

Recent Development of Pervaporation in Japan

(National Institute of
Materials and Chemical Research)

Kensaku Mizoguchi

Recent Development of Pervaporation in Japan

Kensaku Mizoguchi

(NIMC, National Institute of Materials
and Chemical Research, AIST, MITI)

1. Introduction

In general, membrane technology in Japan has remarkably developed in these 20 years. Especially, ones treating water is now in high level and seems to be matured. Water shortage of last summer was a new stimulus for promoting membrane research works.

The researches are now extending to more precise separation of, for example, isomer and proteins. In such cases, not only polymeric materials but also ceramic or carbon ones are attempted.

Concerning pervaporation (PV), water permselective membranes (GFT) are in practical use, PV research works are now concentrating on separation of new targeting substances.

Here, I'd like to introduce, first of all, the outline of membrane technology in Japan (not limited to PV), and then of PV research works.

2. Outline of Membrane Technology in Japan

2.1 From the view point of patent application

Table 1 shows the situation of patent application of membrane technology from each company during these five years¹⁾. Nitto Denko and Mitsubishi Rayon (MRC) has applied averagely more than 60 items every year. Recently, MRC seems to concentrate its research works on membrane, and due to another table, on water cleaner and membrane degassing. Following the same table, Nitto Denko is strong in RO.

Table 2 is relating to the trend in membrane separation method and application field. The number of patents of RO technique is the biggest. Though the one concerning PV is 225 and the fifth biggest, the number is decreasing slightly.

From the view point of application field, the number relating to water cleaner is overwhelmingly large.

2.2 Former National Projects

○The main target system of separation of MITI's National Project for NEW Generation (JISEDAL) during 1981 to 1991 was water/ethanol. Through

such a motivation, PV research works in Japan have been so much promoted. In the project, two types of water permselective membrane were developed with success:

- ① Polyacrylonitrile one, whose surface was exposed to hydrolysis and converted to polyion complex,
- ② Chitosan membrane crosslinked with metal ions.

Both of the two membranes finally had a form of hollow fiber. The performance of them were more than 5,000 in separation factor and 0.5 kg/m²·hr in permeation rate²⁾.

○Aqua-Renaissance '90(1986~1991) - Research and Development of Total System for Water Reuse³⁾

UF and/or MF membranes were combined with a bioreactor for methane fermentation in order to treat exhausted water.

○Research and Development of Oxygen Enrichment Membrane and its Application to Furnace System(1982~1987)

2.3 Recent National Projects

1)MITI Project

○RITE(Research Institute of Innovative Technology for the Earth)Project (1990-)

Concerning membrane technology, main target of the project is CO₂ separation.

○PEC(Petroleum Energy Center) Project(1993-)

Membrane technique has been attempted for precise separation of fractionated components of petroleum. Fifteen teams have been taking part in the project, and three of them are engaged in PV. Other teams are treating mainly organic vapor separation.

○JFCC(Japan Fine Ceramics Center)Project

Separation of high temperature CO₂

2)Project of Ministry of Health and Welfare

○MAC(Membrane Aqua Century 21) and New MAC21⁴⁾

Application of UF, MF and Nanofiltration membrane for tap water purification instead of sedimentation and sand filtration

3. Research Works of PV in Japan

3.1 PV Engineering in Japan

PV plants using GFT membrane have been introduced by MITSUI ZOSEN to industries in these ten years (Table 3). Fig. 1 is the system of Mitsui Zosen⁵⁾. Such industrial applications seem to encourage the PV research works in Japan.

According to a reference (Makusyori Gijutu Taikei, Fuji Technosystem, 1991), Asahi Glass, Sasakura Kikai, Mitsui Zosen and Mitsubishi Rayon have been preparing some types of pV system.

3.2 Permeation Mechanism

In the pervaporation, permeants first dissolve into a membrane and diffuse through it. Therefore, we should investigate ① the solution equilibrium on the liquid side of membrane, and ② the diffusion mechanism.

Iwatsubo et al (our group) analyzed the swelling equilibrium (namely, solution equilibrium) of PV membrane containing ionic groups with generalized Flory-Huggins (F-H) equation. They finally obtained the following approximate equation for a water permselective membrane of water/ethanol system⁶⁾:

$$\alpha \cdot J^{(1/s-1)} \approx \text{const}$$

(α : separation factor, J: permeation flux, s: molar volume ratio of water and ethanol, s=0.31)

From Fig. 2, we can confirm that the gradient of lines obtained is nearly the one predicted. This fact means that the F-H equation is to be applied as a guideline for designing permselectivity.

As for the investigation of diffusion mechanism, we should, first of all, prepare a measuring method of concentration profile in a membrane under separation operation. Iwatsubo et al proposed a new and precise method to get such a profile to measure the dependency of flux on pressure of downstream side phase. Fig. 3 shows an example of concentration profile of water and ethanol in a cellulose acetate membrane. The profile was determined for permeation of single substances⁷⁾.

Through the treatments mentioned above, we elucidated that even in a diffusion process membrane swelling has a large effect.

3.3 PV membranes for Water/ethanol separation

3.3.1 Some materials attempted

1) In order to control the permselectivity, Yamasaki et al attempted to

introduce cyclodextrin(CD), which has a cave with ethanol affinity, into a Polyvinylalcohol(PVA) membrane. By contraries, such membranes showed higher water permselectivity(Fig.4). They thought that the cave has a role of ethanol trapping as well as of a bypass route for smaller size water molecule⁸⁾.

2)A group of Nakagawa proposed recently two types of water/ethanol PV membrane. One type is of Copoly(α -amino-acid) composed of hydrophilic and hydrophobic monomers. They suggested that the free volume formed between α -helix can work as a transport channel of substances, and therefore, permselectivity can be controlled by changing the side chain of amino-acid²¹⁾.

The other material is partially dithiocarbamated Poly(vinyl chloride). The membranes obtained showed water permselectivity.

3)Yanagishita's group tried a new membrane preparation technique using vapor deposition and polymerization.They deposited a thin layer of polyamic acid and polymerised it by heating into dense polyimide.The base membrane was of an asymmetric polyimide. Fig.5 is the apparatus for deposition and Table 4 shows the results of PV of water/ethanol. The membrane was water permselective.The performance was found to be improved²²⁾.

4)Kita et al have tried to use inorganic membranes for separation of water/alcohol.They prepared hydrothermally NaA Zeolite membranes and showed that such membranes could be used as water permselective ones.

3.3.2 Ethanol permselective membranes

1)Uragami's group has proposed two types of membrane and a new membrane separation technique for ethanol permseparation⁹⁾.The first one is related to surface modification. They tried to give higher water repellency on the surface of PTMSP(Poly-1-trimethylsilyl-1-propyne) membrane. For the purpose, a substance(PFA-g-PDMS) the main chain of which is hydrophobic Polyfluoro-acrylate, and Polydimethylsiloxane is grafted on the chain as an anchor, was synthesized and mixed to toluene solution of PTMSP. The solution was cast on a glass plate. Fig.6 is the results of PV and contact angle of the membrane obtained thus. As through the casting, PFA-g-PDMS concentrated on the membrane surface, the contact angle of the surface was increased as well as the ethanol permselectivity.

The second attempt was selectivity control with structure of microphase

separation. A grafted copolymer of methylmethacrylate and dimethylsiloxane(MMA-g-DMS) was prepared changing the content. Fig. 7 shows the effect of DMS content on the permselectivity. According to the TEM observation, when DMS phase changed to continuous one, the membrane was ethanol permselective.

The third one is the application of evaporation(EV). As shown in Fig. 8, a membrane does not contact liquid mixture directly and moreover temperature around the membrane can be controlled independently(TDEV). Seeing the results(Table 5), we can recognize the high performance of TDEV.

2)A type of Zeolite membrane showed much higher ethanol permselectivity. Sano, Yanagishita and coworkers tried to apply Silicalite membrane for separation of water/ethanol and found that this type of membrane showed ethanol preferential property. Fig. 9 is an example of excellent performance of the membrane¹⁰⁾.

3.4 Separation of organic liquid mixture

1)Okamoto and his group have been treating polyimide base membranes. Fig. 10 is the results of PV for benzene(Bz)/cyclohexane(Chx) with some phosphonated polyimide(PhPI), and phosphonated polyphenyleneoxyde(PPO) and polystyrene(PS). Though PhPI is easily cast and crosslinked, the resulted performance is not so high as expected, due to low degree of phosphonation. Meanwhile, the PPO and PS based ones showed a little bit higher performance(Ref. Table 6)¹¹⁾.

2)Yamasaki et al are applying PVA membrane for separation of Bz/Chx. PVA has hydrophilicity, so the polar component Bz can be separated preferentially and the membrane is durable to organic compound as well. As predicted, the membrane was Bz permselective but the flux was very low(Fig 11). The group is now trying to prepare a thin layer of PVA to increase the flux¹²⁾.

3)Yoshikawa is investigating the possibility of separation of Chx/cyclohexanone/cyclohexanol through polyoxyethylene grafting nylon6 membrane. The PV results showed that the membrane rejected Chx. Such type of membrane would be applied to a reaction mixture for the air oxydation of Chx¹³⁾.

4)Nakao, Yamaguchi, Kimura and their group proposed a new preparation technique of membrane called plasma-graft filling polymerization¹⁴⁾. In the

technique, a porous base membrane (polyethylene, $0.02 \mu\text{m}$) was first exposed to air plasma and then grafted polymerized with some vinyl monomer. Through the process, pores of base membrane were filled rigidly (Fig. 12). Such type of membranes are now applied for separation of Bz/Chx where styrene/MMA are used as grafted monomer. Fig. 13 is an example of the results¹⁵⁾.

5) Uragami is trying to apply crosslinked acrylate membrane for PV separation of Bz/Chx¹⁶⁾.

6) Ueyama has attempted PV separation of Bz/Chx, p-xylene/o-xylene and Bz/p-xylene through a ferrierrite membrane. For the last mixture, the membrane showed high performance. The results seem to show that the molecular form difference has an effect of their invasion to the pores because the pore size and molecular size are very similar¹⁷⁾.

3.5 Removal of trace organic compound from water

1) It is an important matter for Japanese people to purify underground water. Underground water has been pointed out polluted with organic chloride which is a detergent for LSI and was spilled out some years ago.

Masuoka and his coworkers (our group) proposed and have investigated a new purification technique for underground water. In the system shown in Fig. 14, air stripping type of PV is applied. Fundamental experiment with a single hollow fiber module of DMS showed that the system could be applied water purification¹⁸⁾.

2) Treatment of polluted water is one of big targets of membrane separation. Mitsui Zosen is now developing a new system using hollow fiber membrane for recycle of phenol. The membrane material is PEBA (Block-copolyetherester amide). Through the pilot test, operation cost of membrane separation was compared with that of incineration method for phenol-contaminated water. The cost was higher for membrane separation, but in the case we can recycle phenol. Totally, the new system is superior to the incineration¹⁹⁾.

3.6) Purification of water by PV

Hitachi group has been engaged in water purification by membrane distillation for cleaning electronic devices, and recycle use of water in a space. For the latter case, pretreatment of urine by active carbon adsorbent to remove surface active substances was found effective for such water purification²⁰⁾.

4. Summary

Though membrane separation research works including PV seem to be matured in Japan, new attempts have been done energetically. Setting new targets of separation would be necessary for more active research works, for example, mixture of organic liquid, and structure or optical isomers, and precise protein separation.

References

- 1) Y. Hashino, New Membrane Technology Symposium, 2-1-1(1996)
- 2) K. Mizoguchi, 「Saikin no Kagakukougaku 41, Maku Bunnri Kougaku」, p239(1989)
- 3) T. Kamizawa, ibid, p257(1989)
- 4) M. Kawasaki, New Membrane Technology Symposium, 3-3-1(1996)
- 5) T. Asada, 「Makusyori Gijutu Taikei, 2, Ouyou siryou Hen」, p353(1991)
- 6) T. Iwatsubo, T. Masuoka and K. Mizoguchi, J. Memb. Sci., 22, 155(1992)
- 7) T. Iwatsubo, T. Yamanaka, S. Yamamoto, K. Mizoguchi and Y. Suda, SEN-I GAKKAISI 44, 367(1988)
- 8) A. Yamasaki and K. Mizoguchi, J. App. Polym. Sci., 51, 2057(1994)
- 9) T. Uragami, New Membrane Technology Symposium, 1-3-1(1996)
- 10) T. Sano, H. Yanagishita, Y. Kiyozumi, F. Mizukami and K. Haraya, J. Memb. Sci., 95, 221(1994)
- 11) T. Kawabata, S. Fujiwara, K. Tanaka, H. Kita and K. Okamoto, Dai 28 Kai Kagaku-Kougaku Kai Syuuki Taikai, S309(1995)
- 12) A. Yamasaki and K. Mizoguchi, ibid, S307(1995)
- 13) H. Okushita, M. Yoshikawa and T. Shimizu, J. Memb. Sci., 105, 51(1995)
- 14) T. Yamaguchi et al, Macromolecules, 24, 5522(1991)
- 15) T. Kai and S. Nakao, Dai 28 Kai Kagaku-Kougaku Kai Syuuki Taikai, S304(1995)
- 16) T. Uragami, H. Okumura, K. Inui and T. Miyata, ibid, S305(1995)
- 17) N. Nishiyama, M. Matsukata and K. Ueyama, ibid, S315(1995)
- 18) T. Masuoka, K. Ogasawara, T. Iwatsubo and K. Mizoguchi, Proc. International Symp. Fiber Sci. and Tech, 281C160(1994)
- 19) M. Kondou, MAKU, 20, 194(1995)
- 20) H. Kurokawa, K. Funabashi, S. Sugawara and R. Futamata, Dai 28 Kai Kagaku-Kougaku Kai Syuuki Taikai, E114(1995)

- 21) T. Nakagawa, K. Shimada and S. Yamada, Proc. International Symp. Fiber Sci. and Tech, 271C19Pa(1994)
- 22) H. Yanagishita, D. Kitamoto, H. Nozoe, T. Nakane, T. Tsuchiya and N. Koura, Proc. Euromemb' 95, I-290(1995)

Table 1 Recent trend of patent application of membrane technology from each company during these 5 years

	(Year)	91	92	93	94	95	Total
日東電工		50	101	76	56	47	330
三菱Rayon		49	42	34	68	111	304
旭化成		38	67	42	42	34	223
Kubota		32	63	25	38	51	209
Toray		32	21	24	37	46	160
N O K		22	36	27	36	37	158
松下電器		31	56	22	27	13	149
Daicel		21	31	22	28	20	122
栗田工業		13	22	20	28	24	107
三菱重工業		16	33	18	22	10	99
日立製作所		19	18	17	17	24	95
富士写真Film		18	39	14	12	3	86
Tokuyama		13	22	15	15	19	64
Organo		8	15	10	23	25	81
荏原製作所		12	30	17	12	7	78
宇部興産		20	22	11	15	8	76
TOTO		5	3	20	31	15	74
旭硝子		7	15	11	15	24	72
東芝		17	12	17	9	16	71
日本碍子		12	10	15	11	14	62
日立Plant Const		6	8	18	20	9	61
Dainihon Ink Chem		8	4	12	16	16	56
Kuraray		15	15	11	3	10	54
三浦工業		6	16	10	7	15	54
松下電工		6	19	10	6	4	45
住友電氣工業		7	8	5	12	10	42
三菱化学		6	2	9	11	12	40
東洋紡績		11	4	2	10	9	36
Yuasa Corporation		11	8	2	7	8	36
Daikin		14	9	10	2	1	36
Japan Milipore		9	7	3	12	4	35
Japan Goretex		6	7	6	6	10	35
Dupont Japan		13	9	2	6	4	34
工業技術院(AIST)		5	5	8	4	11	33
三井造船		2	3	10	8	7	30
Japan Paul		5	3	5	9	7	29
東芝Ceramics		14	7	5	2	1	29
水道機工		1	1	2	15	3	22
Hochst-Celanese		5	1	7	3	6	22
Union Carbide		6	12	2	0	2	22
野村Micro Science		1	2	2	7	7	19
三洋電機		2	4	6	2	3	17
東燃		5	2	7	1	1	16
Dow Chemical		4	4	1	2	5	16
鐘淵化学		2	1	4	3	5	15
Small Total		605	819	616	716	718	3474
Others		357	397	397	351	336	1838
Total		962	1216	1013	1067	1054	5312

Table 2 Recent trend of patent application of membrane technology in separation method and in application field

Separation Method (Year)	91	92	93	94	95	
RO	44	51	78	70	60	303
Membrane degassing	35	68	41	51	62	257
Gas	38	63	36	50	52	239
Ion Exchange	30	50	47	40	72	239
PV	45	54	58	33	35	225
MF	64	30	47	23	42	206
Ceramic Membrane	59	41	39	26	29	194
Oxygen/Nitrogen	51	47	36	26	15	175
UF	26	29	43	39	35	172
Cleaning	25	21	20	22	20	108
MF Hollow Fiber	56	15	8	4	22	105
Dehumidity	26	18	11	20	18	93
Hydrophilicity	17	27	15	12	12	83
Hydrogen	7	9	12	13	16	57
Membrane Distillation	17	3	7	3	8	38
Total						2494
Application Field						
Water Cleaner	58	113	93	18	108	490
Polluted Water Treatment	41	97	27	25	54	244
Cell Separator	44	59	55	40	33	231
Ultrapure Water	13	31	31	23	23	121
Water Purification	1	24	30	31	22	108
Atomic Energy	28	14	6	5	8	61
Medical Use	14	7	3	5	16	45
Water Preparation	9	3	4	5	4	25
Total						1325

Table 3 Introduction of PV Separator in Japan (1988.6)

No	Companies	Solvent	kg/h	Water Content	Setting
1	Ohgaki Distiller	IPA	500	13→0.3(wt%)	1987.5
2	Hitachi Chemical	Mixed	25	1.5→0.05	1987.5
3	Niigata Iron Ind	ethanol	50	33→8	1987.6
4	Kao	solvent A	150	0.5→0.3	1987.12
		solvent B	20	25→1.0	
5	X Medical Comp.	solvents	max 10	to 100ppm	1987.12

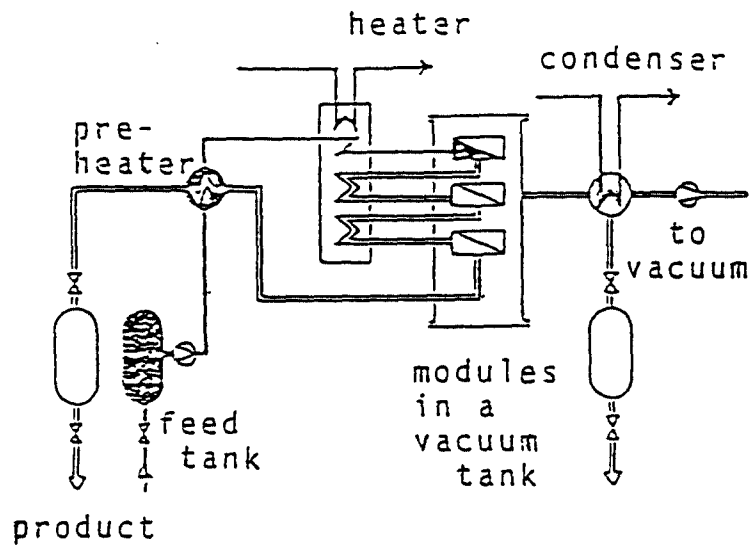


Fig.1 PV separator system

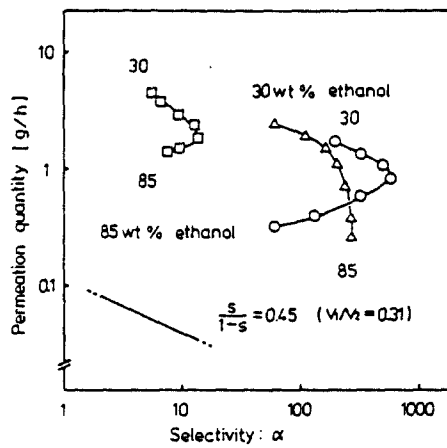


Fig.2 Conformation of α -J relation for water/ethanol

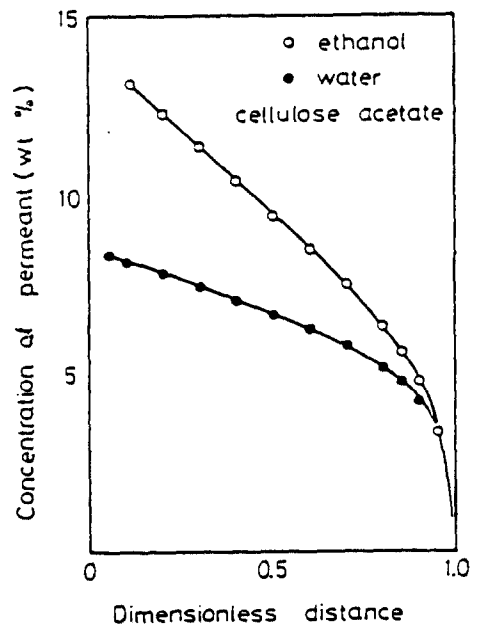


Fig.3 Concentration profile in a membrane

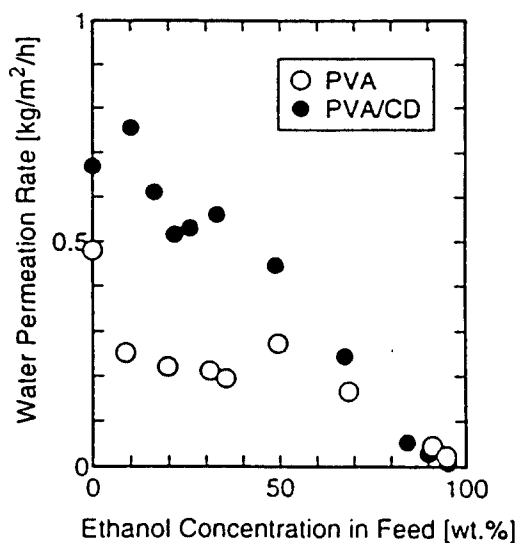


Fig. 4 Effect of addition of CD to PVA membrane

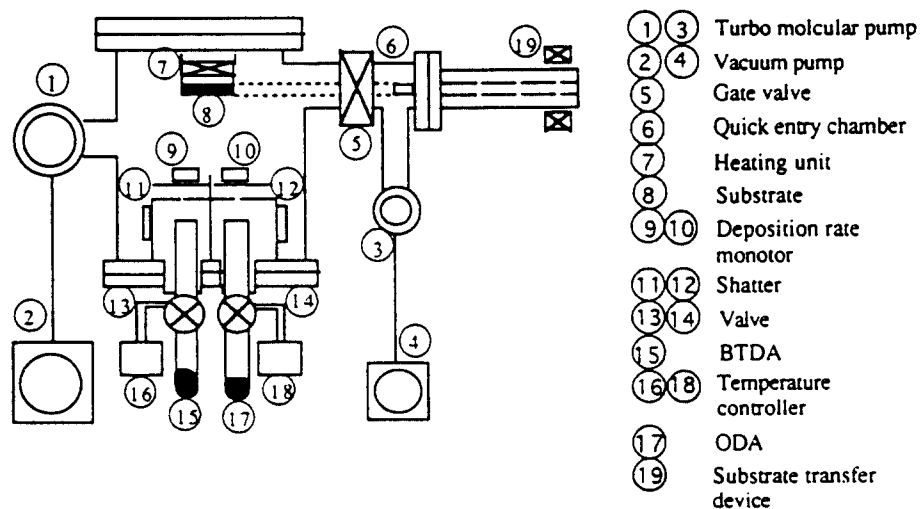


Fig. 5 Vapor deposition and polymerization apparatus

Thickness of deposited layer (μm)	flux ($\text{kg}/\text{m}^2\text{h}$)	separation factor α
supporting membrane	0.19	40
0.05	0.088	360
0.1	0.051	790
0.2	0.037	1300
0.4	0.012	1300
homogeneous membrane (20 μm)	0.002	1300

Table 4 Separation performance of composite membrane

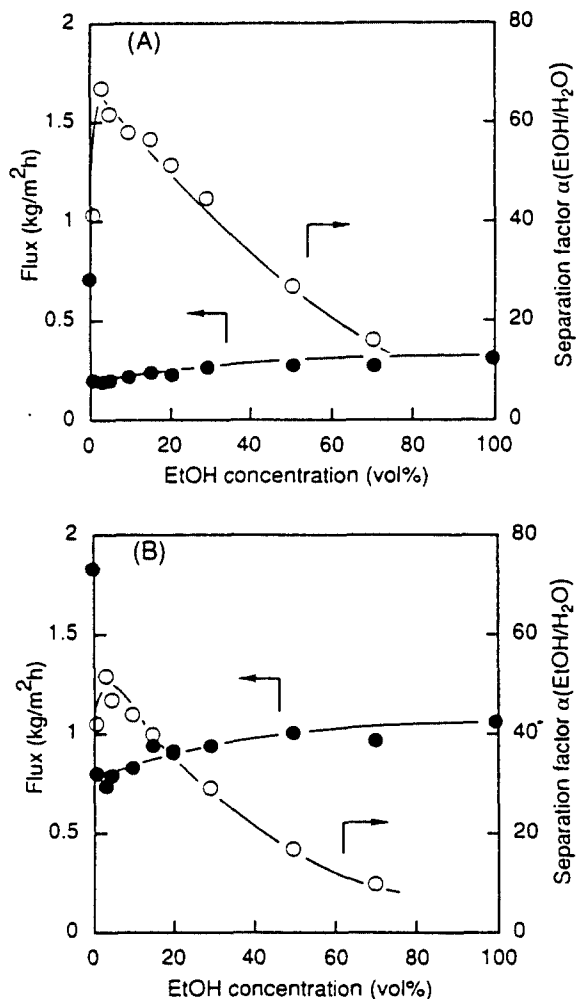


Fig.9 Performance of Silicalite membrane

Table 6 Membrane materials and performance

No	Membrane	l (μ m)	X_B (wt%)	T ($^{\circ}$ C)	Q _f (Kg μ m/m ² h)	$\alpha_{B/C}$ (-)
1	BP-TrMPD	44	50	50	9.1	7.1
3	BP-TrMPD(7%Br)	40	60	50	12	8.2
4	BP-TrMPD(7%Br/A)	23	60	50	2.1	12
5	BP-TrMPD(11%Br)	21	50	50	8.1	8.4
6	BP-TrMPD(11%Br/TC)	21	50	50	5.9	9.4
7	BP-TrMPD(11%Br/A)	24	50	70	0.21	33
8	BP-TrMPD(0.6%Br/A)	15	50	50	1.3	11
10	BP-TrMPD(1.2%Br/DETA)	19	50	70	1.0	18
11	BP-TrMPD(1%P)	31	60	50	18	5.9
12	BP-TrMPD(1%P/TC)	31	60	50	14	6.7
13	BP-TrMPD(1%P/A)	31	60	50	6.8	7.9
14	BP-TrMPD(1.9%P)	27	50	50	9.9	7.3
15	BP-TrMPD(1.9%P/TC)	34	50	70	14	7.4
16	BP-TrMPD(1.9%P/DEA)	26	80	70	0.024	89
21	PPO-P(10%P)/CA(1/1)	40	50	70	24	10
22	PPO-P(10%P/A)/CA(1/1)	45	50	70	23	11
23	PPO-P(11%P/20%Br)/CA(1/1)	27	50	70	9.9	13
24	PPO-P(11%P/20%Br/A)/CA(1/1)	25	50	70	5.9	10
25	PPO-P(11%P/20%Br/EDA)/CA(1/1)	25	50	70	5.8	18
26	PPO-P(11%P/20%Br)/CA(3/2)	25	50	70	32	8.6
27	PPO-P(11%P/20%Br/TC)/CA(3/2)	28	50	70	17	14
28	PS-P(7.3%P)/CA(1/1)		55	78	14	14
29	PS-P(6.1%P)/CA	20	55	77.8	20	12
30	PS-P(10.5%P)/CA	20	55	77.8	24	40
31	PSP/CA	20	55	77.8	16	9.0

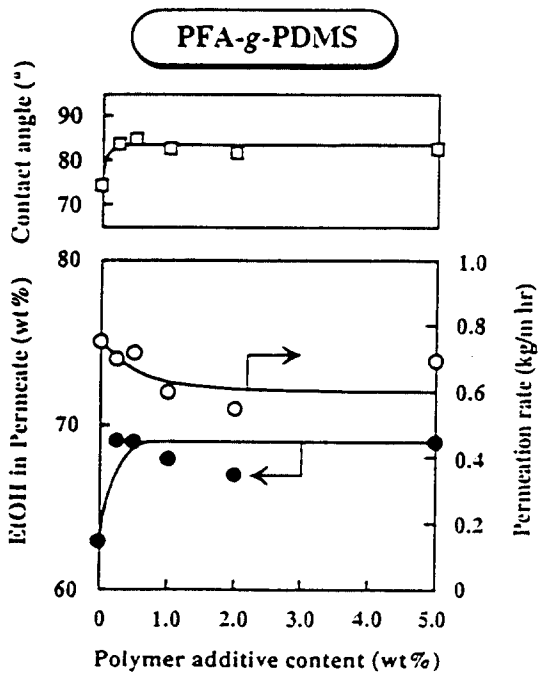


Fig.6 Effect of PFA-g-PDMS content on contact angle and performance

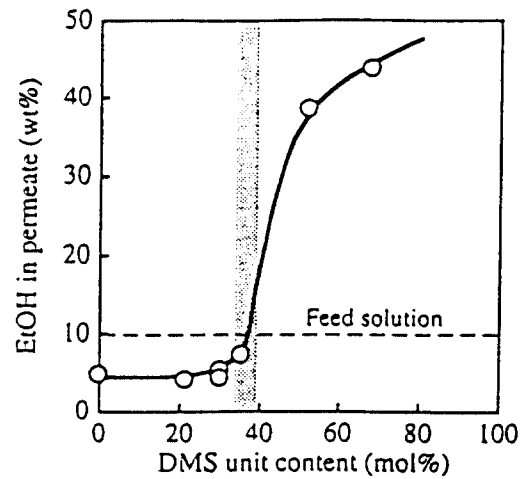


Fig.7 Effect of DMS content on permeation

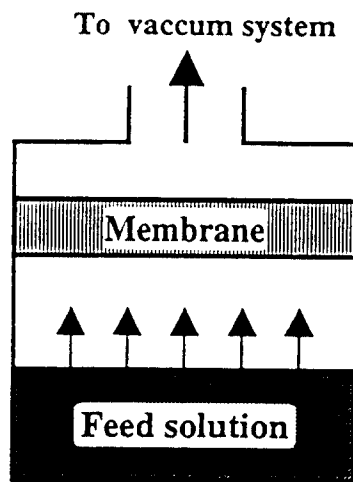


Fig.8 Concept of Evapomeation

Feed	Permeation rate $\times 10^2$ (kg/m ² h)		Separation factor ($\alpha_{\text{EtOH}} / \text{H}_2\text{O}$)	
	PV ^a	TDEV ^b	PV ^a	TDEV ^b
10wt% EtOH	5.33	4.01	7.44	14.36 (2.04) ^c
30wt% EtOH	6.90	6.24	5.79	7.20 (2.02) ^c

a Permeation temperature: 40°C.

b Temperature of feed solution: 40°C, temperature of membrane surroundings: 25°C.

c Values in parentheses are for the feed vapor in EV.

Table 5 Comparison of PV and TDEV

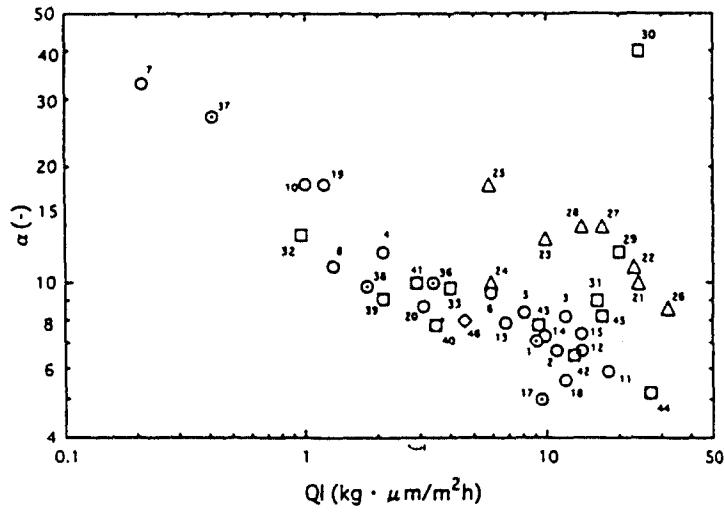


Fig.10 PV performance of phosphonated membranes

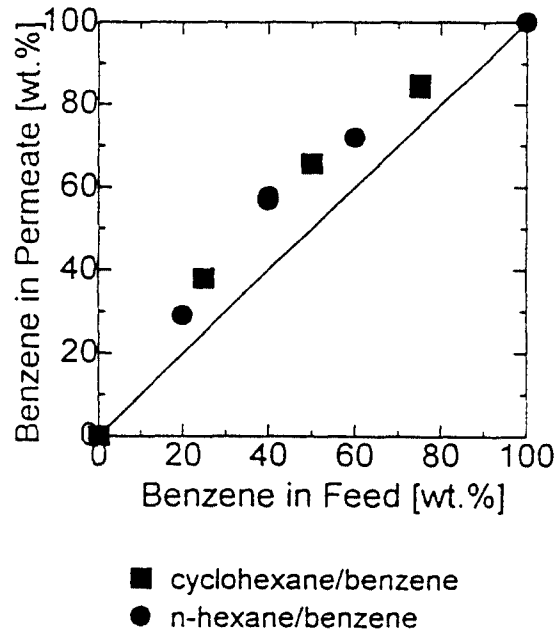


Fig.11 PV performance of PVA membrane for Bz/Chx

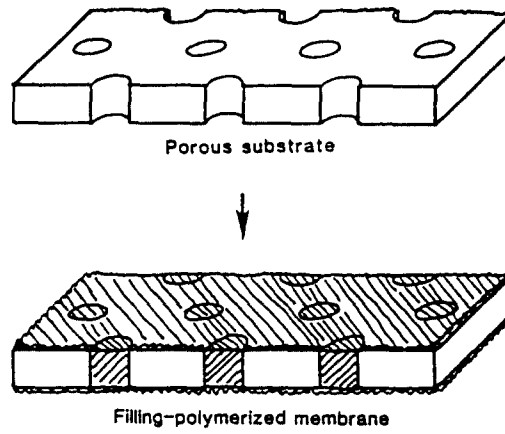


Fig.12 Principle of plasma graft-filling polymerization

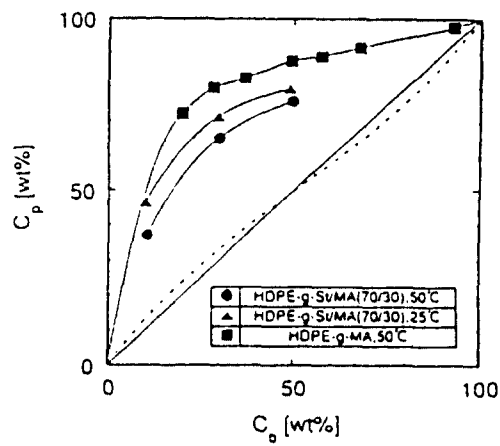


Fig.13 PV performance for Bz/Chx

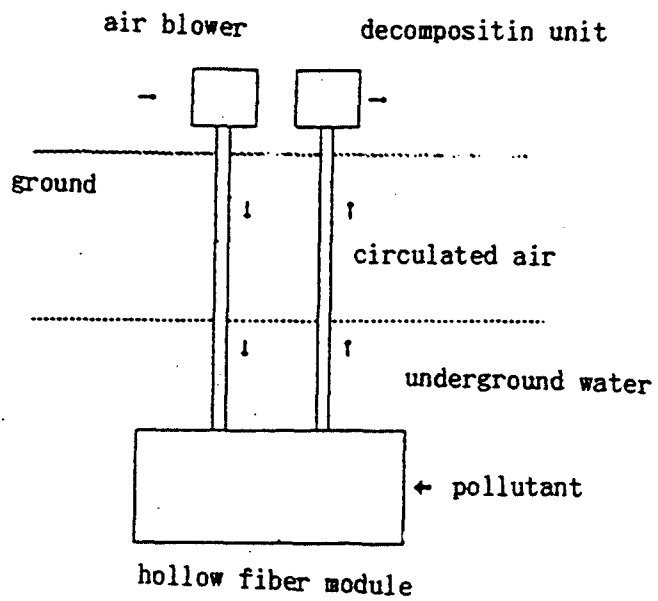


Fig.14 Concept of underground water purification using membrane