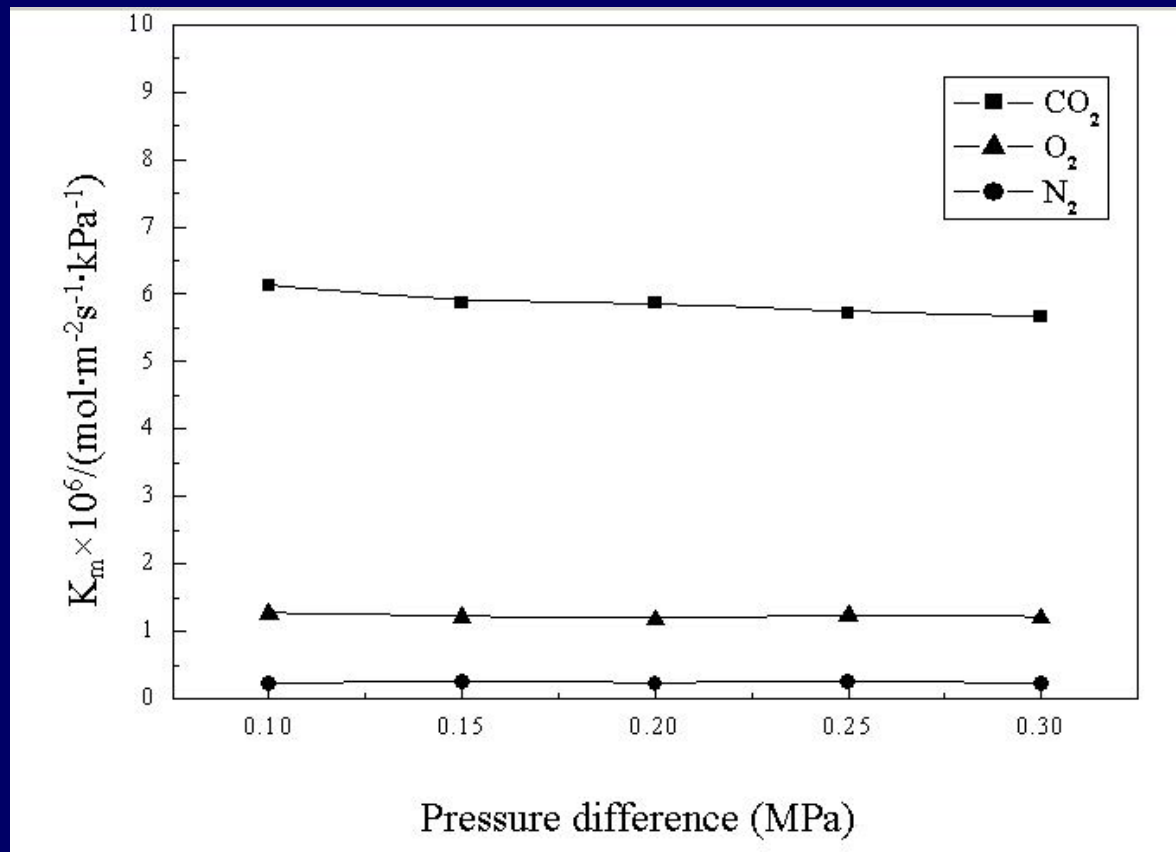


Membrane: Silicone rubber/Polysulfone asymmetric membrane 膜采用 硅橡胶/聚砜非对称膜

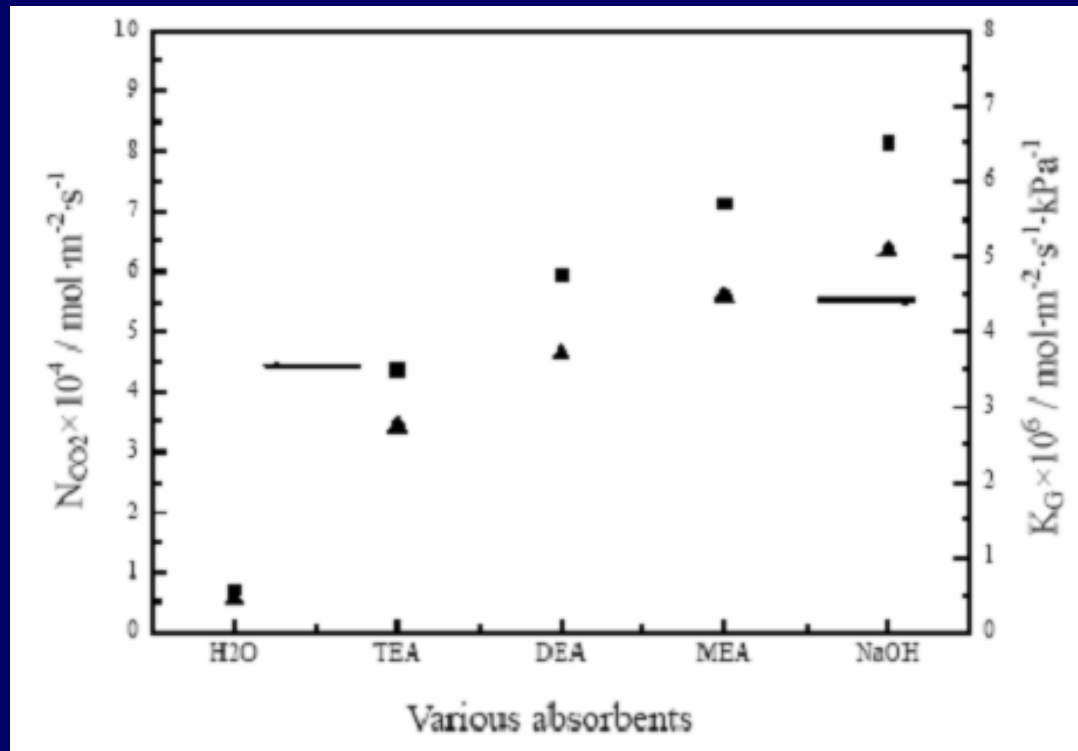
Absorbent: H₂O, TEA, DEA, EA, NaOH solution

吸收液: 水, TEA, DEA, EA, NaOH溶液

Gas permeability of prepared module for membrane absorption 膜的气体渗透性能



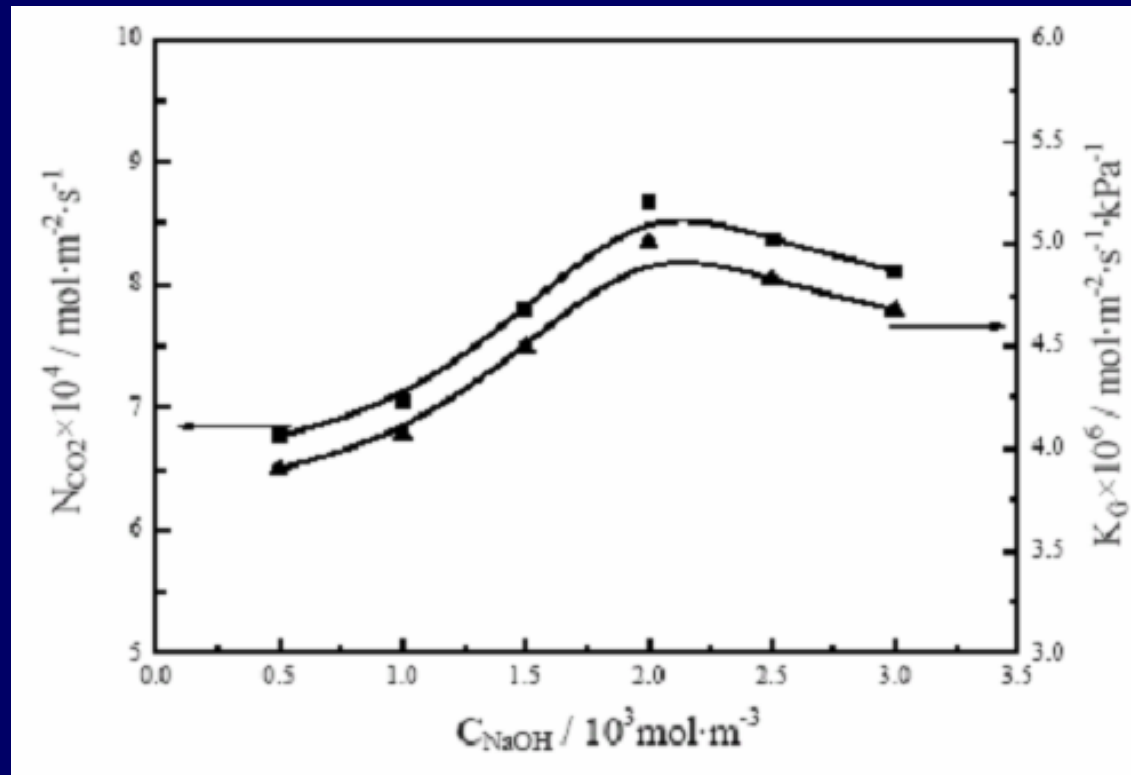
Membrane absorption performance using different absorbent 不同吸收液的影响



Test condition: $C_{\text{absorbent}} 2 \times 10^3 \text{mol} \cdot \text{m}^{-3}$, liquid flow rate $1.39 \times 10^{-6} \text{m}^3 \cdot \text{s}^{-1}$, liquid pressure 0.2MPa, gas pressure 0.16MPa

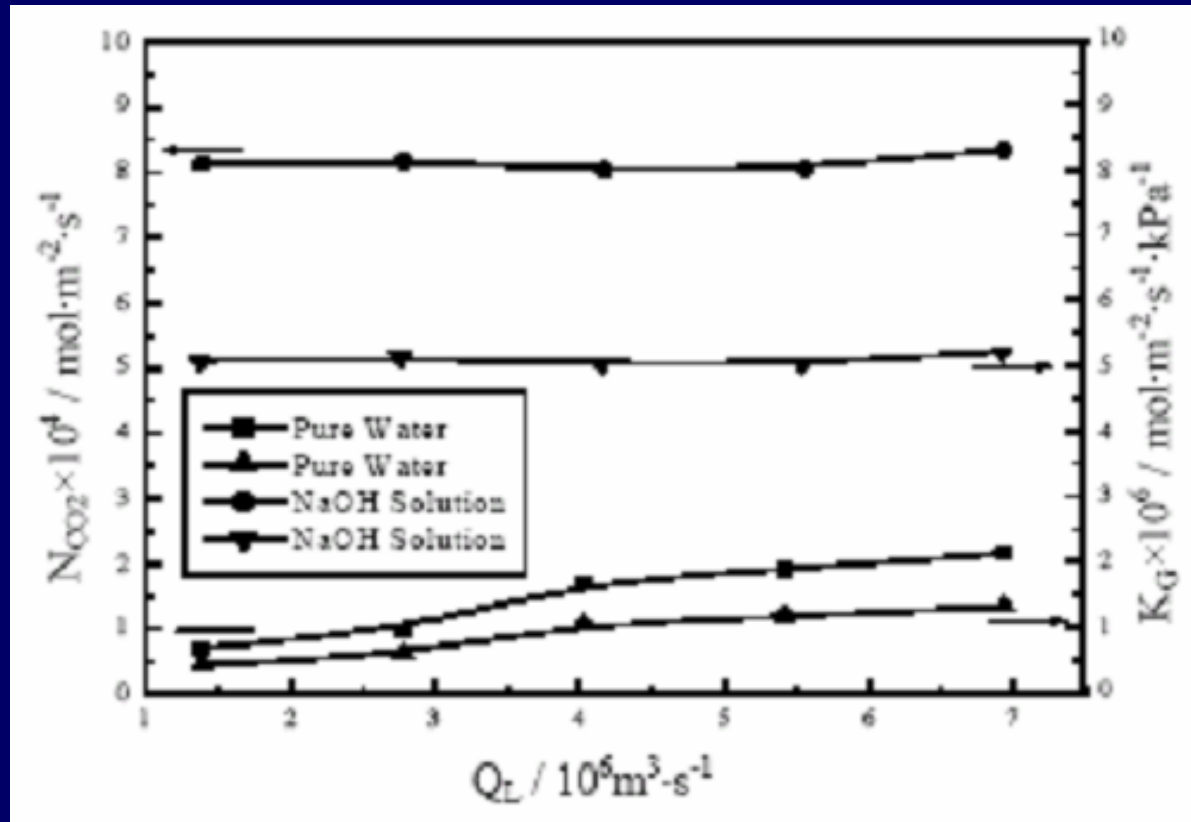
Influence of absorbent concentration on membrane absorption performance

吸收剂浓度的影响



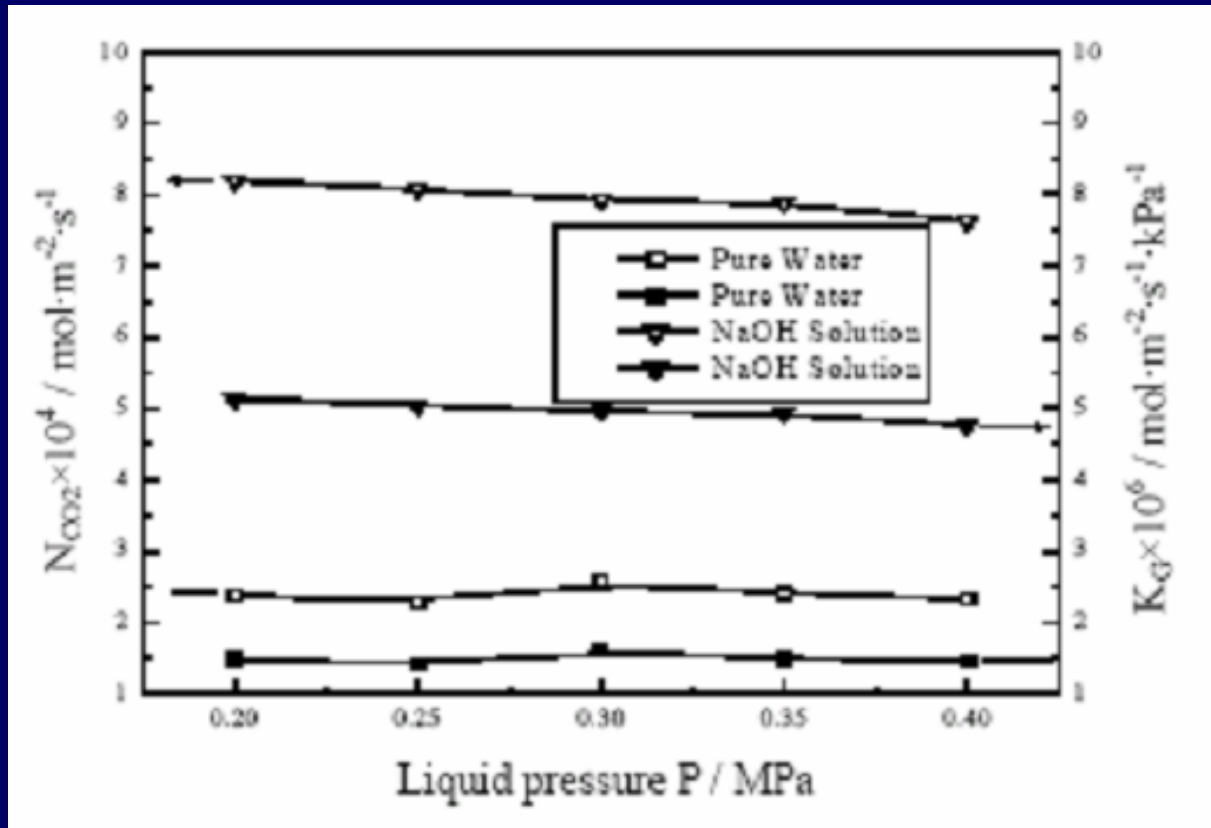
Test condition: liquid flow rate $6.94 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$, liquid pressure 0.2MPa, gas pressure 0.16MPa

Influence of liquid flow rate on membrane absorption performance 液体流速的影响



Test condition: C_{absorbent} 2×10³mol·m⁻³, liquid pressure 0.2MPa, gas pressure 0.16MPa

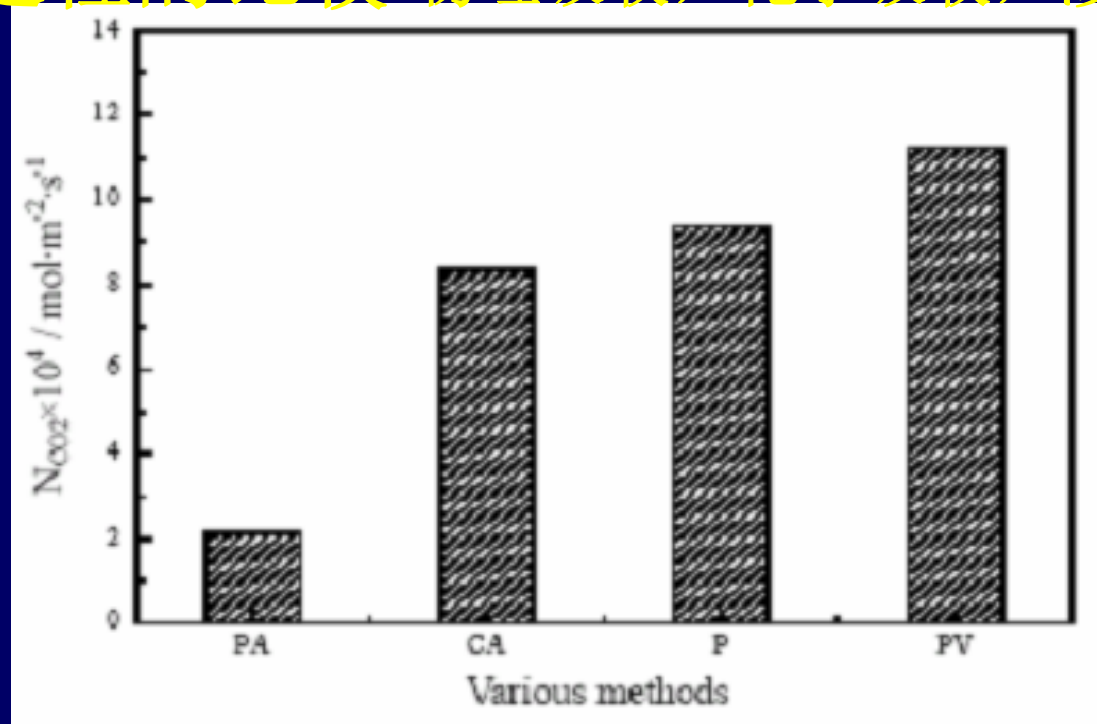
Influence of liquid pressure on membrane absorption performance 液压的影响



Test condition: $C_{\text{absorbent}} 2 \times 10^3 \text{mol} \cdot \text{m}^{-3}$, liquid flow rate $1.39 \times 10^{-6} \text{m}^3 \cdot \text{s}^{-1}$, gas pressure 0.16MPa

Comparison of different separation processes

不同过程的比较 物理吸收，化学吸收，渗透，真空渗透

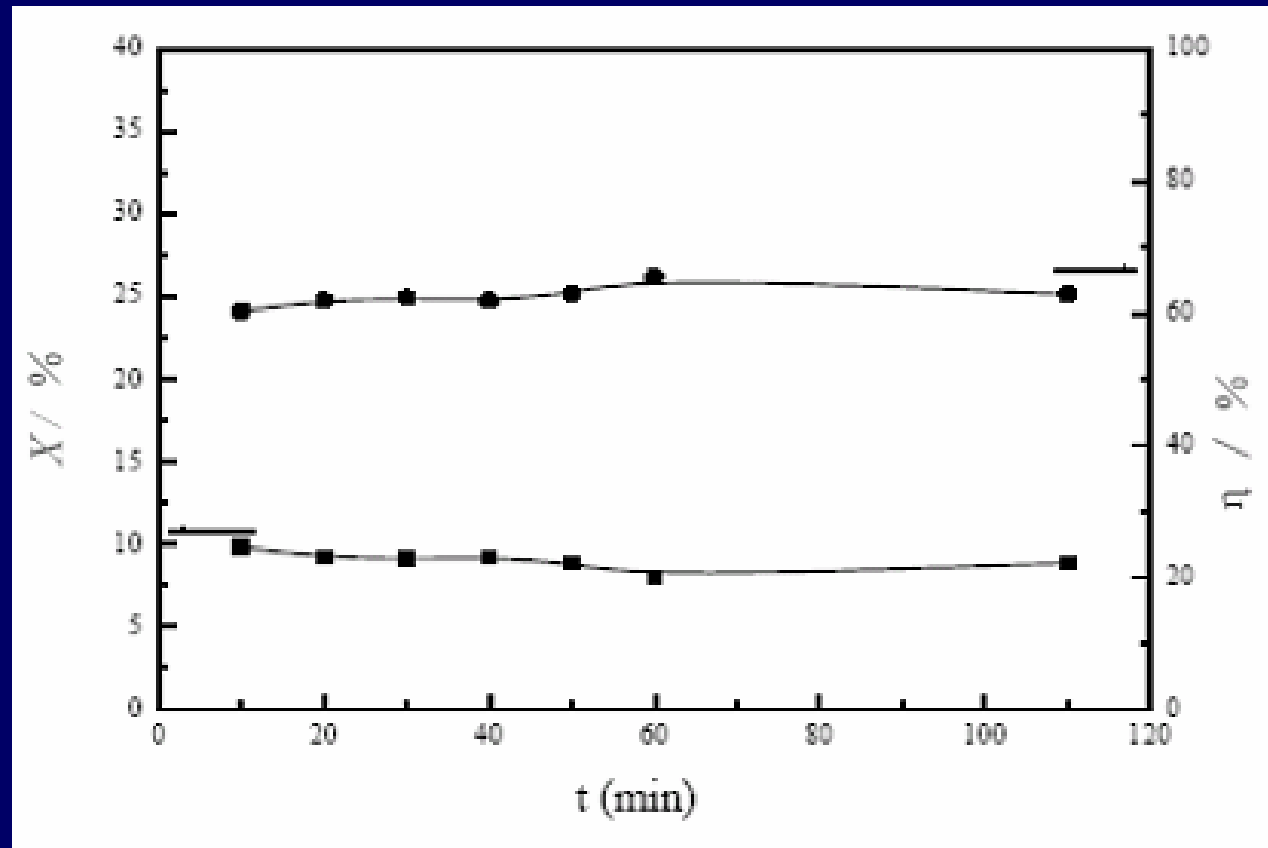


PA: physical absorption; CA: chemical absorption;

P: permeation; PV: vacuum permeation.

CO₂ removal results of membrane absorption

膜吸收脱除CO₂实际效果



Test condition

water , flow rate $2.5\text{m}^3\cdot\text{h}^{-1}$, pressure 0.2MPa;

CO₂ 25% /N₂ 75%, flow rate $0.4\text{Nm}^3\cdot\text{h}^{-1}$, pressure 0.16MPa.

Brief conclusion

CO₂ transfer in liquid phase should be control step during physical absorption, and chemical absorption can greatly accelerate the rate.

物理吸收时CO₂在液体中的传质为控制步骤，化学吸收可以明显促进吸收。

Membrane absorption for CO₂ removal with dense hollow fiber membrane module shows satisfactory application potential.

中空纤维致密膜基吸收脱除CO₂实际可行。



Thank you!

谢谢大家!