Synthesis of Grafted Polydimethylsiloxane Membranes with Fluoroalkyl Methacrylate and their Volatile Organic Compounds Separation Properties

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博士学位請求論文

Synthesis of Grafted Polydimethylsiloxane Membranes with Fluoroalkyl Methacrylate and their Volatile Organic Compounds Separation Properties

（ﾌﾙｵﾛｱﾙｷﾙﾒﾀｸﾘﾚｰﾄｸﾞﾗﾌﾄﾎﾟﾘｼﾞﾒﾁﾙｼﾛｷｻﾝ膜の合成と
それらの膜の揮発性有機化合物の透過性に関する研究）

学位請求者　　三島　聡子

ABSTRACT

MISHIMA, SATOKO. Permeability of Organic Compounds in Silicone Rubber Membrane and Fluoroalkyl Methacrylate Grafted Silicone Rubber Membranes. (Under the direction of Professor Tsutomu Nakagawa.)

Recently, it has been a social problem that ground water and soil are contaminated with volatile organic compounds (VOCs). Removal of VOCs from water by pervaporation has been studied. The membranes that allow VOCs to permeate preferentially can be applied to the removal of very low concentrations of VOCs like chlorinated hydrocarbons from these contaminated water (<1000g/m^3). Pervaporation performance of a membrane is determined by both the sorption and the diffusion characteristics of the permeating components in the membrane. The solubility and diffusivity are achieved by the difference in the membrane solubility and permeability of the feed solution components. Polydimethylsiloxane (PDMS) has been well-known as an excellent polymer membrane material for its high permeability to gases and liquids. Fluorinated polymers have the hydrophobicity based on their low surface energy and their hydrophobic nature was expected to promote the selective adsorption and transport of the organic component in a water solution. In this study, the PDMS membranes were improved using fluoroalkylmethacrylates (FALMA), which has vinyl functional group and easy radical formation, to enhance the affinity of PDMS for chlorinated hydrocarbons. For this improvement, blending of PDMS and poly(FALMA) is difficult due to the low affinity of PDMS for poly(FALMA). There is the possibility of preparing graft or block copolymers of them.

The PDMS membranes were grafted by FALMA using various irradiation source. FALMA had the effect of increasing the selectivity for VOCs. The novel grafted PDMS membrane had the difference of polymer structure by various irradiation methods. The permeation properties of the various grafted PDMS membranes were characterized.

The basic permeation behavior for PDMS membrane was investigated. The hydration effect on the sorption-diffusion mechanism for various organic compounds was investigated in pervaporation through the PDMS membrane. Almost all water molecules are concerned with hydration when the concentration of (water molecules)/(solute molecules) is the same as the hydration number. When the actual concentration was over this concentration, the water molecules hydrate to several solute molecules and the motion of the water molecules is prevented. During pervaporation, the solute was concentrated in the PDMS membrane and the diffusion of water molecules was prevented. It is concluded that not only the volume of penetrate but also the hydration considerably affect on the diffusivity.

The PDMS membrane in which FALMA and alkylmethacrylates (ALMA) were sorbed, was irradiated by UV and utilized in pervaporation. The polymerized FALMA and ALMA were contained in a modified membrane. The contained amounts of FALMA and ALMA were around 1wt%. The almost same values were obtained for each FALMA and ALMA. The sorbed TCE in the modified membrane increased with increasing length of the fluorinated side chain of FALMA, i.e., the number of fluorine atoms. The membrane that showed the best separation performance was the membrane having the highest TCE concentration in the sorbed solution. With increasing feed concentration, water diffusivity decreased. Due to the introduction of a hydrophobic polymer, FALMA, the TCE quantity sorbed into the membrane was so high that the diffusion of water was prevented- in turn, the flux decreased.

The effect of solubility and diffusibility of a monomer on graft polymerization by electron beam according to solubility parameter, octanol-water partition coefficient (Pow) and the molecular volume of the monomer was investigated. The difference in the sorpted amount or grafted amount was little when considering the difference of the solubility parameter and the logPow. The sorpted amount and grafted amount were affected by the molecular volume. The sorpted amount for ALMA that have low molecular volume was high. The sorpted amount for FALMA that have high molecular volume was low. Compared to each other in the same group of FALMA or ALMA, the sorpted and grafted amount for the monomer which has low molecular volume was high, and the sorpted and grafted amount for monomer which has high molecular volume was low. The various grafted amounts were obtained for FALMA and ALMA in different from the modification by UV irradiation. The pervaporation for the PDMS membrane, PDMS membrane irradiated by electron beam, grafted PDMS membranes was investigated. It is thought that the PDMS membranes were made brittle by electron beam irradiation. FALMA grafted PDMS membranes showed excellent sorption and pervaporation separation performance.

The PDMS membrane was improved by the graft polymerization with 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA) by plasma, which had a long n-fluoroalkyl chain and the effect on increasing the selectivity for VOCs. The plasma technique does not require a high installation cost for the energy source. The radical formation is easily performed on the surface of the polymer. The treatment time is short, within a few minutes. The degree of grafting and oxidation simultaneously increased with plasma power. The flux of the grafted PDMS membrane increased with increasing plasma power. The degree of grafting increased with increasing plasma irradiation time. The flux of the grafted PDMS membrane was constant regardless of the plasma irradiation time. When the PDMS membranes were irradiated at 10W for 180s and grafted, the grafted membranes were not brittle and the permselectivity increased. Because the grafted amount of the plasma grafted PDMS membrane was little and the advantage of rubbery PDMS membrane remained, the relationship between the feed concentration and the permeate concentration was observed to be linear.

The sorption and diffusion for various VOC-water mixture during pervaporation through the PDMS membrane and HDFNMA grafted PDMS membrane by plasma preirradiation were investigated. The TCE flux was prevented by benzene during pervaporation of the TCE-benzene-water mixture through the grafted PDMS membrane.Permselectivity is determined by the sorption and the diffusion characteristics of the permeating components in the membrane. The permselectivity of PCE and toluene was high. Because the solute quickly permeates in the rubbery membrane like PDMS, permselectivity was not affected by diffusivity. Solubility significantly affects the permselectibity during pervaporation through the hydrophobic rubbery membrane.

The PDMS membrane was grafted by HDFNMA using a ^{60}Co source. The PDMS membrane and HDFNMA are irradiated simultaneously. The grafted amount by simultaneous irradiation was more than by preirradiation methods, and the permeation behavior will be expected to be differ from the rubbery untreated PDMS membrane and the grafted membranes by preirradiation method. The grafted and polymerized HDFNMA by a ^{60}Co simultaneously irradiation was swollen but not dissolved in solvent, different from poly(HDFNMA) grafted by electron beam and plasma preirradiation. The grafted PDMS membranes had a microphase-separated structure, i.e., a separated structure of PDMS and grafted HDFNMA. The grafted PDMS membrane showed great separation performance. The permeability of the PDMS phase was significantly great and that of the poly(HDFNMA) phase was too low to affect the whole permeation of the grafted PDMS membrane directly. The permeation on the surface of poly(HDFNMA) and PDMS played important role because of poly(HDFNMA) had a much stronger affinity for TCE than for water. The permeability and permselectivity of TCE on the surface of poly(HDFNMA) and PDMS were high. At a high concentration of TCE solution, TCE was sufficiently sorbed into the membrane, so that the diffusion of water was prevented by the TCE molecules; in turn, the permselectivity of TCE was increased significantly. The permeation behavior was differ from rubbery untreated PDMS membrane and the little grafted PDMS membrane by preirradiation.

In this study, the permeation properties of the grafted PDMS membranes by various irradiation methods were characterized. The permeation behavior was differ from rubbery untreated PDMS membrane and the little grafted PDMS membrane by preirradiation. Not only solute properties and interaction but also membrane structure effected on the permeation behavior.

Further, Poly(1-Trimethylsilyl-1-Propyne) PMSP membrane was filled with polyHDFNMA (PHDFNMA) and investigated the sorption-diffusion mechanism in pervaporation compared to the grafted PDMS membrane. The separation performance was

increased due to introduce hydrophobic porymer, PHDFNMA, compared to PMSP membrane. At low feed concentration, the diffusivity of ethyl butanoate (EBU) molecule was much lower than that of water due to the larger molecular size of EBU. As EBU was sorbed enough into the membrane, the diffusion of water was prevented by the EBU molecules, in turn, the permselectivity of EBU was increased significntly. At high feed EBU concentration, the diffusion of water increased and the diffusion of EBU decreased to be constant as the PHDFNMA-filled PMSP membrane was plasticized. In case of the HDFNMA grafted PDMS membrane by simultaneous irradiation, the membrane was not plasticized because the PDMS membrane is rubbery polymer but crosslinked. Because the PMSP membrane is glassy polymer but has high solubility for organics, the PHDFNMA-filled PMSP membrane was plasticized and the permeation behavior was differ from the grafted PDMS membrane.

BIOGRAPHY

The author, Satoko Mishima, was born in Tokyo, Japan, on December 7, 1966. She graduated from Shonan High School, Kanagawa, Japan, in March of 1985.

She matriculated at Meiji University, Kawasaki, Japan, in April of 1986 and graduated from Meiji University in March of 1990, receiving a Bachelor of Science degree in Industrial Chemistry.

She joined the Ministry of Trade and Industry, Tokyo, Japan, as a government official.

Since April of 1992, she worked at Kanagawa Environmental research center, Hiratsuka, Japan as a research worker. She investigate environmental pollution and treatment. From April of 1995, she was given the direction for the treatment of organic compounds by pervaporation from Professor Tsutomu Nakagawa.

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Chapter 1. Introduction

1.1 Background

Pervaporation is known as the process which separate the objective liquid from liquid mixture by permeation into membrane and vaporation from it. The pervaporation was used as the method that concentrate the protein solution in membrane bag by vaporizing water in the old days. From 1950s, pervaporation has been studied seriously[1~3]. The separation of close boiling components using pervaporation was reported by Kammermeyer et al.[3], Binning[2] was investigated for the pervaporation through dense organic membrane. Up to now, pervaporation has used as practical process in the separation of water/ethanol mixture[4]. The pervaporation membrane separation technique is a fractionation process which uses a dense polymeric membrane as a separation barrier between the liquid feed and permeate vapor. The pervaporation separation process is potentially useful when distillation is difficult to use, such as the fractionation of azeotropic mixtures, close boiling components, thermal decomposition and isomeric mixtures. Therefore, pervaporation with organophilic membranes is an interesting alternative process to distillation or solvent extraction for the separation and the concentration of diluted organic compounds and is of growing interest for industrial applications. The litertures about pervaporation for volatile organic compounds (VOCs) mixture or using silicone polymer and fluorinated polymer are given in Table 1.1. An example of this kind of separation are the treatment of process water, which are a side stream in the technical production of a minor component[5] and temperature sensitive volatiles like aroma compounds[6~12]. Extraction of VOCs from water and various solution by pervaporation has been actively studied in view of treatment[13~38] , membrane structure and permeation behavior[4,6,7,9~12, 39~62] .

Volatile organic compounds (VOC) represented by trichloroethylene (TCE), tetrachloroethylene (PCE) and benzene have been widely used in detergents for metals and cleaning, etc.[13,14]. Recently, it has been a social problem that ground water and soil are contaminated with chlorinated hydrocarbons. Their toxicity has been clarified for

Table 1.1 Litertures about pervaporation for volatile organic compounds (VOCs) mixture or using silicone polymer and fluorinated polymer

Authors	Journal	Vol.	Page	Year	Membrane material	VOC	Contents	Reference number
T. Nakagawa, et. al	Sen'i Gakkaishi	51	123	1995	Poly[(trimethylsilyl)methyl methacrylate-co-n-butyl acrylate]	1,1,2-Trichloroethane, Trichloroethylene, Tetrachloroethylene	Synthesis, Permeability	4
K. Meckl, et. al	J. Membr. Sci.	113	81	1996	Polyether-block-polyamide, Polydimethylsiloxane, Polybutadiene	Aniline	Operating condition	5
A. Baudot, et. al	J. Membr. Sci.	158	167	1999	Polydimethylsiloxane filled with silicalite, Polyether-block-polyamide	Ethyl acetate, diacethyl, S-Methyl thiobutanoate, etc	Permeation behavior	6
M. K. Djebbar, et. al	J. Membr. Sci.	146	125	1998	Polyether-block-polyamide	Ethl acetate, Ethyl propionate, Ethyl butyrate	Permeation behavior	7
K. Riedl, et. al	J. Membr. Sci.	139	155	1998	Polyvinylidene fluoride, Nylon, Polysulfone, Polyethersulfone	Apple juice	Analysis and evaluation of permeation	8
A. Baudot, et. al	J. Membr. Sci.	120	207	1996	Polydimethylsiloxane filled with silicalite, Polyether-block-polyamide	Methylthiobutanoate, diacethyl	Permeability	9
J. Börjesson, et. al	J. Membr. Sci.	119	229	1996	Polydimethylsiloxane, Polyoethylmethylsiloxane, Polyether-block-polyamide	Ethyl ethanoate, Ethyl butanoate, Ethyl hexanoate, etc	Permeability	10
N. Rajagoplan, et. al	J. Membr. Sci.	104	243	1995	Polydimethylsiloxane-polycarbonate, Polyether-block-polyamide, Pervap-1070	Methyl anthranilate	Permeability	11

T. Lamer, et. al	J. Membr. Sci.	80	251	1994	Polydimethylsiloxane	Ethyl ethanoate, Ethyl butanoate, Ethyl hexanoate, etc	Permeation behavior	12
S. Yamahara, et. al	Maku (Membrane)	18	69	1993	Various	VOC	Application	13
T. Yamaguti, et. al	Kagaku-kougyo (Chemical Industry)	47	51	1996	Various	VOC	Application	14
J. Jou, et. al	J. Membr. Sci.	162	269	1999	Polyvinyl acetate Hollow fiber	Trichloroethylene, Chlorofolm	Analysis and evaluation of permeation	15
I. Abou-Nemeh, et. al	J. Membr. Sci.	158	187	1999	Polydimethylsiloxane, Hollow fiber	Trichloroethylene	Analysis and evaluation of permeation	16
A. M. Urtiaga, et. al	J. Membr. Sci.	156	275	1999	Polydimethylsiloxane, Hollow fiber	Chloroform	Analysis and evaluation of permeation	17
L. M. Vane, et. al	J. Membr. Sci.	153	233	1999	Silicone polymer	1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene	Operating condition	18
U. Hömmerich, et. al	J. Membr. Sci.	146	53	1998	PERVAP1137	Methl t-butyl ether	Operating condition	19
R. O. Crowder, et. al	J. Membr. Sci.	145	173	1998	Polydimethylsiloxane, Hollow fiber	Chloroform	Analysis and evaluation of permeation	20

S. Schnabel, et. al	J. Membr. Sci.	142	129	1998	Polydimethylsiloxane, Hollow fiber	Chloroform, n-Butanol	Operating condition	21
R.W. Baker, et. al	J. Membr. Sci.	137	159	1997	Polydimethylsiloxane	Trichloroethylene, Toluene, Ethyl acetate etc.	Analysis and evaluation of permeation	22
M. Rodríguez, et. al	J. Membr. Sci.	137	45	1997	VitonR, Hollow fiber	Valeric acid	Analysis and evaluation of permeation	23
T. K. Poddar, et. al	J. Membr. Sci.	132	229	1997	Silicone polymer, Hollow fiber	Dichloromethane	Operating condition	24
M.G.Liu, et. al	J. Membr. Sci.	111	227	1996	Silicone polymer, Hollow fiber	Trichloroethylene	Modeling of permeation	25
J.G.Wijmans, et. al	J. Membr. Sci.	109	135	1996	Polydimethylsiloxane, Plyolefin	Trichloroethylene, Benzene, Toluene, etc.	Analysis and evaluation of permeation	26
S. B. McCray, et. al	Proc. 7th Int. Conf. Pervaporation Process Chem. Ind.		422	1995	Polyimides, Poly(arylene ether) benzimidazols	Trichloroethylene	Operating condition	27
D. Yang, et. al	J. Membr. Sci.	103	195	1995	Silicone polymer, Hollow fiber	Trichloroethylene, Tluene	Analysis and evaluation of permeation	28
K. Ogasawara, et. al	Ground warter	37	47	1995	Silicone polymer, Hollow fiber	Chlorinated hydrocarbon	Simulation of Operating condition	29

C. Visvanathan, et. al	Ind. Eng. Chem. Res.	34	3956	1995	Silicone polymer, Hollow fiber	1,1,1-Trichloroethane, Trichloroethylene	Operating condition	30
C. Dotremont, et. al	Desalination	95	99	1994	Polydimethylsiloxane filled with silicalite	Trichloroethylene, Chloropropane, Chlorofolm etc.	Analysis and evaluation of permeation	31
P. J. Hickey, et. al	J. Membr. Sci.	97	53	1994	Silicone polymer, Spiral wound	Dichloromethane	Operating condition, Cost	32
P. J. Hickey, et. al	J. Membr. Sci.	88	47	1994	Spiral wound	VOC	Modeling of permeation	33
B. K. Srinivas, et. al	Comput. Chem. Eng.	17	957	1993	Silicone polymer, Polyvinyl alchol, etc. Hollow fiber	Trichloroethylene, Chloroform	Operating condition	34
A. R. J. Andrews, et. al	Environ. Sci. Technol.	27	1139	1993	Silicone polymer, Hollow fiber	Trichloroethane, Trichloroethylene, Tetrachloroethylene etc.	Operating condition	35
M. L. Jacobs, et. al	Proc. A WMA Annu. Meet.	86	1	1993	VaporSepTM	Tetrachloroethylene, Benzene, Methylene chloride etc.	Operating condition	36
A. Shimazu, et. al	KankyokagakuKaishi	6	1	1993	Silicone polymer, Spiral wound	Chloroform, Bromodichloromethane,	Operating condition	37
J. G. Wijmans, et. al	Environmental Progress	9	262	1990	Spiral wound	1,1,2-Trichloroethane, Chloroform, Ethyl acetate, etc.	Operating condition, Cost	38

J. Kim, et. al	J. Membr. Sci.	169	185	2000	Polyimide with fluorinated alkyl side groups	Chloroform, Dichloromethane, Toluene, etc.	Synthesis, Permeability	39
M. Hoshi, et. al	J. Appl. Polym. Sci.	74	983	1999	Crossliked poly[acrylate-co-acrylic acid]	1,1,2-Trichloroethane, Trichloroethylene, Tetrachloroethylene	Synthesis, Permeability	40
C. H. Park, et. al	J. Appl. Polym. Sci.	74	83	1999	Poly[acrylonitrile-co-vinylphosphonic acid]	Pyridine	Synthesis, Permeability	41
C. K. Yeom, et. al	J. Appl. Polym. Sci.	73	601	1999	Polydimethylsiloxane additional crosslinked	Chloroform, Dichloromethane, Tetrachloromethane etc.	Permeation behavior	42
T. Johnson, et. al	J. Membr. Sci.	155	133	1999	Natural rubber	Chloroform, Dichloromethane, Tetrachloromethane	Permeation behavior	43
S. D. Doig, et. al	J. Membr. Sci.	154	127	1999	Polydimethylsiloxane filled with silicalite	Toluene, Hexadecane, Ethyl decanoate, etc.	Permeation behavior	44
M. Hoshi, et. al	J. Appl. Polym. Sci.	71	439	1999	Crossliked polyurethane	Phenol	Synthesis, Permeability	45
M. Hoshi, et. al	J. Appl. Polym. Sci.	69	1483	1998	Crossliked poly[acrylate-co-acrylic acid]	1,1,2-Trichloroethane, Trichloroethylene, Tetrachloroethylene etc.	Synthesis, Permeability	46
A. Jonquiémres, et. al	J. Membr. Sci.	147	59	1998	Polyurethaneimide-block-copolymers	Methl t-butyl ether, Ethyl acetate, Ethanol	Permeation behavior	47

D. Hofmann, et. al	J. Membr. Sci.	144	145	1998	Polydimethylsiloxane, Polyether-block-polyamide	Heptane, Benzene	Permeation behavior	48
T. Nakagawa, et. al	Sen'i Gakkaishi	53	427	1997	Modiificated poly[1-trimethylsilyl-1-propyne] by fluoroalkyl methacrylate	Chloroform	Synthesis, Permeability	49
M. Bennett, et. al	J. Membr. Sci.	137	63	1997	Polydimethylsiloxane organofunctionalised	Chloroform, Pyridine, Phenol, etc	Synthesis, Permeability	50
W. W. Y. Lau, et. al	J. Membr. Sci.	134	209	1997	Oligosilylstyrene-co-polydimethylsiloxane	Chloroform, Dichloromethane, 1,2-dichloroethane	Synthesis, Permeability	51
Y. Sun, et. al	J. Membr. Sci.	134	117	1997	Poly[bis(trifluoroethoxy)phosphazene], Poly[bis(phenoxy)phosphazene]	Benzene, Tluene, Xylene, etc.	Permeation behavior	52
M. V. Chandak, et. al	J. Membr. Sci.	133	231	1997	Polydimethylsiloxane filled with silicalite or hydrophobic zeolite	1,1,1-Trichloroethane, Trichloroethylene	Permeation behavior	53
M. Hoshi, et. al	J. Appl. Polym. Sci.	65	469	1997	Polyurethane	Phenol	Synthesis, Permeability	54
C. Leger, et. al	J. Membr. Sci.	120	135	1996	Polydimethylsiloxane composited ceramic	Chloroform, Toluene, Acetone, etc.	Synthesis, Permeability	55
K. Jian et. al	J. Membr. Sci.	117	117	1996	Poly(vinylidene fluoride)	Benzene, Tluene, Xylene	Synthesis, Permeability	56

C. Dotremont, et. al	J. Membr. Sci.	104	109	1995	Polydimethylsiloxane filled with hydrophobic zeolite	Chloroform, acetone, 2-propanol	Permeation behavior	57
S.Goethaert, et. al	J. Membr. Sci.	78	135	1993	Polydimethylsiloxane filled with silicalite or hydrophobic zeolite	Chloroform, Dichloromethane, Tetrachloromethane	Permeation behavior	58
Y. Fang, et. al	J. Appl. Polym. Sci.	54	1937	1994	Polyethersulfone modified with fluoroteromer	Chloroform	Synthesis, Permeability	59
J. Schauer	J. Appl. Polym. Sci.	53	425	1994	Poly(2,6-dimethyl-1,4-phenylene oxide)	Trichloroethylene, 1,4-dioxane, Cyclohexane, etc.	Synthesis, Permeability	60
T. Yamaguchi, et. al	J. Membr. Sci.	95	39	1994	Alkyl acrylate plasma-grafted porous polyethylene	1,1,2-Trichloroethane, Chloroform	Synthesis, Permeability	61
M. Hoshi, et. al	Sen'i Gakkaishi	47	644	1991	Crossliked poly[acrylate-co-acrylic acid]	1,1,2-Trichloroethane, Trichloroethylene, Tetrachloroethylene	Synthesis, Permeability	62
S. Kimura, et. al	Maku (Membrane)	8	177	1983	Polydimethylsiloxane	Dioxane, 2-propanol, acetone, etc.	Permeability	64
L. Bueso, et. al	J. Appl. Polym. Sci.	75	1424	2000	Polydimethylsiloxane with Polymethylhydrogensiloxane	Ethanol	Swelling behavior	65
Y. K. Hong, et. al	J. Membr. Sci.	159	29	1999	Polydimethylsiloxane composited ceramic	2-propanol	Synthesis, Permeability	66

I. F. J. Vankelecom, et. al	J. Membr. Sci.	158	289	1999	Polydimethylsiloxane composited porous polyvinylidenfluoride	Ethanol, t-Butanol	Synthesis, Permeability	67
C. B. Almquist, et. al	J. Membr. Sci.	153	57	1999	Polydimethylsiloxane	Dimethy methylphosphonate, Diethy methylphosphonate,	Permeation behavior	68
L. Liang, et. al	J. Membr. Sci.	114	227	1996	Polydimethylsiloxane-polystylene interpenetrating polymer	Ethabol	Synthesis, Permeability	69
D. Roizard, et. al	J. Membr. Sci.	113	151	1996	Oligohydrogenopolysiloxane-co-polyorgano phosphazene	n-Butanol	Synthesis, Permeability	70
T. Miyata, et. al	J. Appl. Polym. Sci.	61	1315	1996	Polydimethylsiloxane Polystylene interpenetrating polymer	Ethanol	Permeation behavior	71
T. Miyata, et. al	Macromol.	196	1211	1995	Methyl methacrylate-co-Polydimethylsiloxane	Ethanol	Permeation behavior	72
T. Miyata, et. al	Polymer Preprints, Japan	45	1970	1996	Fluoroalkyl methacrylate-co-Polydimethylsiloxane	Ethanol	Permeation behavior	73
M. Nakamura, et. al	J. Membr. Sci.	36	343	1988	Copolymers of tetorafluoroethylene with Alkylvinyl ethers	Ethanol	Synthesis, Permeability	74

several years[13,14]. Their discharge has been regulated and the use of substitutes has been considered[13,14]. The purification of water contaminated with VOCs is desired and has been studied[13,14]. Pervaporation is an attractive and potentially cost-competitive alternative to traditional methods (e.g., aeration, adsorption on activated carbon, photolysis and ozonization) for removing low concentrations of organic solvents from waste water and has been expected to remove a number of VOCs including trichloroethylene (TCE), tetrachloroethylene (PCE), chloroform, 1,1,2-trichloroethane, benzene and toluene from dilute aqueous feed solutions.

1.2 Membrane material

In the removal of very low concentrations of VOCs like chlorinated hydrocarbons from these contaminated water (<1000g/m3), the use of pervaporation applications with membranes that allow VOCs to permeate preferentially has been considered for several years[13~62]. The high selectivity of pervaporation makes it potentially very interesting for continuous recovery of VOCs under compatible conditions. The remove of VOCs using the various membranes with permselectivity for organic compounds, e.g., silicone rubber[5,6,9~12,16~18,20~22,24~26,28~32,34,35,37,42,44,48,50,51,53,55,57,58], polyethel-block-polyamide (PEBA)[5~7,9~11], crosslinked poly(acrylate-co-acrylic acid)[40,46,62] and poly[n-butyl acrylate-co-(trimethylsilyl)methyl methacrylate][4] were studied. Recently, various composite membrane have been developed[5,13,14,37,55,59,61,66,67]. T. Yaaguchi, et al.[61], reported the pervaporation for VOCs/water mixture using plasma-graft filling polymerized membrane.

Polydimethylsiloxane (PDMS) has been well-known as an excellent polymer membrane material for its high permeability to gases and liquids[63~68] and most widely used because of its ease of preparation into different shapes and relatively small thickness[5,16,20,24,28,37,50,51,55,63,70]. The pervaporation ability of PDMS membrane to remove VOCs from water with very high separation factors has been recognized as a result of several early studies[5,6,9~12,16~18,20~22,24~26,28~32,34,35,37,42,44,48,50,51,53,55,57,58].

Pervaporation performance of a membrane is determined by both the sorption and the diffusion characteristics of the permeating components in the membrane. The solubility and diffusivity are achieved by the difference in the membrane solubility and permeability of the feed solution components. The molecular size of VOCs is larger than that of water; hence, it is desirable to enhance the selectivity of PDMS for VOCs by solubility rather than diffusivity. Therefore, the study of the pervaporation of VOCs from water has focused on the use of organophilic and elastomeric (rubbery) polymers, including PDMS and its copolymers[42,50,51,65,69~73]. The synthesis of PDMS copolymers and its improvement by the incorporation of fillers such as silicates and zeolites[6,9,53,57,58] have been expected and studied. C. Dotremont et al.[31,57,58] improved the solubility of the PDMS membrane for chlorinated hydrocarbons by incorporation of a filler (silicate).

Fluorinated polymers have the hydrophobicity based on their low surface energy and the hydrophobic nature of fluorinated polymers was expected to promote the selective adsorption and transport of the organic component of an organic/water feed solution[8,39,49,52,56,59,67,73,74]. The fluorinated polymer membranes generally have low permeability and no placticality[8,39,49,52,56,59,67,73,74]. The various membranes were synthesized to enhance their permeability. Y. Fang et al.[59], modified the surface of polyethelsulfone with fluorinated polymer and applied to the separation of chloroform/water mixture by pervaporation. The pervaporation for VOCs/water mixtures with asymmetric poly(vinylidene fluoride) was reported by K. Jian et al.,[56]. The improvement of PDMS membrane by fluorinated compounds has been expected to enhance the permselectivity for VOCs.

1.3 Composition incompatible polymers

In this study, the PDMS membranes were improved using fluoroalkyl methacrylates (FALMA), which has vinyl functional group and easy radical formation, to enhance the affinity of PDMS for chlorinated hydrocarbons. For this improvement, blending of PDMS and poly(FALMA) is difficult due to the low affinity of PDMS for poly(FALMA). There is the possibility of preparing graft or block copolymers of them. Graft and block copolymers, compared to mixtures of the corresponding polymers, often make it possible to join incompatible polymers in that form[75].

Graft polymerization is a method of conducting the growth of the graft chain by polymerization starting with reactive radicals produced in the membrane[76,77]. Generally, a vinyl monomer has been used in graft polymerization. Irradiation by gamma rays, electron beams, ultraviolet light and plasma has been well-known as a means of radical formation [76,77]. In this study, the PDMS membrane was grafted with FALMA by gamma rays, electron beams, ultraviolet light (UV) and plasma. UV can be operated easily and not so affect the strength of membrane. In UV irradiation, the effects of the fluoroalkyl side chain on increasing of the chlorinated hydrocarbon partition coefficient into the membrane were determined with fluorinated n-alkylmethacrylate and non-fluorinated n-alkylmethacrylate. A radiation source has high energy and the possibility of industrial use[74]. Gamma ray radiation which has suitable energy and can control the degree of grafting in order to obtain compatible flux and selectivity has been studied[78~91]. Electron beam has high energy and is able to effectively graft-polymerize in quantity[92~103]. The plasma technique which does not require a high energy source and is easily performed, has been studied[61,104,105]. Preirradiation and simultaneous irradiation have been known as methods of radiation-induced graft polymerization[77]. The plasma technique does not require a high installation cost for the energy source. The radical formation is easily performed on the surface of the polymer. The treatment time is short, within a few minutes. Preirradiation is a method in which the monomer is reacted with the polymer which has been irradiated in advance[77]. The preservation of radicals is necessary for this method. Simultaneous irradiation is a method in which the monomer and polymer are irradiated simultaneously[77]. It is expected to synthesize a more useful membrane material by combining the PDMS and fluorinated polymer. Graft polymerization is a useful method to combine the polymeric materials with incompatible chemical and physical properties. In this study, simultaneous irradiation was studied by gamma irradiation and preirradiation was investigated by electron beam or plasma irradiation.

The difference of grafted polymer structure by preirradiation and simultaneous irradiation, and their permeation properties were investigated.

Membranes that have a phase-separated structure in a composite with PDMS and the incompatible polymers are interesting. Several papers reported on membranes which were prepared by casting of the block copolymer and graft copolymer solutions or crosslinking them. The membranes were more hydrophobic at the air-side surface than at the glass-side surface[72]. While the membranes in which the incompatible polymer domains are homogeneously dispersed are thought to be better for evaluation of the permeation of the membrane and application to a membrane process, the preparation of the membranes composed of a homogeneous mixture of incompatible polymer domains is difficult. Simultaneous irradiation was expected to make homogeneous mixture of incompatible polymer domains. In this study, the novel membranes which have phase-separated structure in composite with PDMS and the incompatible polymer were synthesized by gamma ray simultaneous irradiation and their permeation properties were investigated.

1.4 Goal and origination of this research

In this study, the PDMS membranes were improved by graft polymerization of FALMA, which had the effect of increasing the selectivity for VOCs, using various irradiation source. The grafted PDMS membrane had the difference of polymer structure by various methods was characterized and applied for pervaporation.

The basic permeation behavior for PDMS membrane was investigated. The permeation behavior , particularly for an aqueous solution with a hydrophilic solute, can be also affected by the hydration of water to the solute. The physical and chemical properties of an aqueous solution is interesting depending on its application and has been extensively studied [107~120]. Their properties are mainly due to a hydrophobic interaction. Water molecules are always moving. The motion of water molecules in an aqueous solution containing a solute is affected by the water and solute interaction, and differ from that in pure water. This interaction (the water hydration of a solute) is important for the kinetic properties of a solution. The transitional motion of water molecules in a diluted aqueous solution was considered in several reports [103,116]. For permeate transport, the sorption-diffusion mechanism is important. The hydration may effect the diffusivity of the solute molecules during permeation. The relationships between hydration and permeation of various organic compounds during pervaporation in a PDMS membrane can be interesting to consider. The pervaporation through a PDMS membrane and the hydration effect on the sorption-diffusion mechanism for various organic compounds were investigated.

The effect of monomer properties on the graft polymerization and the separation properties for chlorinated hydrocarbons was investigated. FALMA were used to modify a PDMS membrane by UV irradiation. The effect of fluoroalkyl chains on the separation of chlorinated hydrocarbons through the modified membranes was determined. Solubility and diffusivity of monomer for membrane are important for preirradiation method. Solubility is affected by the chemical affinity of monomer for membrane. Also, the molecular volume is closely concerned with difusibity of organic compounds. Hence, for preirradiation method, solubility parameter, Octanol- water partition coefficient (Pow) and molecular volume are important. The PDMS membranes was grafted with FALMA and Alkylmethacrylates (ALMA) by electron beam preirradiation method. Then, the effect of solubility and diffusibity of monomer on graft polymerization were investigated.

The prediction of permeation is important for the treatment, extraction and quantitative analysis. The linear relationship between the feed concentration and the permeate concentration could be used for easy quantitative analysis. To account for the permeation through the non-porous membrane, a solution-diffusion mechanism is important factor. For predicting permeation, a solution-diffusion mechanism is proposed and has been studied[12,52,53,57,58,65]. The need for hydrophobicity data in the studies of organic compounds can be traced back at least to the turn of the century. The hydrophobicity is used to indicate the physical property of the molecule which governs its partitioning into the non aqueous portion of an immiscible or partially immiscible solvent pair[106]. Pow has been generally used in expressing hydrophobicity. The hydrophobicity, Pow, is closely related to the solubility of organic compounds[12]. Also, the molecular volume is closely related to the diffusivity of organic compounds which permeate. The relationship between the feed concentration and the permeate concentration in pervaporation through the plasma-grafted PDMS membranes, and the solution-diffusion mechanism for various VOCs were investigated.

Next, the grafted membranes which have high grafted amount and phase-separated structure in composite with PDMS and the incompatible polymer, FALMA were synthesized. The grafted membranes were expected to have differ permeation properties from PDMS membrane due to their membrane structure. While the membranes in which the incompatible polymer domains are homogeneously dispersed are thought to be better for evaluation of the permeation behavior, the preparation of the membranes composed of a homogeneous mixture of incompatible polymer domains is difficult. Simultaneous irradiation was expected to make homogeneous mixture of incompatible polymer domains. In this study, the novel membranes which have phase-separated structure in composite with PDMS and FALMA were synthesized by gamma ray simultaneous irradiation and their permeation properties.

In this study, the pervaporation through the grafted membranes by gamma ray simultaneous irradiation was investigated and compared to the PDMS membrane and the grafted PDMS membranes by preirradiation method.

Further, Poly(1-Trimethylsilyl-1-Propyne) PMSP membrane was filled with PHDFNMA and investigated the sorption-diffusion mechanism in pervaporation compared to the grafted PDMS membrane.

1.5 References

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Chapter 2. Theoretical Background

2.1 Theory of permeation through the membranes[1,2]

2.2.1 Sorption-Diffusion theory

Graham[2] explained the permeation behavior of gas such as oxygen, hydrogen through the rubber film by the mechanism described below. The cell is divided into two parts with the homogeneous non-porous membrane which doesn't contain low molecule. The one part is introduces gas and the other is kept low pressure. Under this state, first, the adsorption and absorption of gas to the membrane surface of the upstream side are became. These two processes are gather together and called sorption or solution. After this sorption, gaseous molecule moves in the membrane and reach the membrane surface of the downstream side. This transport, diffusion is caused by the gradient of low molecule concentration among both the surfaces of the membrane, i.e., the gradient of chemical potential according to the expression by heat dynamics. The low molecule which reached on a membrane surface of the downstream side evaporates from the membrane surface to the vapor-phase. The process of the transport of such a low molecule is called permeation. According to Graham, the permeation is the complex process which contains sorption (solution) and diffusion. Such a mechanism which explains permeation is called a sorption-diffusion theory.

Langmuir[3] explained the relationship between the adsorption amount, C and equilibrium pressure, p at fixed temperature adsorption isotherm as follows.

$$C=C_{mon}bp/(1+bp) \qquad (2.1.1)$$

where C_{mon} and b denote the amount of gaseous one molecule layer on the surface of polymer and the absorption rate constant of gas to the adsorption rate constant ratio, respectively. The formula of this type often stands up when solute adsorption to solid in solution.

W. Henry (1774~1836) found following relation to the gas solution in liquid.

$$C=kP \qquad (2.1.2)$$

where, C and P denote the absorption amount of gas and equilibrium pressure, respectively. This formula is called Henry's low and proportional constant, k is called a Henry's law constant. In sorption of gas to the rubbery amolfus polymer, it is thought that the absorption is the predominant process and Henry's low stands up.

2.1.2 The basic formula of the permeation

When the diffusion is caused only in the perpendicular direction to the membrane, the permeation behavior through the non-porous homogeneous membrane is given by the following Fick's second low.

$$\partial C/\partial t=\partial/\partial x(D\partial C/\partial x) \qquad (2.1.3)$$

where C and D denote low molecular concentration and diffusion coefficient respectively.

$$C=C_0,\ 0<x<l,\ t=0 \qquad (2.1.4)$$

C_0 is the early stage concentration, l is membrane thickness and the starting point of the x axis is a surface of the membrane of the upstream side. At x=0, when the permeation starts, C is kept equilibrium concentration C_∞ which corresponds to the pressure p_∞ of the vapor-phase at once and this value continues for the measurement. For the measurement, the swelling of the membrane can be ignored and in the membrane surface on the downstream side, concentration is kept at C_0. That is, the boundary condition is as follows.

$$C=C_\infty,\ x=0,\ t>0 \qquad (2.1.5)$$

$$C=C_0,\ x=l,\ t>0 \qquad (2.1.6)$$

By the condition that D is constant, $D=D_0$, and $C_\infty >> C_0 \sim 0$

$$Q_t / (l C_\infty) = D_0 t / l^2 - 1/6 - 2/\pi^2 \sum (-1)^n / n^2 \exp(-D_0 n^2 \pi^2 t / l^2) \qquad (2.1.7)$$

Q_t is the permeation amount at the time t. When time t is long and the condition is close to steady state,

$$Q_t = D_0 C_\infty / l\, (t - l^2 / 6D_0) \qquad (2.1.8)$$

The permeation rate Js under the steady state is defined as follows.

$$Js \equiv \lim_{t \to \infty} dQ_t/dt \qquad (2.1.9)$$

By eq. (2.1.8).

$$Js = D_0 C_\infty / l \qquad (2.1.10)$$

When it is supposed that the solubility coefficient of gas to polymer is S, the relation between concentration C_∞ and P_∞ is given eq. (2.1.11)

$$C_\infty = Sp_\infty \qquad (2.1.11)$$

When S is constant, i.e. the sorption of gas to polymer is conducted by Henry' low of eq. (2.1.2), Js is shown by eq. (2.1.12).

$$Js = D_0 S_0 p_\infty / l \qquad (2.1.12)$$

When a product right side D_0 and S_0 is represented by P_0, P_0 is shown as follows from eq. (2.1.12).

$$P_0 \equiv D_0 S_0 = J_s l / p_\infty \qquad (2.1.13)$$

Because P_0 is constant, it is called a permeability constant and it is calculated from the gradient of the straight line part of the permeation curve. The relation stands up under the assumption of the constant diffusion coefficient D.

When D is a function only with concentration, i.e. the system is called Fick type, the relationships are introduced as follows[4,5]. Eq. (2.1.10) is shown as follows.

$$\overline{Js}\,(C_\infty) = D(C_\infty) C_\infty / l \qquad (2.1.14)$$

But, $D(\overline{C_\infty})$ is integral diffusion coefficient.

$$\overline{D}(C_\infty) \equiv 1 / C_\infty \int_0^{C_\infty} D(C)dC \qquad (2.1.15)$$

But, D(C) is the mutual diffusion coefficient which is a function with concentration. When D depends on the concentration, the sorption isotherm do not often become a straight line. At this time, solubility coefficient S is defined by eq. (2.1.11). But differ from the case following the law of the henry, S becomes a function with concentration (or pressure) and the following is introduced by eq. (2.1.14).

$$\overline{P}(C_\infty) \equiv \overline{D}(C_\infty) S(C_\infty) = Js(C_\infty) l / p_\infty \qquad (2.1.16)$$

$\overline{P}$ in this equation is a function with concentration, like $\overline{D}$, S. $\overline{P}(C_\infty)$ is called an mean permeability coefficient. $\overline{P}(C_\infty)$ is found from the permeation rate under the steady state, like P_0.

Permselectivity of a polymer for gas A to B is argued by the ideal separation coefficient α to define next. That is

$$\alpha_{A/B} \equiv (Y_A/Y_B) / (X_A/X_B) \qquad (2.1.17)$$

But, Xi and Yi denote the concentration of component i represented by the mole fraction of the upstream side and the downstream side, respectively. When the pressure on the downstream side is much lower compared with the pressure on the upstream side, the α is approximately shown as follows.

$$\alpha_{A/B} = \overline{P}_A / \overline{P}_B \qquad (2.1.18)$$

But, $\overline{P}i$ is the mean permeation coefficient of component i. Referring to eq. (2.17), it is possible to write α dividing into two parts as follows.

$$\alpha_{A/B} = (\overline{D}_A/\overline{D}_B)(S_A/S_B) \qquad (2.1.19)$$

The ratio of the diffusion coefficient and the solubility coefficient is called diffusion selectivity and solubility selectivity respectively. Diffusion selectivity is affected by the physical factor like the polymer chain movement and the stuff condition of polymer segment. On the other hand, solubility selectivity is affected by the chemical and physical interaction of gaseous molecule and the polymer segment. Permselectivity is often considered and argued dividing into two pieces of contribution as shown in eq. (2.1.19).

2.1.3 Sorption

The kinetic property of sorption is described as follows. The sorption quantity to the polymer membrane under the constant pressure increases in the time. Finally, it is saturated and reaches equilibrium sorption quantity. In case of the diffusion that is one dimensional diffusion with no volume change under an equilibrium temperature system, the diffusion of sorpted molecule is shown by the Fick's second law as follows.

$$\partial C/\partial t=\partial/\partial x(D\partial C/\partial x) \qquad (2.1.3)$$

where, C, t, x and D denote the amount of the sorpted molecules in the polymer represented by the weight concentration (g/cm^3), time, a distance to the direction of the diffusion and a diffusion coefficient, respectively. The diffusion is caused only in the perpendicular direction to the membrane in consideration of the very thin polymer membrane compared with the size. Because it is supposed that the concentration in the polymer membrane is homogeneously, the concentration of early stage Ci at time 0 is given eq. (2.1.20)

$$C=C_i \qquad (-l/2<x<l/2,\ t=0) \qquad (2.1.20)$$

where, l denote membrane thickness. When the polymer membrane is under the equilibrium liquid condition, the concentration of the membrane surface in the equivalent to the pressure p reaches the membrane surface concentration Cf, immediately. That is

$$C=C_f \qquad (x = \pm l/2,\ t>0) \qquad (2.1.21)$$

In case that diffusion coefficient is independent of the concentration, eq. (2.1.3) is solved under the boundary condition of eq.s (2.1.20) and (2.1.21).

$$C(t)/C(\infty)=1-\sum^{x} 8 / \{(2n+1)^2\pi^2\}\exp|-D(2n+1)^2\pi^2 t / l^2| \qquad (2.1.22)$$

where, C(t) and C(∞) denote sorption amount at the time t and ∞, respectively. Relationship between the amount of sorpted molecules C in the polymer membrane under the liquid condition over the glass transition point and pressure p is expressed by the Henry's low (eq.2.1.23) which is well applied to the absorption of gas to liquid.

$$C=k_D p \qquad (2.1.23)$$

where k_D denote a Henry's law solubility constant. In the polymer membrane which is doing lively segment exercise under equilibrium state, sorpted molecules are homogeneously dispersed in the system. The following is possible to confirm. By the fact that this membrane is under the liquid condition, the sorpted amount and the pressure show straight line relation and follow the Henry's low.

The sorption gas to the polymer membrane under the glass condition is shown by another sorption mechanism. When the polymer which has a lot of free volume and is doing lively segment exercise is cooled and under the glass condition, it has frozen free volume (micro void). The polymer membrane under the glass condition consists of the part where segment movement is frozen up and the part of above-mentioned micro void. The former is expressed by the Henry's sorption mechanism of eq. (2.1.23), the latter is expressed by the adsorption of molecule to micro void, i.e. Langmuir's adsorption mechanism. The sorption mechanism is called a dual-mode sorption mechanism, well-known as the sorption mechanism of the polymer membrane under the glass condition and confirmed to fit actually to the experiment[6~11].

$$C=k_D\, p + C_{H'}\, bp\, /\, (1+ bp) \qquad (2.1.24)$$

where $C_{H'}$ and b denote the hole saturation constant of Langmuir adsorption (related to the quantity of micro void) and the Langmuir affinity constant.

2.1.4 Diffusion

When the interaction of diffusion molecule and the polymer membrane is strong, the concentration dependence of the diffusion coefficient is well observed. When the concentration dependence is small, the average diffusion coefficient D is shown by the following equation approximately.

$$D=1\, /\, C_f \int_0^{C_t} D(C)dC \qquad (2.1.25)$$

When the concentration dependence of the diffusion coefficient is changing to hundreds or thousands times high, the approximate method of the Crank has high precision. The diffusion coefficient D_a in the early stages of sorption is given as follows.

$$D_a(C_f)=5/3\, C_f^{-3/5} \int_0^{C_f} C^{2/3}\, D(C)dC \qquad (2.1.26)$$

The diffusion coefficient D_d in the early stages of adsorption is given as follows.

$$D_d(C_i)=1.85C_i^{-1.85}\int_0^{C_f}(C_f-C)^{0.85}D(C)dC \qquad (2.1.27)$$

2.1.5 Pervaporation

The pervaporation is performed as follows. The feed solution is introduced one side of the membrane and the other side was kept under the vacuum or flushed the inactive gas, and then the components permeate into the membrane, is vaporized and extracted. The sorption to membrane, the diffusion in the membrane and volatility of the component affect the permselectivity.

That is, pervaporation is the method combined the membrane permeation and the discreet distillation. The characteristic of pervaporation is shown below.

(1)Because pervaporation does not need heating, it can be applied to the separation concentration of the thermal decomposition and thermal spoilage liquid.

(2)Because pervaporation is different from the reverse osmosis and the ultra filtration which is the same liquid separation method and needless to pressurize, the pressure densization of the membrane is not caused.

(3)The isolation isn't necessary because penetrated material is obtained as pure material ideally and is not diluted different from the dialysis method.

(4)The membrane in pervaporation has the two layer structure which consists of swollen layer and the dense separation activated layer, because the feed solution is introduced one side of the membrane and the other side is kept low pressure. This is one of the biggest characteristics of this method and along with the characteristic of (2) that the pressure densization is not caused, is thought to be the favorable point for the permeation rate and the membrane lifetime.

(5)There are two way of pouring carrier gas and making a vacuum in pervaporation. There is a limit in the flow rate as the mass even if the flow on the capacity is made high, because the pressure of the permeate side is low.

(6)There is not an influence of the several atm pressurization of feed solution but when making a degree of the decompression on the permeate side higher, in appropriate pressure range, the permeate rate is increased by the decompression.

(7)The permeate rate is in reverse proportion to the membrane thickness. On the other hand, the separation efficiency is relationless in membrane thickness. The thickness of separation activation layer is relationless in membrane thickness.

(8)Pervaporation is useful separation process for azeotropic mixtures and close boiling components which have different properties, for example, polarities.

(9)It is mentioned that the pervaporation is an effective separation method in view of energy balance when the feed concentration of objective component is below 30wt%.

Binning[12] defined that the one part of membrane close to the feed solution is a solution phase and the other part of membrane close to the vapor side is vapor phase. When considering a membrane from the crossing direction, the most of the membrane is solution layers and is swollen by feed solution. That is, in the solution phase the permeation liquid dissolves under the condition of solution. On the other hand, in the vapor phase the permeation liquid is dispersed under the condition of steam. Up to now, generally, solution phase is called swollen layer and vapor phase is called separation activated layer. All the processes of the separation by pervaporation are composed of the following five processes.

(1)The solution molecules selectively dissolves to the membrane surface of the upstream side.

(2)After this dissolution, the molecule penetrates into the membrane.

(3)The penetrate molecules selectively dissolves on the boundary surface of the swollen layer and the separation activated layer.

(4)The molecules actively diffuse in the separation activated layer.

(5)The molecules which reached on the membrane surface of the downstream side, adsorpt and evaporate. The analysis of above mentioned process of the membrane separation is extremely important to consideration of the characteristic, the use of pervaporation and the more required membrane efficiency.

In view of the structure of the membrane, the physic and chemical properties (the degree of the crystallization, polarity and so on) of the membrane are extremely important to consider the permeation. The chemical properties of the membrane affect the hydrophilicity and hydrophobicity balance of the membrane and influence on the permselectivity. The hydrophilicity and hydrophobicity balance of the membrane can be adjusted by the chemical modification, cross-linking, co-polymerization, grafting, hydrogen bonding and so on. The permeability is enhanced by the function groups in the polymer membrane which breaks the combination of penetrates. On the other hand, the permeability is low in the membrane which enhances the combination of penetrates. For example, the permeability of water is high in the membrane with hydrophilic groups (-OH, -NH2, -COOH and so on) which brakes the cluster of waters. However, the hydrophobic groups in the membrane increase the cluster of waters and decrease the water permeability[13~15]. Also, the combination of the penetrates depends on the properties of coexistent solvent and the temperature of solution[16,17]. The control of the combination of the penetrates can enhance the permselectivity. If it is supposed that the components permeate through the polymer membrane following to the sorption - diffusion model, the process of the permeation is approximately divided to the three parts (1) the dissolving into the membrane of the components, (2) the diffusion in the membrane, (3) the adsorption outside the membrane. (1) and (3) depends on the solubility of the components. (2) is affected by the diffusivility of the components. It is important for separation to utilize the difference of the solubility or the diffusivility of the components. Also, when the difference of both can be used ideally, the permselectivity can be more enhanced.

2.1.6 The basic formula of the permeation in pervaporaion[1,2,18]

The permeation rate of component i Q_i is proportional to the concentration gradient of the component i and shown by the following Fick's first low.

$$Q_i=-D(C_i)dC_i/dx \qquad (2.1.28)$$

where $D(C_i)$, Q_i and C_i denote the diffusion coefficient, the permeation rate and the liquid concentration of the component i in the membrane at distance x from the membrane surface of the upstream side, respectively.

The fick's second low is given as follows.

$$dC_i/dt=D(C_i)d/dx(dC_i/dx)=D(C_i)d^2C_i/dx^2 \qquad (2.1.29)$$

Here, diffusion coefficient $D(C_i)$ is shown as follows.

$$D(C_i)=D_0\exp(\tau C_i) \qquad (2.1.30)$$

where D_0, τ denote the diffusion coefficient at concentration 0 and a constant which is the standard of the plasticization of the membrane by the penetration components, depended on temperature, respectively.

When the boundary condition of $dCi/dt=0$ in the permeation under the steady state, $C_i=C_1$ in $x=0$ and $C_i=C_2$ in $X=l$, the permeation rate J_i under the steady state is given as follows by substituting eq. (2.1.30) for eq. (2.1.30) and integrating it.

$$J_i=Q_i=D_0/\tau l\,(\exp\tau C_1-\exp\tau C_2) \qquad (2.1.31)$$

Also, the concentration distribution in the film is shown as follows.

$$C_i=1/\tau\ \ln\{\exp\tau C_1-x/l(\exp\tau C_1-\exp\tau C_2) \qquad (2.1.32)$$

If it is supposed that the concentration on the surface of the liquid and the membrane is under the equilibrium in view of heat dynamics, the following equation stands up.

$$C_1=C^*(p^0) \qquad (2.1.33)$$

$$C_2=C^*(p_2) \qquad (2.1.34)$$

where C^* shows a function. p^0 and p_2 denote the saturated steam pressure of solution and the steam pressure on the downstream side, respectively. Using these equations, eq.s (2.1.31), (2.1.32) are shown by p^0, p_2.

On the other hand, permeation coefficient Pi is shown as follows.

$$P_i=J_il/\Delta p=D_0/\tau\Delta p\,(\exp\tau C_1-\exp\tau C_2),\qquad \Delta p=p^0-p_2. \qquad (2.1.35)$$

When eq.s (2.1.33), (2.1.34) are following the Henry's law that are $C^*(p)=SP$, eq.s (2.1.31), (2.1.32), (2.1.35) become the function of p^0 and p_2.

$$J_i=D_0/\tau l\,(\exp\tau Sp^0-\exp\tau Sp_2) \qquad (2.1.36)$$

$$C_i=1/\tau\ \ln\{\exp\tau Sp^0-x/l(\exp\tau Sp^0-\exp\tau Sp_2) \qquad (2.1.37)$$

$$P_i=D_0/\tau\Delta p\,(\exp\tau Sp^0-\exp\tau Sp_2) \qquad (2.1.38)$$

eq. (2.1.39) suggests that it is not possible to consider with dividing a permeability coefficient into the solubility coefficient and the diffusion coefficient in pervaporation

Considered to be the same as gas permeation, it becomes as follows.

$$Q_i l = -\int_{C_1}^{C_2} D(C_i)dC_i \qquad (2.1.39)$$

$$Q_i = P_i(p_1 - p_2) / l \qquad (2.1.40)$$

where p_1 and p_2 denote the steam pressure on the side of the high concentration and the side of the low concentration, respectively.

eq. (2.1.41) given by eq.s (2.1.39) and (2.1.40).

$$P_i = \{ \int_{C_1}^{C_2} D(C_i)dC_i \}(p_1 - p_2) \qquad (2.1.41)$$

By substituting this equation for eq. (2.1.42), the following equation is given.

$$Q_i l = R = P_i(p_1 - p_2) = \int_{C_1}^{C_2} D(C_i)dC_i \qquad (2.1.42)$$

where R denote the ratio of permeation rate.

When the concentration average diffusion coefficient $\overline{D_i}$ is defined by the following equation, permeability coefficient Pi and the ratio of permeation rate R are shown by eq.s (2.1.44) and formula (2.1.45), respectively.

$$\overline{D_i} = \int_{C_1}^{C_2} D(C_i)dC_i / (C_1 - C_2) \qquad (2.1.43)$$

$$\overline{P_i} = D_i \{(C_1 - C_2) / (p_1 - p_2)\} \qquad (2.1.44)$$

$$\overline{R_i} = D_i (C_1 - C_2) \qquad (2.1.45)$$

If the diffusion does not depend on the concentration of the permeation component, $\overline{Di}$ may be the diffusion coefficient D.

For the permeation in pervaporation, by $p1 \gg p2$, eq.s (2.1.43), (2.1.44) and (2.1.45) are shown as follows.

$$\overline{D_i} = \int_{C1}^{C2} D(C_i)dC_i / C_i \qquad (2.1.46)$$

$$P_i=\overline{D_i}(C_1 / p_1) \qquad (2.1.47)$$

$$R=\overline{D_i}\,C_1 \qquad (2.1.48)$$

When C_1/p_1 is assumed S_1(apparent solubility coefficient), the following equation is given.

$$P_i=\overline{D_i}\,S_1 \qquad (2.1.49)$$

It is possible to show permeation coefficient P_i as the product the concentration

average diffusion coefficient $\overline{Di}$ and the apparent solubility coefficient S_1.

In pervaporation, also, the permeation rate can be described by considering the gradient of chemical potential (μ) to be the driving force. Tentative illustration for the permeation of pervaporation is given in Fig. 2.1. It is possible to show the permeation rate of component i as the product the concentration, the degree of the movement m_i and the driving force as shown in eq. (2.1.50) following to the sorption -diffusion theory.

$$Q_i=-C_i m_i(d\mu/dx) \qquad (2.1.50)$$

$$m_i=D_{i,T} / RT \qquad (2.1.51)$$

Where $D_{i,T}$ denote the heat dynamic diffusion coefficient.

The concentration in the membrane is not being constant to the direction of the membrane thickness, and it pictures a gentle curve and decreases in the direction of the permeation flow. The heat dynamic equilibrium is formed on the surface of the membrane and feed solution, that is, it supposes that the chemical potential of the component i on the surface of membrane in feed side is equal to the chemical potential of the component i in the feed solution ($\mu_{i,1}=\mu_{i,0}$). In the case, it is considered that the concentration of the component i in the membrane in the upstream side can be detected by the sorption equilibrium measurement. When the dissolving becomes later than diffusing because of the resistance, i.e. the concentration polarization in the liquid boundary phase, the concentration in upstream side of membrane is often lower than the equilibrium sorption concentration in membrane. When membrane thickness is thin, this resistance increase. As the concentration of one component in feed solution is very low and the permselectivity for the component is high, the concentration polarization is easily caused.

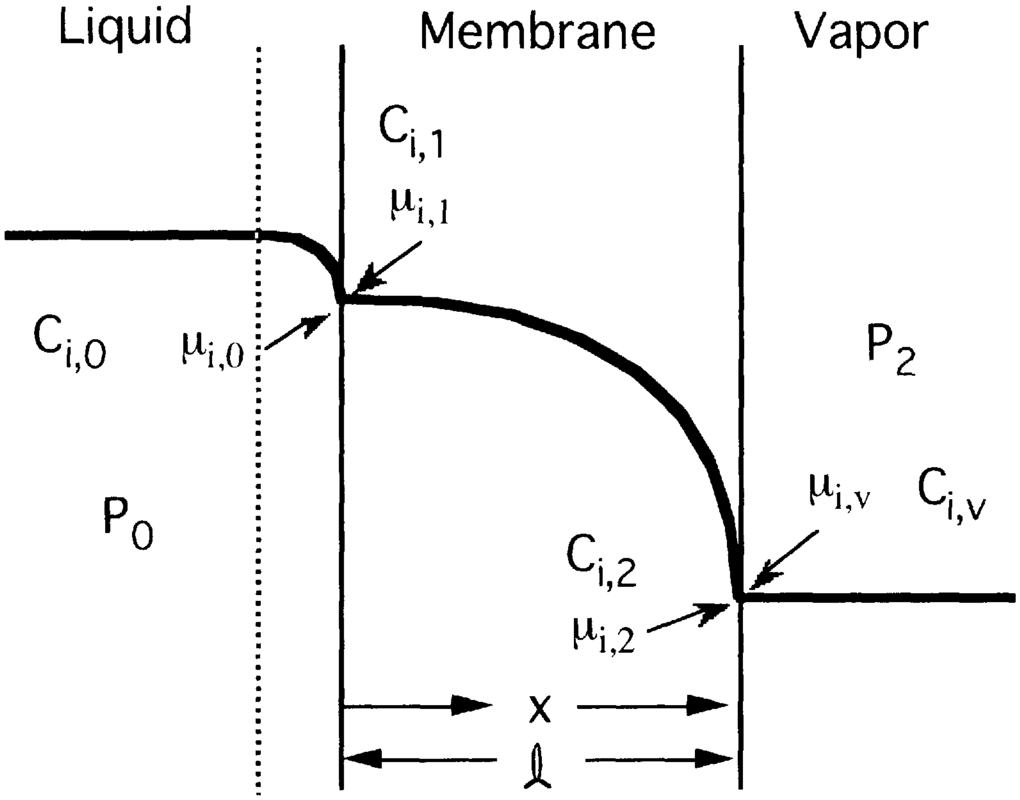

Fig.2.1 Chemical potential gradient for preferentially permeating component across the membrane.

The degree of the (mole) movement of low molecule m_i shown by the eq. (2.1.51) contained $D_{i,T}$. $D_{i,T}$ is related to the Fick diffusion coefficient by the following eq. (2.1.52).

$$D_i = D_{i,T} (\ln a_i / \ln C_i) \qquad (2.1.52)$$

In isotherm, chemical potential is given by a function with activity and pressure. Chemical potential for component i is given by eq. (2.1.53). Incidentally, a_i is activity of the component i.

$\mu_i = \mu_{i,0} + RT \ln a_i + V_i(p_i - p_{ref})$ (2.1.53)

Where V_i is a partial molar volume of component i. p_i are the pressure of the component i. Therefore, the driving force in the direction of the membrane thickness, i.e. in the direction of the x axis becomes as follows.

$d\mu_i/dx = RT\,(d\ln a_i/dx) + V_i(dp_i/dx)$ (2.1.54)

The pressure term of eq. (2.1.54) can be omitted because the pressure difference between the upstream side and the down stream side is about 1 atm and it is $RT\Delta\ln a_i >> V_i\Delta p_i$ in usual pervaporation.

Therefore, it is possible to show driving force as follows.

$d\mu_i/dx = RT\,(d\ln a_i/dx)$ (2.1.55)

Consequently, the permeation rate of the component i is shown by the following eq. (2.1.56).

$Q_i = -C_i D_{i,T}\,(d\ln a_i/dx)$ (2.1.56)

This relationship is the equation which is often used to consider the permeation model through the homogeneous membrane.

The permeation rate J_i under the steady state can be expressed as follows by Fick's first law (2.1.28).

$J_i = D_i(C_{i,1} - C_{i,2})/l$ (2.1.57)

$C_{i,1} = K_{i,1}\,C_{i,0}$ (2.1.58)

$C_{i,2} = K_{i,2}\,C_{i,v}\exp[-V_i(P_0 - P_2)/RT]$ (2.1.59)

Where $C_{i,1}$ and $C_{i,2}$ denote the concentration of component i on the membrane surface of the upstream side and the downstream side. $C_{i,0}$ and $C_{i,v}$ denote the concentration of component i in the feed solution and the vapor side. K_i is the partition coefficient. V_i is a partial molar volume of component i. P_0 and P_2 are the total pressure of the upstream side and downstream side.

Then, $[-V_i(P_0 - P_2)/RT]$ becomes very small, and the exponential term becomes nearly equal to 1.

$C_{i,2} = K_{i,2}\,C_{i,v}$ (2.1.60)

The activity of downstream side of the component i, $a_{i,v}$, is given as follows.

$$a_{i,v}=\gamma_{i,v} C_{i,v}= p_{i,2} / p^{\bullet}_{i} \qquad (2.1.61)$$

Where $p_{i,2}$ and $p^{\bullet}_{i}$ denote vapor pressure of the component i in the downstream side and the saturated vapor pressure of component i. $\gamma_{i,v}$ is activity coefficient of downstream side of the component i.

$p_{i,2}$ becomes nearly equal to 0 when the pressure of downstream side is close to 0. Then, the concentration on the downstream side ($C_{i,v}$) is almost 0. In case of pervaporation, adsorption is comparatively fast caused and the concentration in membrane on the downstream side ($C_{i,2}$) is almost 0. eq. 2.1.57 becomes

$$J_i=D_i K_{i,l} C_{i,0}/l \qquad (2.1.62)$$

Where

$$P_i=D_i K_{i,l} \qquad (2.1.63)$$

$$J_i=P_i C_{i,0}/l \qquad (2.1.64)$$

This relationship is the equation which is often used to consider the permeation of pervaporation through the homogeneous membrane. In this study, this equation is used as basic equation.

2.2 Graft polymerization[19,20]

2.2.1 Simultaneous irradiation

A. Rabee, G. Odian et. al.[20], offered several possible grafting mechanisms in simultaneous irradiation. The dependence on monomer changes with increasing does rate as does the dependence of grafting rate on does rate. The initiation of graft polymerization involves the involves the formation of primary polymeric alkyl radicals (P·) by radiolysis of the polymer (P):

$$P \xrightarrow{\text{radiation}} P\cdot \qquad (2.2.1)$$

followed by addition to monomer to form the propagating radical:

$$P\cdot + M \xrightarrow{k_i} M\cdot \qquad (2.2.2)$$

Propagation can be depicted in general terms as

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot \qquad (2.2.3)$$

Assuming that terminating occur by bimolecular coupling and/or disportionation of propagating radiation as follows:

$$M_n\cdot + M_m\cdot \xrightarrow{k_t} \text{dead polymer} \qquad (2.2.4)$$

This will occur, however, only if the primary radicals undergo a destructive side reaction with some species Z:

$$P\cdot + Z \xrightarrow{k_2} \text{destruction of primary radicals} \qquad (2.2.5)$$

Reaction (2.2.4) may involve reaction with other radicals or with some inhibitor present in the system or the conversion of the primary alkyl radicals into unreactive alkyl radicals (via successive hydrogen abstractions toward unsaturated groups present initially in the polymer or formed during irradiation)\ or some other reaction.

Under these conditions, the initiation rate is the rate of eq.(2.2.2):

$$R_i = k_i [P\cdot][M] \qquad (2.2.6)$$

On assuming a steady state in the concentration of primary radical $[P\cdot]$, i.e., that the rate of formation of primary radicals eq.(2.2.1) equals their rates of destruction eqs. (2.2.2) and (2.2.6), yields

$$k_1[P]GI = k_2[P\cdot][Z] + k_i[P\cdot][M] \qquad (2.2.7)$$

The left-hand side of eq.(2.2.7) is the rate of eq.(2.2.1) where G is the G valve for primary radical formation (number of radicals formed per 100eV), I is the radiation dose rate, and k_1 is a constant which includes various conversion factors such that $k_1[P]GI$ will have units of moles per liter-second as do the other rates.

solving eq.(2.2.7) for $[P\cdot]$ and substituting into eq.(2.2.6) yields R_i as

$$R_i=\{k_1k_i[M][P]GI\}/\{k_2[Z] + k_i[M]\} \qquad (2.2.8)$$

In the usual case $k_i[M]>>k_2[Z]$, the initiation rate R_i is independent of monomer and the grafting rate R_p is given as follows

$$R_p=k_p[M](R_i/2k_t)^{1/2} \qquad (2.2.9)$$

The concentration of primary polymer radicals is given by $[P\cdot]=K[P]$ which, when combined with eqs.(2.1.63) and (2.1.65), yields

$$R_p=k_p|M|(Kk_i|P||M|/2k_t)^{1/2} \qquad (2.2.10)$$

for the rate of graft polymerization.

The actual mechanism for the lowered rate of monomer addition to primary radicals relative to recombination of primary radicals may be due to the monomer concentration not being sufficiently high. In the systems, the polymerization rates decreased in proportion to the decrease in monomer concentration as monomer was diluted with solvent until a critical low monomer concentration was reached. After that critical monomer concentration, the polymerization rates decreased much more rapidly than expected based on a simple dilution effect. The situation involves the competition between reactions (2.2.11) and (2.2.12):

$$P\cdot + P\cdot \text{ or } P\cdot + H\cdot \rightarrow \text{primary radical recombination} \qquad (2.2.11)$$

$$P\cdot + M \text{ or } H\cdot + M \rightarrow \text{initiation} \qquad (2.2.12)$$

Since inhibition is monomer-dependent while primary radical recombination is monomer-independent, the later becomes increasingly more competitive as the monomer concentration decreases. Interestingly, this critical monomer concentration was reached earlier (i.e., at a higher concentration) as the radiation dose rate increased. (Is it a coincidence that the order of dependence of rate on monomer in the system increases with increasing dose rate.) The competition between reactions (2.2.11) and (2.2.12) favors primary radical recombination as the dose rate increases, since that process is second-order in the radical concentration while initiation is only first-order. Above the critical monomer molecules to scavenge all primary radicals which begin to difference from their cages. But below the critical monomer concentration, this is no longer the case and primary radical recombination becomes important.

An energy transfer mechanism involving energy transfer may be responsible for the increased orders of dependence of rate on monomer. Such energy transfer eq. (2.2.13) completes with the formation of primary radicals eq.(2.2.14).

$P - \text{radiation} \rightarrow P^* - B \rightarrow P + B^* \rightarrow$ energy dissipation by B^* (2.2.13)

$P\cdot - M \rightarrow$ initiation (2.2.14)

Here P and S are polymer and solvent, respectively, P* and S* are the corresponding excited species, and M is monomer. Energy transfer results in a decrease in the rate of initiation. The extent of energy transfer increases with the concentration of benzene. Thus, the initiation rate is inversely dependent on monomer concentration.

For excision energy transfer, the initiation rate would be first order in monomer, i.e.,

$R_i \propto 1/(\text{energy transfer}) \propto r^3 \propto 1/|B| \propto |M|$ (2.2.15)

For energy transfer by the Förster mechanism, one would predict a second-order dependence of the initiation rate on monomer:

$R_i \propto 1/(\text{energy transfer}) \propto r^6 \propto 1/|B|^2 \propto |M|^2$ (2.2.16)

The energy transfer from exited polymer to monomer would result in a dependence of the initiation rate on monomer, yielding a higher order of energy transfer would depend on the mechanism of energy transfer.

The dose rate increases indicates that the mode of termination is changing from the usual bimolecular coupling and/or disproportionation of propagating radicals

$M\cdot + M\cdot - k_t \rightarrow$ termination (2.2.17)

to reaction of a propagating radical with a primary radical

$M\cdot + P\cdot - k_{t0} \rightarrow$ termination (2.2.18)

The latter reaction is referred to as primary radical termination and has been observed in homopolymerizations of monomer carried out in high viscosity media. Further, as Chapiro pointed out, primary termination becomes increasingly important at high dose rates as the concentration of primary radicals increase. Primary termination may be especially important in high viscosity systems (such as a grafting system) where primary radicals would have grater mobility than the larger-sized propagating radicals.

The kinetics of polymerization where termination occurs exclusively by primary termination lead to the expression for the graft rate

$$R_p=k_p k_i [M]^2/k_{t0} \qquad (2.2.19)$$

which shows the grafting rate to be second-order in monomer and independent of dose rate.

G. odian et al.[21], studied the case of graft polymerization proceeding in a polymer film of thickness L in 100% monomer by simultaneous irradiation method.

The other two dimensions of the film are large relative to L such that only two-sided (one-dimensional) diffusion need be considered; diffusion of monomer from the four edges of the film are relatively unimportant. Applying Fick's second law of diffusion, one obtains a mass balance on the monomer contained in a thickness of infinitesimal size within the polymer film as

$$R_p+(dc/dt)=D(d^2c/dx^2) \qquad (2.2.20)$$

where R_p is the rate of monomer disappearance (i.e., graft polymerization) in that thickness, dc/dt is the change in the monomer concentration in that thickness with time and $D(d^2c/dx^2)$ is the difference in the rates of diffusion in and out of that thickness. In eq. (2.2.20), x is the distance from the center of the film, c is the concentration of monomer in the film, and D is the diffusivity of the monomer within the polymer.

In the usual grafting experiment, the polymer and monomer are equilibrated prior to irradiation. After equilibration and prior to the start (time=0) of the irradiation, all of the terms in eq. (2.2.20) have valves of zero throughout the whole film thickness. The monomer concentration is its equilibrium or maximum valve M and is the same throughout the whole film thickness. The situation changes quite drastically with the start of the irradiation. The rate of graft polymerization very quickly (almost) instantaneously) reaches a maximum valve and then begins to fall as the monomer concentration (responced by dc/dt) decreases. Diffusion of monomer occurs simultaneous as the Dd2c/dx2 term increases with time from its zero value. Finally, the monomer-polymer system reaches a steady-state condition in which the monomer concentration and grafting rate become constant and independent of time. The dc/ct term is zero at steady state, and eq. (2.2.20) becomes

$$R_p=D(d^2c/dx^2) \qquad (2.2.21)$$

The steady state of the grafting system does not imply that the monomer concentration and grafting rate are constant and uniform throughout the whole thickness of the polymer film. both of these quantities show a distribution profile throughout the film thickness with maximum values at the film surfaces and minimum values in the center of the film. The steady state refers simply to the fact that monomer concentration and R_p profiles have reached constant valves and do not undergo further changes. The monomer concentration and grafting rate at any thickness of differential size in the film are constant.

From ordinary free radical polymerization considerations, the grafting rate at any differential thickness in the film will be given by

$$R_p=(k_p/k_t^{1/2})R_i^{1/2}c \qquad (2.2.22)$$

where R_i is the rate of initiation (i.e., radical production in the polymer) and k_p and k_i are the rate constants for propagation and bimolecular termination. Combination of eqs. (2.2.1) and (2.2.22) yields as follows

$$d^2c/dx^2=[(k_p/k_i^{1/2})(R_i^{1/2}/D)]c \qquad (2.2.23)$$

Two boundary conditions (BC) must be satisfied by eq. (2.2.23).

These are BC_1: at $x=0$, $dc/dx=0$ (2.2.24)

BC_2: at $x=L/2$, $c=M$ (2.2.25)

The first boundary condition states that there is no concentration gradient at the center of the polymer film since diffusion from both sides meet at the center thickness. The second boundary condition states that for a film of thickness L, the monomer concentration at the surface is equal to the equilibrium concentration M.

One should note that the experimentally determined grafting rate is not Rp but is instead the average volumetric grafting rate $\overline{Rp}$ averaged over the entire thickness of the polymer film. The average grafting rate is thus given by

$$\overline{Rp}=(2/L)\int_0^{L/2} Rp\,dx \qquad (2.2.26)$$

where R_p is defined by eq. (2.2.22).

Combination and rearrangement of eq.s (2.2.21), (2.2.22), (2.2.26) yields

$$\overline{R_p}=[(k_p/k_i^{1/2})R_i^{1/2} M)]\mathrm{tahn}A / A \qquad (2.2.27)$$

where

$$A=[(k_p/k_i^{1/2})(R_i^{1/2}/D)]^{1/2} L/2 \qquad (2.2.28)$$

Equation (2.2.27) shows the general relationship among the questions R_p, R_i, M, L, $k_p/k_i^{1/2}$, and D and can be used to interpret and analyze experimental data in grafting systems. Equation (2.2.27) can be meaningfully expressed in a graphical manner by a log-log plot of R_p versus A. This is equally applicable to all polymers and monomers under all conditions of initiation rate, film thickness and reaction temperature. The R_i valve is determined by the radiation intensity and the G valve of the monomer. The valves of M, D, and $k_p/k_i^{1/2}$ are determined by the particular combination of polymer, monomer, and temperature. The average grafting rate $\overline{Rp}$ is then determined by the film thickness and all of the parameters in accordance with eq (2.2.27). Equation (2.2.27) has defined by the values of A.

2.2.2 Preirradiation

In bulk polymerization using preirradiation method, polymer radicals are terminated mostly by coupling, and the contributions of chain transfer to monomer and disproportionation are significant[22]. It is considered that the ratios of coupling in grafting reactions are identical with those of bulk polymerization. It is quite difficult to estimate the apparent chain transfer constant in heterogeneous systems. The fact that observed values of Mn of graft chains are terminated by coupling[20]. The nature of coupling processes of graft radicals may appear to be quite different from that of homopolymer radicals in solutions; single ends of graft radicals are fixed on the trunk polymer end, consequently, the transitional diffusion of center of masses is hindered. The rate-determining step in coupling reactions between polymer radicals is not the transitional diffusion of their center of mass but the segmental motions of active ends around the chain centers. Hence, it would be probable that the coupling probability of graft radicals is influenced by chain length in ways somewhat similar to homopolymer radicals in solutions. The molecular weight distribution of graft chains is one of the most important factors in characterizing graft copolymers. The detail several factors which influence the molecular weight distribution of graft chains was studied by simulating the grafting reaction with various models employing Monte Carlo technique by T. Yasukawa et al[22].

Moreover, the bulk polymerization using preirradiation method is affected by the reaction temperature, the physic and chemical properties of monomer, and the affinity of monomer to polymer like as simultaneous irradiation[19].

2.3 Molecular dynamics for aqueous solution

The molecular dynamics of liquid water is interesting and important in many areas of sciences. The scattering of X-rays from the free surface of liquid water in equilibrium with water vapor has been analyzed by A. H. Narten et al.[23], The thermodynamic properties estimated for the model structure are in essential agreement with those of liquid water. The X-ray diffraction data on liquid water presented the yield information on the average atomic arrangement around any oxygen atom taken as the origin. The water model retains the hexagonal symmetry of the ice-like network. The model has properties which are not in disagreement with the thermodynamic properties of water, and it may be helpful in the interpretation of the many strange properties of water. D. F. Coker et al.[24], present the results of using infrared predissiciation spectroscopy based on bolometric detection to study clusters of water molecules. The clusters are formed by expanding water vapor in helium from a wide range of source pressures and temperatures. Measurements are made using a color center laser as the source of infrared radiation and a cryogenic bolometer as detector. This method has proven very useful for a wide range of van der Waals clusters[23] and has given rovibrational spectra and estimated predissiciation lifetimes for several dimmers. by varying the source conditions it is possible to identify the dimmer vibrational modes and watch their transformation, as the cluster size increases, towards the type of vibrational spectrum found in liquid water. The combined intra-inter molecular potential surface indicated an excellent description of water dimmer and trimmer vibrational frequencies. By postulation of pair wise additive potentials between rigid water molecules and molecular dynamics techniques on a system of a few hundred molecules the structural and dynamically correlation in pure water has been studied[23,24,25]. The result of all these studies has been to show that the water structure can be thought of as a network of hydrogen bonds. These hydrogen bonds are not perfectly formed as ice crystal. Unlike the case of ice crystals, in liquid water, one is required to set down a "definition" of a hydrogen bond. A. Geiger et al.[24], simulated the molecular dynamics for liquid water. Water has to be considered as a large macroscopic space-filling network enclosing a few small bonded but isolated clusters.

O. Ya. Samoilov[26] mentioned the exchange of water molecules in the immediate vicinity of the ions. An examination of the action of ions on the transitional motion of the water molecules closest to the ions may be offered as a basis for a general approach to the study of ion hydration in aqueous solutions. The properties of aqueous electrolyte solutions depend in large measure on the interaction of ions with the molecules of the water. This interaction is known as the hydration of ions and extremely important both for the equilibrium properties of solutions and for properties that are known as kinetic properties (viscosity, diffusion, etc.). When studying the hydration of ions it is common to consider ions as bonding a certain number of water molecules of the solution. Attempts have been made to describe hydration in terms of the number of water molecules bound to ions, the so-called hydration numbers. The entire total effect of hydration of ions may be divided into two parts: "primary" hydration that consists chiefly in the firm binding of the water molecules by the ion; and " secondary" hydration which amounts to the polarization, due to the action of the field of the ion, of the water not included in the primary hydration. An examination of the action of ions on thermal agitation and above all of the so-called transitional motion of the water molecules of the solution closest to the ions may be offered as a basis for such a general approach to the study of ion hydration in solutions. The transitional motion of water molecules relative to the ion in its immediate vicinity should be regarded as the exchange of water molecules of the solution that are closest to the ion. If the exchange occurs relatively rarely, the hydration of the ion is considerable. As the frequency of the exchange grows the hydration of the ion weakens. The magnitudes defining the frequency of exchange of water molecules near the ion are, according to the suggested point of view, the quantitative characteristics of ion hydration in solutions. Water molecules are always moving. The motion of water molecules in an aqueous solution containing a solute is affected by the water and solute interaction, and differ from that in pure water. This interaction (the water hydration of a solute) is important for the kinetic properties of a solution. For pure water, the water molecules exchange in the vicinity of each other almost immediately. The mean time in an equilibrium position is denoted as τ. The value of the activation energy of the exchange is denoted as E. In the case of an aqueous solution, the mean time that a water molecule is in the closest equilibrium position to the ion in the structure of the solution is denoted as τ_i. The value of the activation energy of the exchange of the closest molecules is denoted as $E+\Delta E_i$. The following relation is then obtained [26,27].

$$\tau_i/\tau=\exp(\Delta E_i/RT) \qquad (2.3.1)$$

In the case that the solute is an organic compound, the interaction between water molecules and a hydrophobic group or a hydrophilic group is as follows:

$$\Delta E_i=\Delta E_1+\Delta E_2 \qquad (2.3.2)$$

The activation energy of the exchange of the water molecules connected to hydrophilic group is denoted as ΔE_1. The activation energy of the exchange of the water molecules connected to hydrophilic group is denoted as ΔE_1. When $\Delta E_i>0$ is the magnitude of the ratio $\tau_i/\tau>1$, i.e., the time that the water molecules connect in the vicinity of a solute molecule in the solution is longer than the time adjacent to the vicinity of a water molecule in pure water. The motion of the water molecules are prevented by the solute vicinity. When $\Delta E_i<0$ and the ratio $\tau_i/\tau<0$, the water molecule adjacent to the solute becomes more mobile than in pure water. In the case of an aqueous solution of organic compounds, generally, the water molecules adjacent to the solute becomes less mobile than in pure water.

Hydrogen bond formation of water molecules in aqueous solutions is thought to form clusters with "ice-like" structure that are stabilized by the presence of a hydrophobic group[25]. Pauling[28] suggested that liquid water has a structure, or range of structures, which consist of a framework of ordered water to contain non hydrophilic molecules in the voids. Liquid water can be regarded as a "water hydrate," consisting of some such framework as is found in the clathrate crystals, which the enclosed sites occupied by unbonded water molecules. The frameworks in question may be thought of as based upon a pentagonal dodecahedron of 20 water molecules, each participating in 3 hydrogen bonds, one such bond lying in each of the 30 edges of the solid figure. The inside of such a dodecahedron contains a void of about 5Å in unobstructed diameter. These are "large" voids (6 Å or more of free diameter), as contrasted with the "small" ones in the dodecahedra. The properties of enthalpies and entropies which are derived for framework and interstitial water, respectively, also seem physically reasonable[29]. H. S. Frank et al.[28], gave a statistical-thermodynamic treatment to Pauling's model for liquid water. In liquid water, some molecules be in a "third state," and if this third state is taken into consideration the shortcomings of the simple model can be remedied.

On the basis of a quantitative assessment of the hydrophobic effect from the standard free energy, enthalpy, and entropy of solution of a large number of gaseous non polar non electrolytes, The hydrophobic effect that arises through a methane group in n-alkanes is primarily an enthalpic effect that arises through a methylene/water interaction[30]. On the other hand, polar solute species with hydrogen bonding ability are also expected to show enthalpy changes for solutes in water. By N. Nishi et al.[30], Stability of hydrate clusters in aqueous solution has been studied.The hydrophobic effect of a methylene group was evaluated on the basis of the quantitative assessment of the hydrophobic effect from the standard free energy, enthalpy, and entropy of solution . On the other hand, the hydrogen bonding ability of a polar solute was also studied. The trend is observed that ethanol-ethanol association is attributed to the hydrophobic hydration of an ethyl group of an ethanol molecule in aqueous environment.

The decreases in entropy is due to the tendency of the water dipoles in the layer of water adjacent to the hydrocarbon solute to orient with respect to the dipoles in the water molecules in the next water layer. This effect does not exist in the bulk liquid away from a surface or hydrocarbon molecule because of the symmetry of the electric field in which a given water molecule finds itself. According to this theory, then, the number of water molecules that can be packed around the hydrocarbon molecule is an important quantity in the partition function for the hydrocarbon solution. In view of hydrophobic bonding, also used this number of water molecules in the first water layer as being a factor in hydrocarbon solubility[31]. The number of water molecules that can be packed around a given hydrocarbon solute molecule is depending on the solute conformation and the assumed water structure. The number is related to the surface area of the solvent cavity if the surface is defined in such a way that it passes though the centers of the water molecules momentarily adjacent to the solute. This idea of cavity surface, while slightly idealized, can be more easily calculated. For a spherical cavity the free energy ΔG for transferring a molecule from the gas phase to the solvent is approximated as follows[32].

$$\Delta G=4\pi r^2\,\sigma-\varepsilon \qquad (2.3.3)$$

where r is the cavity radius, σ is the solvent surface tension, and ε is the solute-solvent interaction energy. Then c'/c, the ratio of molecules in the solvent to molecules in the gas phase, is given by the Boltzmann distribution

$$c'/c=e^{-\Delta G/kT} \qquad (2.3.4)$$

Since that time, the liner relationship between the solvent surface tension for non polar solvents and the logarithm of the gas solubility has been amply verified. R. B. Hermann[31,32] studied the correlation of hydrocarbon solubility in water and the free energy change with solvent cavity surface area. The free energy was assumed to be linearly related to the number of water molecules that can be packed around a given hydrocarbon molecule. The cavity surface area is a better parameter than experimental molar volume in correlating solubilities.

The hydration number of water molecules is what can be packed around the partition function for the hydrocarbon solution. The hydration number of water molecules will depend on the solute conformation and the assumed water structure. The hydration number is also related to the surface area of the solute that passes through the centers of the water molecules which can be affixed to the solute. The bulk water is the water molecules that are not adjacent to the solute and have no interaction .

The solutes in aqueous non electrolyte solutions may be derived into two classes according to the predominant thermodynamic property in the mixing process with water^{26}. These are termed typically aqueous and typically non aqueous. The former solutes are those which exhibit in solution anomalous thermodynamic properties as found only in aqueous solution and are typified by relative magnitudes of excess enthalpy ΔH and excess entropy $T\delta S$ in such a manner as $|T\Delta S|>|\Delta H|$ (e.g., alchols and amines). On the other hand, the letter solutes in aqueous solution indicate the properties which are similar to those of normal non aqueous solutes and the relation between the two thermodynamic functions is characterized as $|\Delta H|>|T\Delta S|$. Therefore, it is possible to interpret the thermodynamic properties in terms of direct interaction between water and solute molecules in the case of typically non aqueous solution. However, those of typically aqueous solution are for the most part attributed to change of water structure around solute molecule rather than the interaction between water and solute. Especially, structualization of water by incorporation of non polar molecule that belongs to typically aqueous solute is called hydrophobic hydration^{27,33}. This phenomenon is accompanied by large entropy loss and negative enthalpy change in the course of hydration. It was confirmed explicitly that hydrophobic hydration at infinite dilution and hydrophobic interaction at higher concentration play predominant roles for the molecules having both polar and non polar groups. This fact could be predicted by thermodynamic measurement. They recognized so many hydration phenomena of non electrolyte solutions are related to the hydrophobic hydration or interaction. Moreover, it is difficult to obtain the microscopic structures or energetic interaction distributions from ordinary experiments but they can be related to macroscopic or thermodynamic properties by computer simulation. By

K. Nakanishi et al.[34], Monte Carlo calculations have been carried out for an infinitely dilute aqueous solution of tertiary butylalchol (TBA). The bulky tertiary aikyl group of TBA can occupy cavities in the network structure of water effectively. While such large volume contraction at infinite dilution of TBA is mainly due to cavity effect, there is a further contribution from hydrophobic hydration. This is more clearly seen by comparing the partial molar enthalpy at infinite dilution which is more negative than that for methanol. This is attributable to the hydrophobic hydration of the non polar group which is larger in TBA. The hydrophobic hydration at infinite dilution may be characterized by a large negative terminal value of partial molar excess enthalpy as the extension of its rapid decrease in dilute aqueous solution. Excess enthalpy data for the water-TBA mixture indicate that the dissolution of TBA into water is exothermic in dilute solution and tends to be positive in the TBA rich region. The introduction of one TBA molecule into pure water leads to shift of the equilibrium. If the hydrophobic to hydrophobic ratio in the molecule is large, there will be a larger volume decrease. This is the hydrophobic hydration effect of hydrophobic groups to promote effective cavity filling. This effect seems to be especially large when the molecule in question has methyl groups. By H. Tanaka et al.[35], a molecular dynamics calculation on aqueous solution of urea has been carried out using constant temperature technique and Monte Carlo calculation. Instead of the possibility to form strong hydrogen bonding as estimated from the potential function, it is found that urea molecule could enter into the water structure without any appreciable distortion. This fact was confirmed by the angular dependence of any distribution function around the urea molecule. The hydrophilic region does not show a large energetic stabilization between water molecules and the system is stabilized slightly by including urea-water interaction. In contrast to this, the energy for water molecules in the hydrophobic region (above and bellow the plane containing urea molecule) becomes lower than that of pure water, although this region is small and water molecules cannot form a strong hydrogen bond with urea. This fact reveals that the role of each functional region, which may be either hydrophobic or hydrophilic, is similar to that of alcohol in aqueous solution, although the whole hydration structure of urea molecule is somewhat different from that of alcohol. Reflecting strong interaction of urea-water, the diffusion coefficient for shell water molecules in the vicinity of urea. Moreover, the hydration structure around urea continues for a long times, though the energetic relaxation time is very short. R. A. Kuharski et al.[36], also studied the effect of urea on water structure. Only very small differences are obtained between the properties of water molecules in the solvate region of urea and bulk, and these difference can be assigned to direct urea-water interactions, with no substantial perturbation of water-water interactions. There are only small differences between water in the vicinity of urea and bulk water, and furthermore, that these small differences are the reseal of direct interactions between urea and water molecules with no substantial urea-induced perturbation of water-water interactions. The quantities considered, including bonding energies, pair interaction energy distributions, and hydrogen bonding, show that water molecules in the solvate shell of urea have properties which are very similar to those of bulk water. Urea has little effect on water structure, in contact to the inference from several experiments that urea acts as a water structure breaker.

Thus, the solute in aqueous solution effect on the molecular dynamics of the around water and the physical and chemical behavior of the solution.

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Chapter 3. Permeation Behavior of Solute Organic Compounds and Water in Polydimethylsiloxane

3.1 Introduction

The basic permeation behavior for Polydimethylsiloxane (PDMS) membrane was investigated. The permeation behavior, particularly for an aqueous solution with a hydrophilic solute, is affected by the hydration of water to the solute. The physico-chemical properties of an aqueous solution is interesting depending on its application and has been extensively studied [1~14]. Their properties are mainly due to a hydrophobic interaction.

Water molecules are always moving. The motion of water molecules in an aqueous solution containing a solute is affected by the water and solute interaction, and differ from that in pure water. This interaction (the water hydration of a solute) is important for the kinetic properties of a solution. The transitional motion of water molecules in a diluted aqueous solution was considered in several reports [9,10].

For pure water, the water molecules exchange in the vicinity of each other almost immediately. The mean time in an equilibrium position is denoted as τ. The value of the activation energy of the exchange is denoted as E. In the case of an aqueous solution, the mean time that a water molecule is in the closest equilibrium position to the ion in the structure of the solution is denoted as τ_i. The value of the activation energy of the exchange of the closest molecules is denoted as $E+\Delta E_i$. The following relation is then obtained [9,10].

$$\tau_i/\tau=\exp(\Delta E_i/RT) \qquad (3.1)$$

In the case that the solute is an organic compound, the interaction between water molecules and a hydrophobic group or a hydrophilic group is as follows:

$$\Delta E_i=\Delta E_1+\Delta E_2 \qquad (3.2)$$

The activation energy of the exchange of the *water molecules connected to hydrophilic group* is denoted as ΔE_1. The activation energy of the exchange of the water molecules connected to hydrophilic group is denoted as ΔE_1. When $\Delta E_i>0$ is the magnitude of the ratio $\tau_i/\tau>1$, i.e., the time that the water molecules connect in the vicinity of a solute molecule in the solution is longer than the time adjacent to the vicinity of a water molecule in pure water. The motion of the water molecules are prevented by the solute vicinity. When $\Delta E_i<0$ and the ratio $\tau_i/\tau<0$, the water molecule adjacent to the solute becomes more mobile than in pure water. In the case of an aqueous solution of organic compounds, generally, the water molecules adjacent to the solute becomes less mobile than in pure water.

Hydrogen bond formation of water molecules in aqueous solutions is thought to form clusters with an "ice like" structure that are stabilized by the presence of a hydrophobic group. The hydrophobic effect of a methylene group was evaluated on the basis of the quantitative assessment of the hydrophobic effect from the standard free energy, enthalpy, and entropy of solution [7]. On the other hand, the hydrogen bonding ability of a polar solute was also studied [7]. The hydration number of water molecules is what can be packed around the partition function for the hydrocarbon solution. The hydration number of water molecules will depend on the solute conformation and the assumed water structure. The hydration number is also related to the surface area of the solute that passes through the centers of the water molecules which can be affixed to the solute [11,12]. The bulk water is the water molecules that are not adjacent to the solute and have no interaction [9].

For permeate transport, the solution-diffusion mechanism is important. The hydrophobicity is closely concerned with the solubility of the organic compounds[15~21]. Also, the molecular volume is closely concerned with the diffusivity of the organic compounds[15~21]. The hydration may effect the diffusivity of the solute molecules during permeation.

PDMS is well known as an excellent polymer membrane material due to its high permeability to gases and liquids. The permeate molecules permeate quickly in rubbery membranes like PDMS, and the permselectivity was not so affected by the diffusivity of a sole molecules. Solubility significantly affects the permselectibity during pervaporation through a hydrophobic rubbery membrane. However, the relationships between hydration and permeation of various organic compounds during pervaporation in a PDMS membrane can be interesting to consider.

In this chapter, the hydration effect on the sorption-diffusion mechanism for various organic compounds through the PDMS membrane which is basic important phenomena for permeation behavior was investigated.

3.2 Experimental

3.2.1 Pervaporation experiment

Table 3.1 Phisico-chemical properties of solute organic compounds

Compound	Formula	Molecular weight	Molecular volume (cm^3 / mol)	Hydration number of water
Acrylonitrile	CH_2CHCN	53.06	65.83	
Isopropanol	$CH_3CHOHCH_3$	60.09	76.42	17[10,11,12]
Acetic acid	CH_3COOH	60.05	57.23	12[10,11,12]
n-Butyl amine	$CH_3(CH_2)_3NH_2$	73.13	98.55	20[10,11,12]

Commercial PDMS membranes (Fuji Systems Corporation), 50μm thick, were used throughout this work. isopropanol, acrylonitrile, acetic acid and n-butyl amine (Special grade, Wako Pure Chemical Industries, Ltd.) were used as received. The physico-chemical properties of the solutes used in this study are shown in Table 3.1.

The pervaporation experiments were performed in a previous study [22,23] using the continuous-feed type method at 25°C. The feed solution was circulated through the cell and the feed tank. The effective membrane area in the cell was 19.6cm^2. The pressure at the permeation side was kept below 10Torr by vacuum pumps. Upon reaching steady state flow conditions, the permeate was collected in traps cooled by liquid nitrogen (-196°C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate, flux(J), was obtained using eq.(3.3)

$$J=Q/At \qquad (3.3)$$

where Q is the amount permeated during the experimental time interval t and A is the effective surface area. The solute flux was calculated from the total flux and the permeate composition. The concentration of solute in the feed and permeate solution was determined by gas chromatography using an FID detector. The enrichment factor, βpv, was calculated as

$$\beta pv = Y/X \qquad (3.4)$$

where X and Y denote the concentration of solute in the feed and permeate solution, respectively.

3.3 Results and discussion

3.3.1 Pervaporation for various aqueous solution

The pervaporation properties of various solute aqueous solution were determined in this study.

The relationships between the solute concentration in the feed and permeate are shown in Fig.3.1. The permeate concentrations of isopropanol and acrylonitrile, which are not dissociable, were increased with feed concentration. The relationship was linar. The permeate concentration of acetic acid and n-butyl amine, which are dissociable, were significantlly increased with feed concentration.

The relationships between the feed solute concentration and the enrichment factor (βpv) are shown in Fig.3.2. The enrichment factors of isopropanol and acrylonitrile were constant with feed concentration. The enrichment factors of acetic acid and n-butyl amine were below 1 at a low feed concentration, however, for a high feed concentration, they were significantly increased with feed concentration.

3.3.2 Hydration effect on the solution-diffusion mechanism

The flux as a function of the feed isopropanol concentration is shown in Fig.3.3 for the aueous isopropanol solution. The isopropanol flux was increased with increasing feed concentration. The water flux increased until the maximum at a feed isoropanol mole fraction

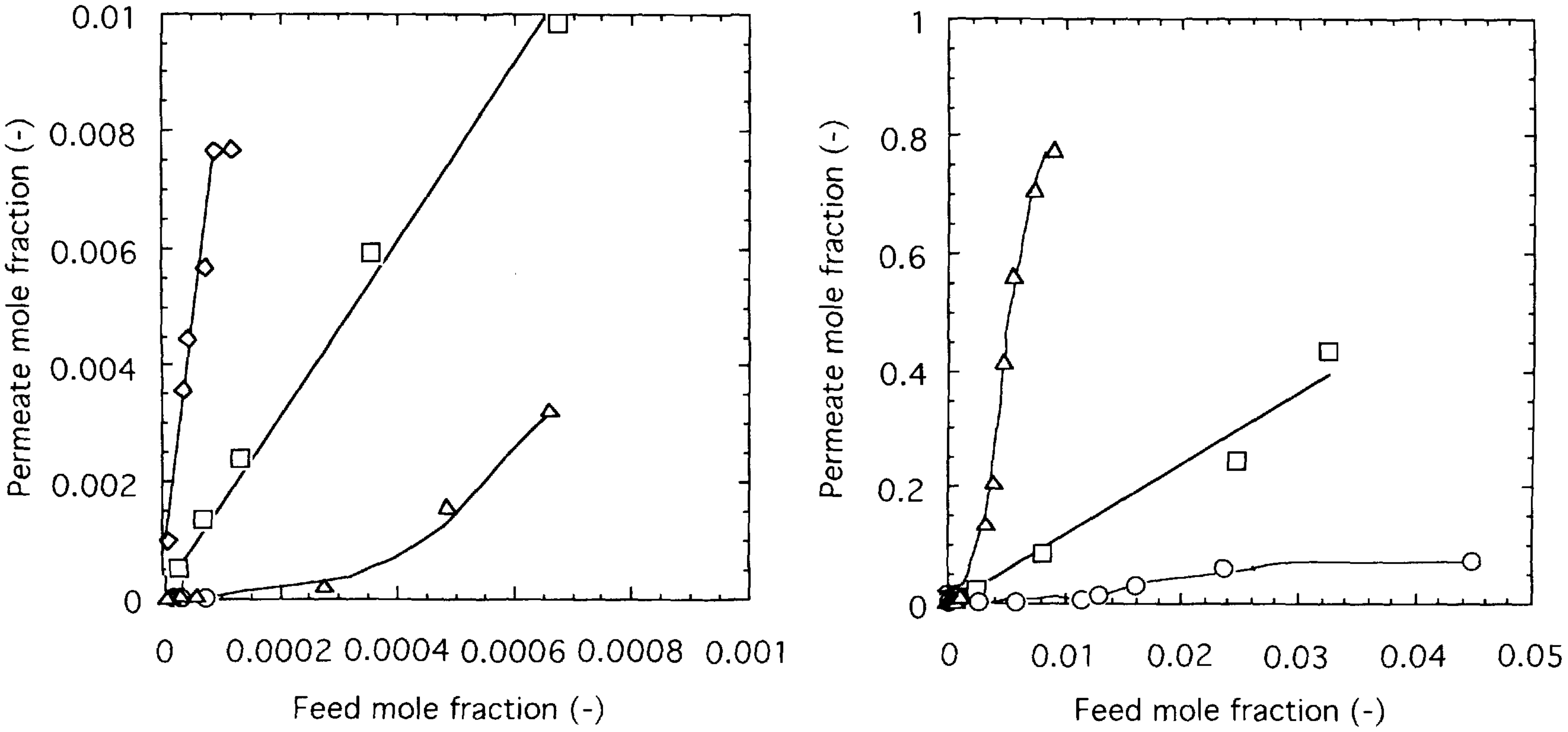

Fig. 3.1 Relationship between solute concentration in feed and permeation during pervaporation.: (□) isopropanol, (◇) acrylonitrile (○) acetic acid, (△) n-butyl amine.

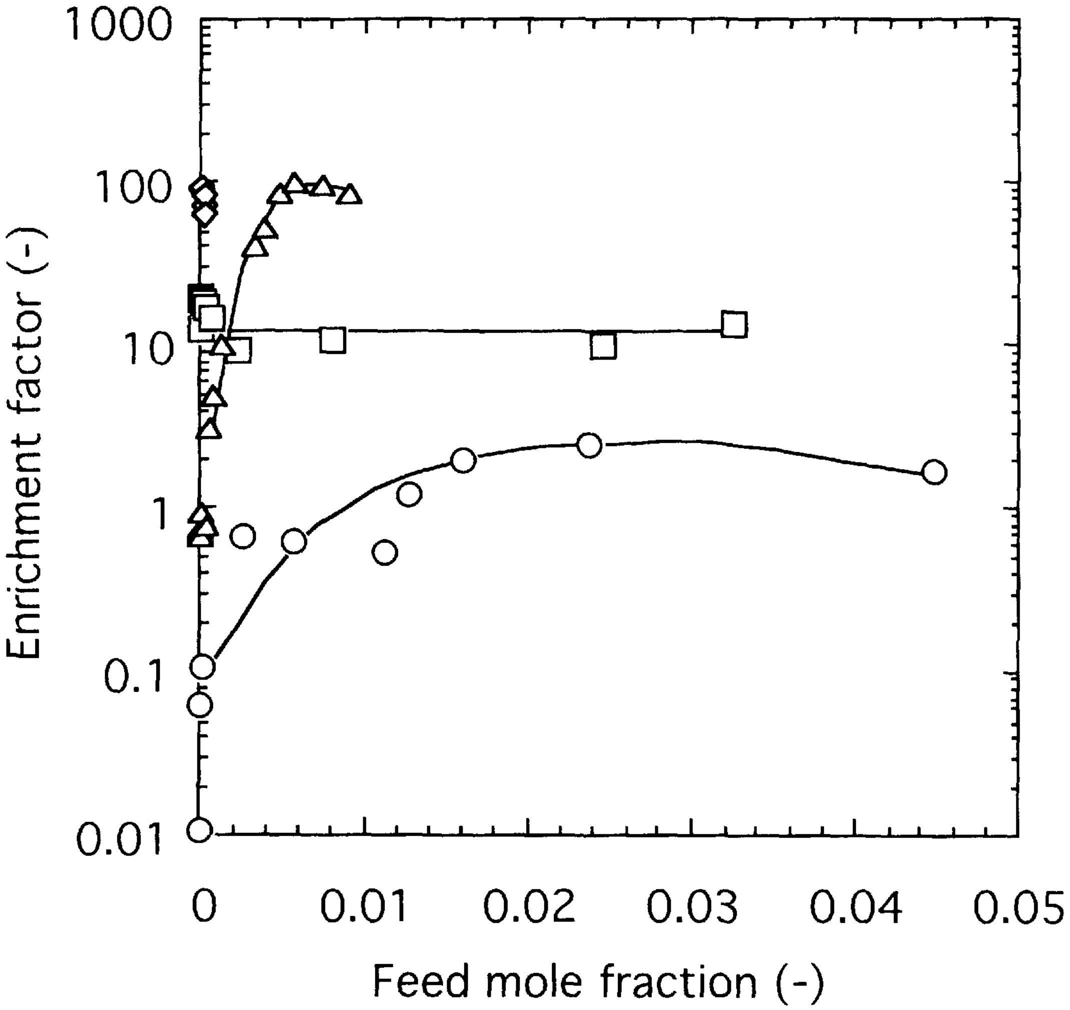

Fig. 3.2 Effect of feed concentration on the enrichment factor (β_{pv}) during pervaporation.: (□) isopropanol, (◇) acrylonitrile (○) acetic acid, (△) n-butyl amine.

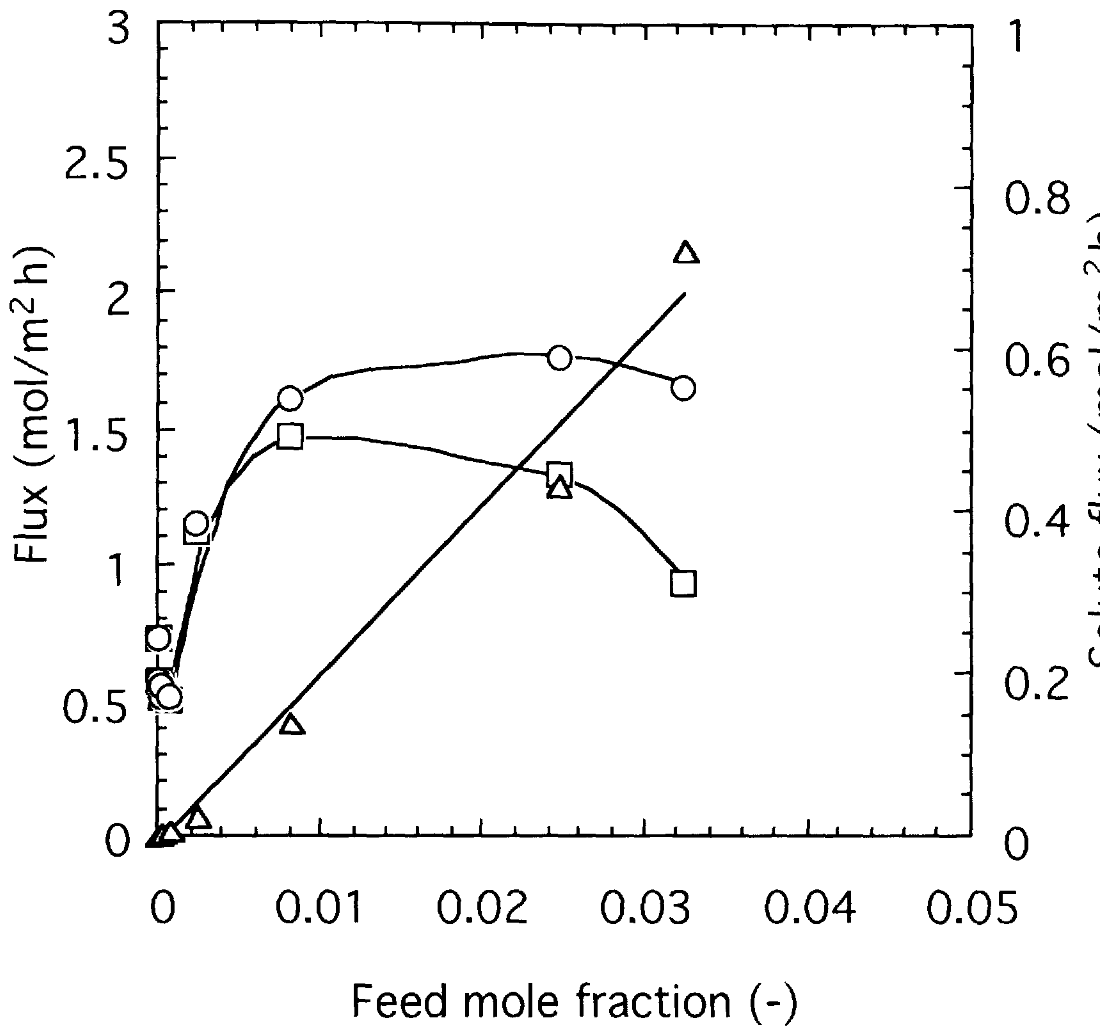

Fig. 3.3 Effect of feed concentration on flux for isopropanol-water mixtures during pervaporation.: (□) water flux, (○) total flux, (△) isopropanol flux.

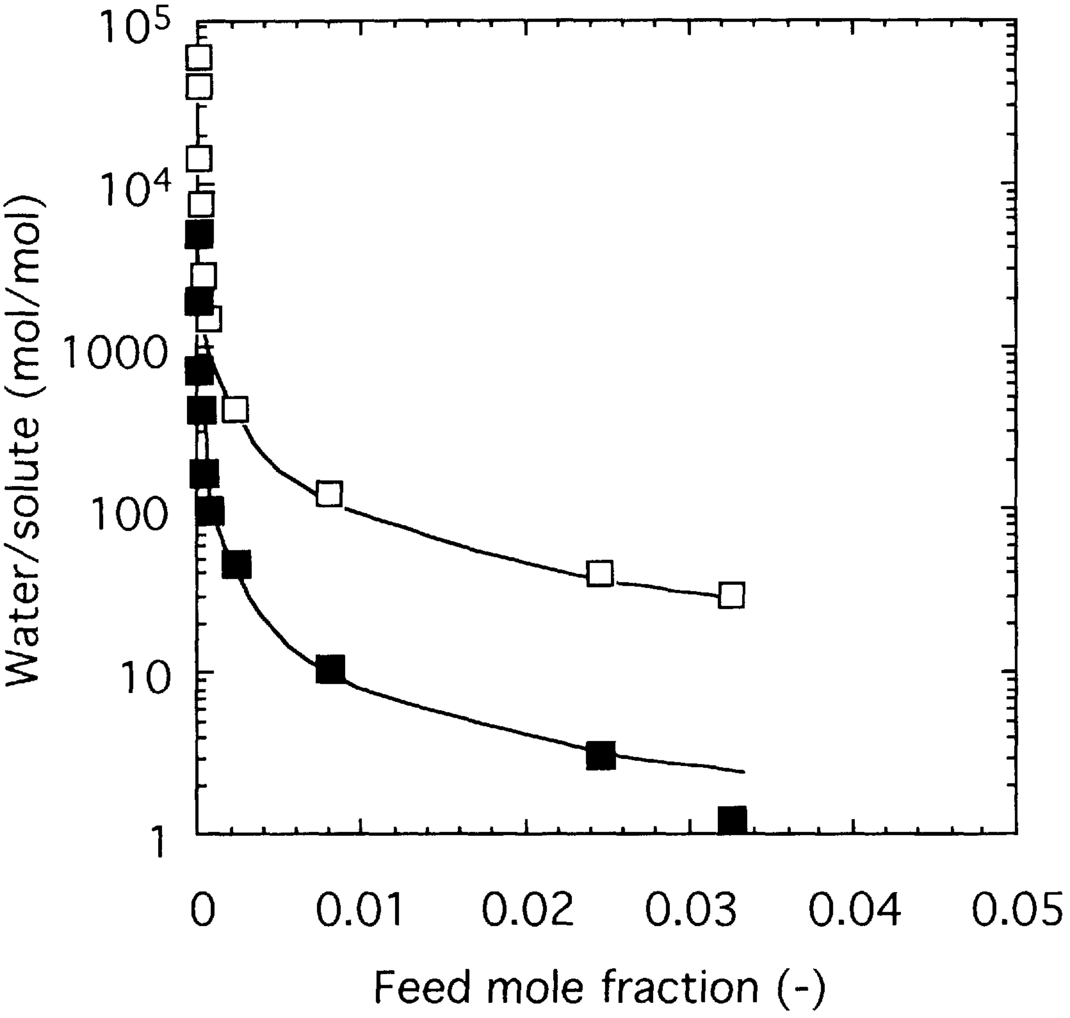

Fig. 3.4 Relationship between feed Isopropanol concentration and water molecular number/isopropanol molecular number in feed or permeate solution: (□) in feed , (■) in permeate.

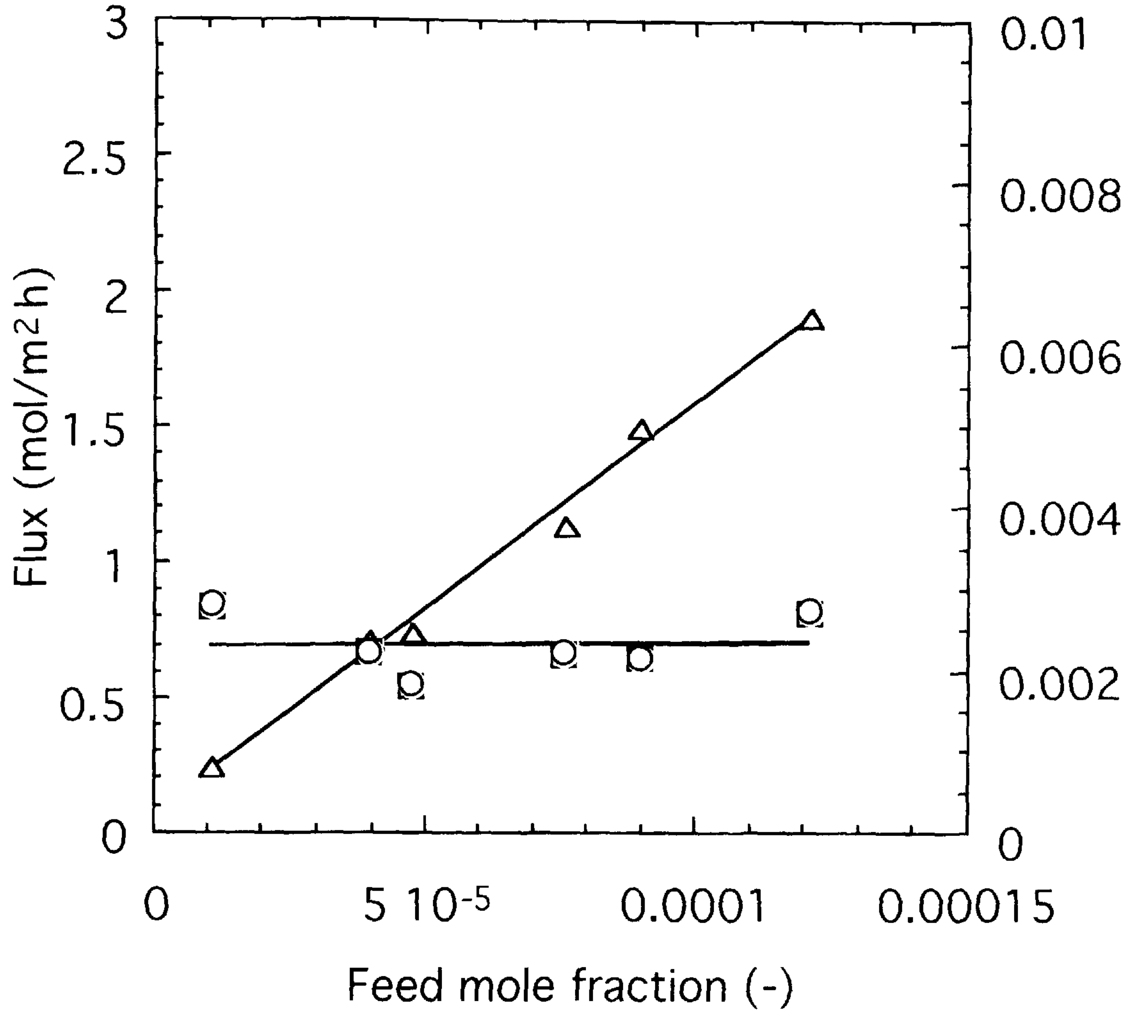

Fig. 3.5 Effect of feed concentration on flux for acrylonitrile-water mixtures during pervaporation.: (□) water flux, (○) total flux, (△) acrylonitrile flux.

of 0.01 and then decreased with increasing feed concentration.

The liquid water has a distribution of hydrogen-bond clusters and space [13,14]. The organic compounds dissolve in the space of the liquid water. The water molecules hydrate the solute molecules. The motion of the water molecules are prevented in the vicinity of the solute.

The number of water molecules per one solute in the feed or permeate solution as a function of the feed isopropanol concentration is shown in Fig.3.4. The water flux increased until a maximum at the feed isoropanol mole fraction of 0.01 because the water diffusion was promoted by hydration. However, in the high feed concentration , mole fraction>0.01, the isopropanol solution was concentrated in the PDMS membrane and the permeate concentration was over 0.08 mole fraction. The hydration number for various solutes is shown in Table 3.1. The hydration number of water molecules on isopropanol is 17. The 0.059 mole fraction describes that 17 water molecules per one isopropanol molecule exist. In the 0.059 mole fraction, almost all water molecules are involved in hydration. When the concentration is over the 0.059 mole fraction, one water molecule is adjacent to several solute molecules and the motion of the water molecules is prevented. Hence, it is considered that when the feed mole fraction is greater than 0.01, the isopropanol solution was concentrated in the PDMS membrane and the diffusion of water molecules was prevented.

The total flux increased until a maximum at the feed isoropanol mole fraction of 0.01 and then decreased with increasing feed concentration due to the effect of water flux.

The flux as a function of the feed acrylonitrile concentration is shown in Fig.3.5 for the acrylonitrile solution. The acrylonitrile flux was increased with increasing feed concentration. The water and total flux were constant with low feed concentrations.

The flux as a function of the feed acetic acid concentration is shown in Fig.3.6 for the aqueous acetic acid solution. The water flux increased until the maximum feed acetic acid mole fraction of 0.025 and then decreased with increasing feed concentration.

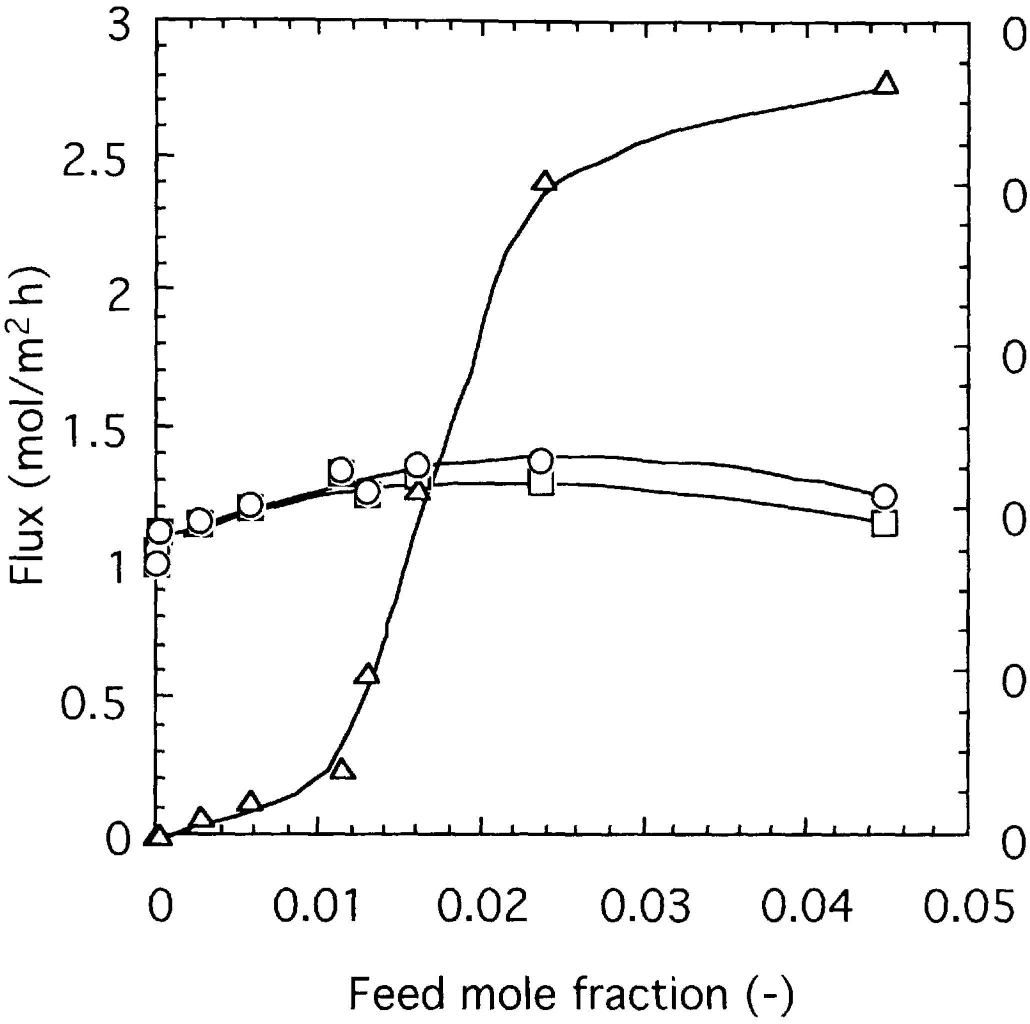

Fig. 3.6 Effect of feed concentration on flux for acetic acid-water mixtures during pervaporation.: (□) water flux, (○) total flux, (△) aetic acid flux.

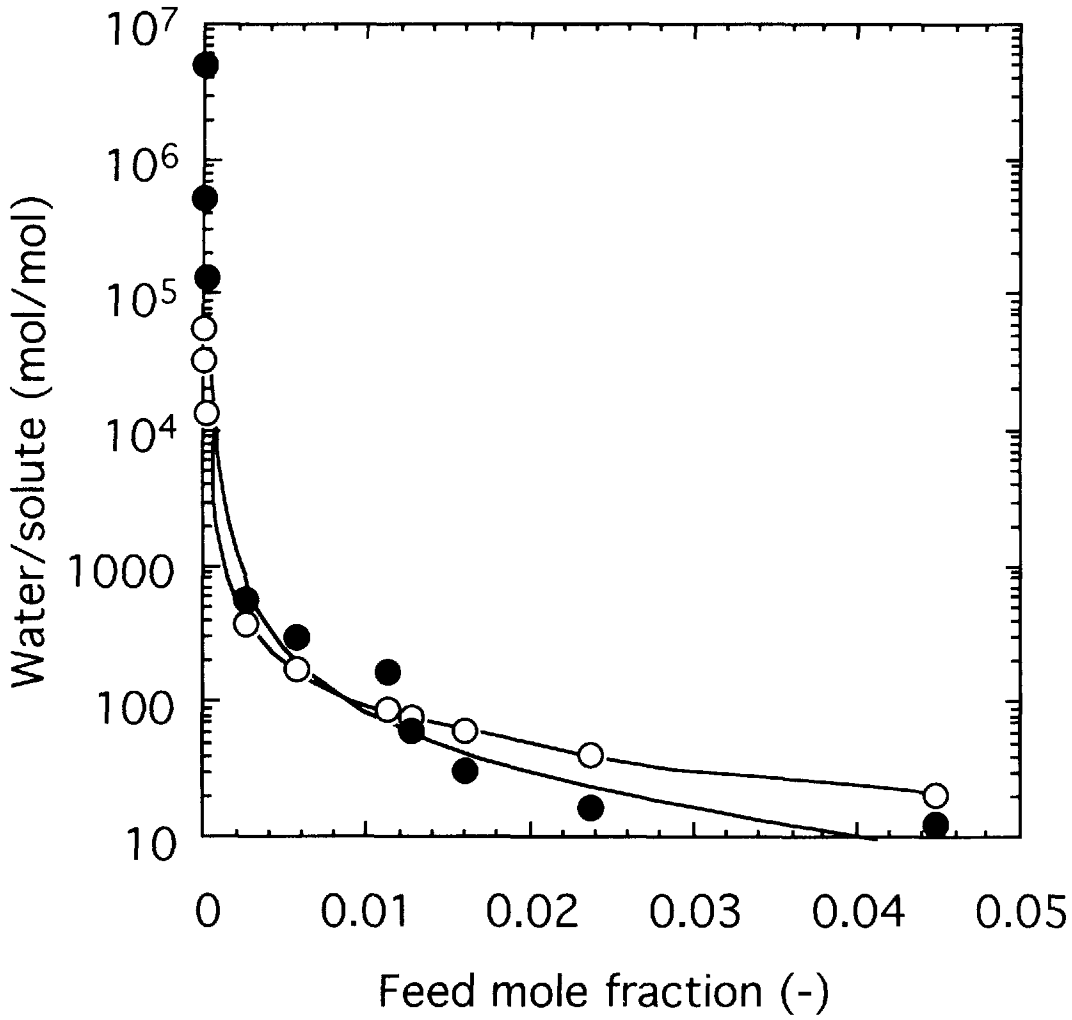

Fig. 3.7 Relationship between feed acetic acid concentration and water molecular number/acetic acid molecular number in feed or permeate solution: (○) in feed, (●) in permeate.

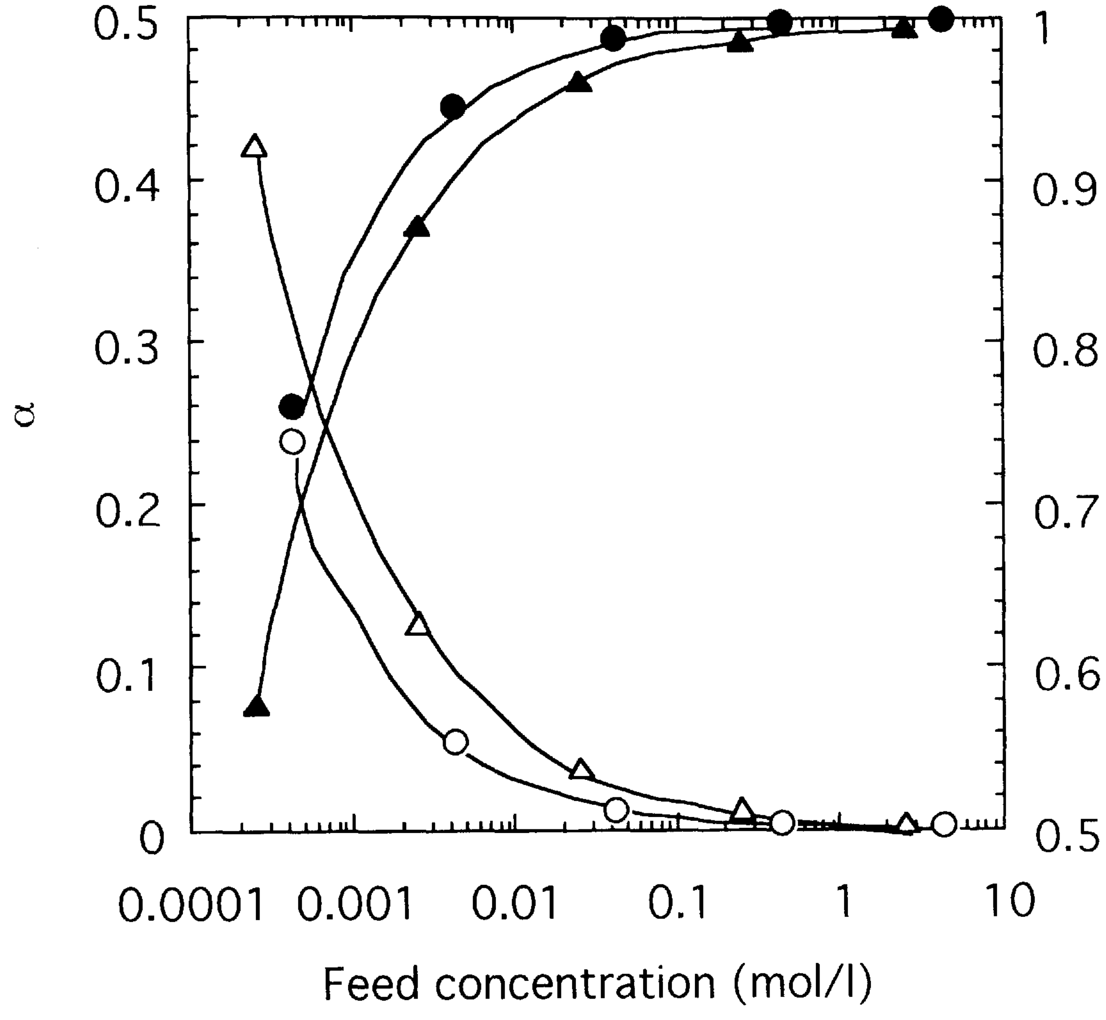

Fig. 3.8 Relationship between feed solute concentration and the degree of dissociation (α) or 1-α in feed.: (○) α for acetic acid, (●) 1-α for acetic acid, (△) α for n-butylamine, (▲) 1-α for n-butyl amine.

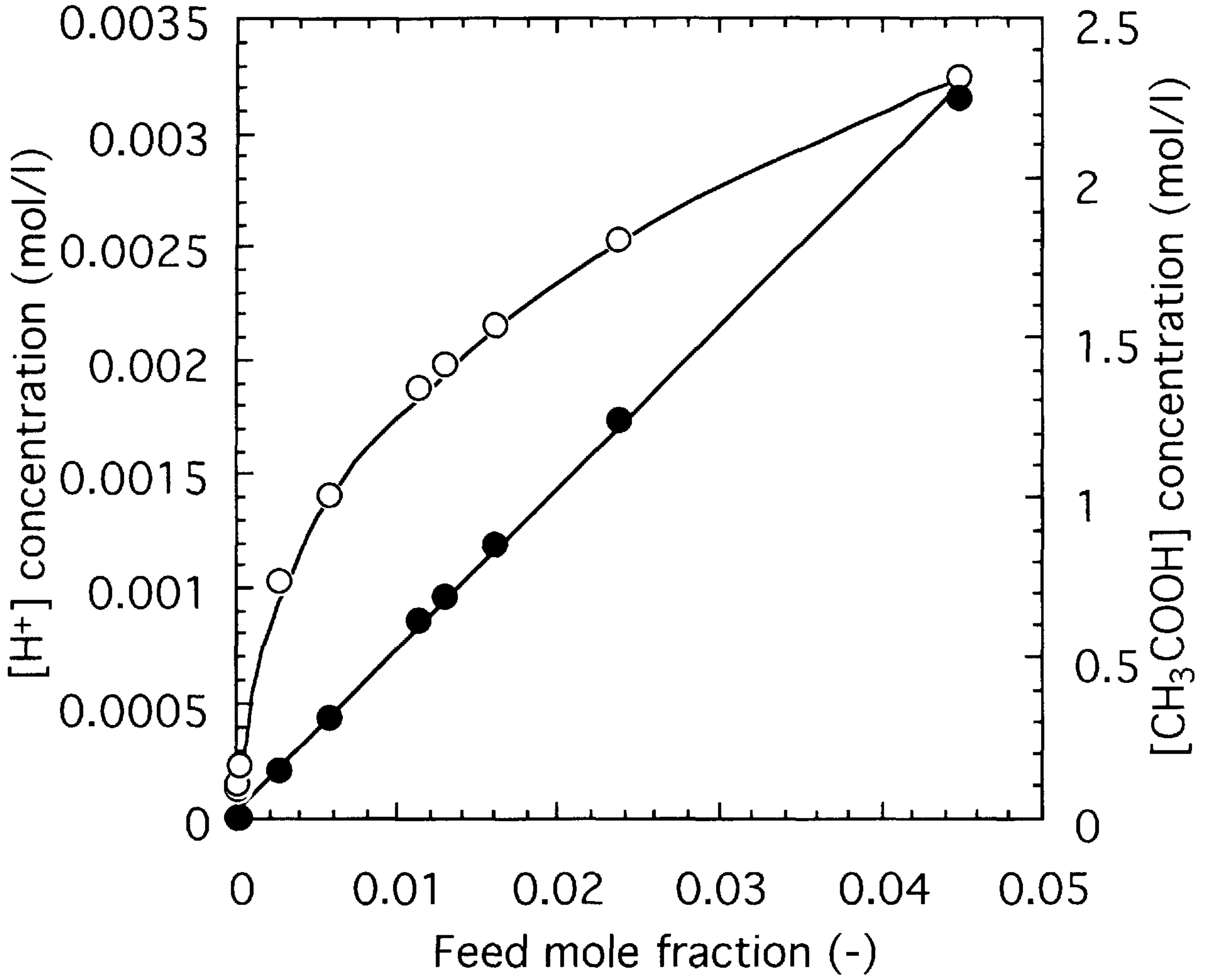

Fig. 3.9 Relationship between feed acetic acid concentration and [H^+] concentration or [CH_3COOH] concentration.: (○) [H^+], (●) {CH_3COOH}.

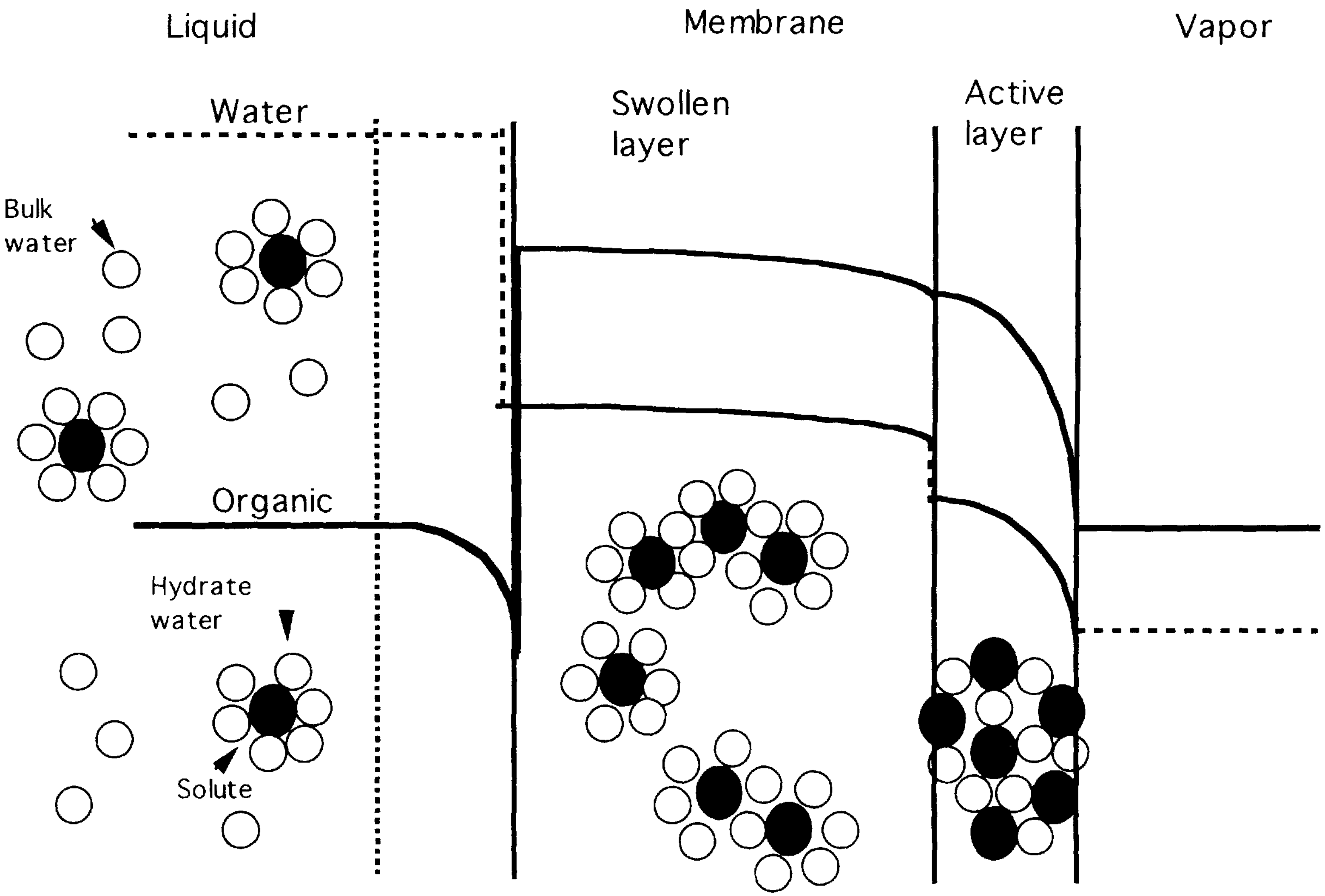

Fig. 3.10 Tentative illustration of the permeation through the PDMS membrane for solute-water mixture.

The number of water molecules per one solute in the feed or permeate solution as a function of the feed acetic acid concentration is shown in Fig.3.7. The water flux increased until the maximum at a feed acetic acid mole fraction of 0.025 because the hydration promoted water diffusion. When the feed concentration was over 0.025 mole fraction, the acetic acid solution was concentrated in the PDMS membrane and the permeate concentration was over 0.06 mole fraction. The hydration numbers for various solutes are shown in Table 1. One acetic acid molecule is hydrated to 12 water molecules. Almost all water molecules are involved in hydration at the 0.077 mole fraction. When the concentration was over 0.077 mole fraction, one water molecule hydrates several solute molecules and the motion of the water molecules are prevented. When the feed acetic acid concentration was over 0.025 mole fraction, the acetic acid solution was enriched in the PDMS membrane and the diffusion of water molecules was prevented by hydration of the solute molecules.

The total flux increased until the maximum feed acetic acid mole fraction of 0.025 and then decreased with increasing feed concentration due to the effect of water flux.

The acetic acid flux was significantly increased with increasing feed concentration. During the permeation of the aqueous acetic acid solution, acetic acid, acetate ion, and water molecules penetrate through the membrane. The degree of dissociation as a function of the feed acetic acid concentration is shown in Fig.3.8. The, proton or acetate ion as a function of the feed acetic acid concentration is shown in Fig.3.9. When the acetic acid mole fraction was below 0.01, the concentration of permeate solution was below 0.01 mole fraction and the degree of dissociation is high. Hence, the permeation of acetate ion controlled the total acetic acid permeation.

For the permeate transport, a solution-diffusion mechanism plays an important role. During the permeation of a dilute organic solution through the PDMS membrane, the permeate molecules quickly penetrate in a rubbery membrane like PDMS. Hence, the solubility significantly affects the permselectibity. Therefore, the permselectivity of acetate ion is not very high. Furthermore, the diffusivity of water, which is a small molecule, is high. The enrichment factor of acetic acid was below 1 at a 0~0.01 feed mole fraction. At a

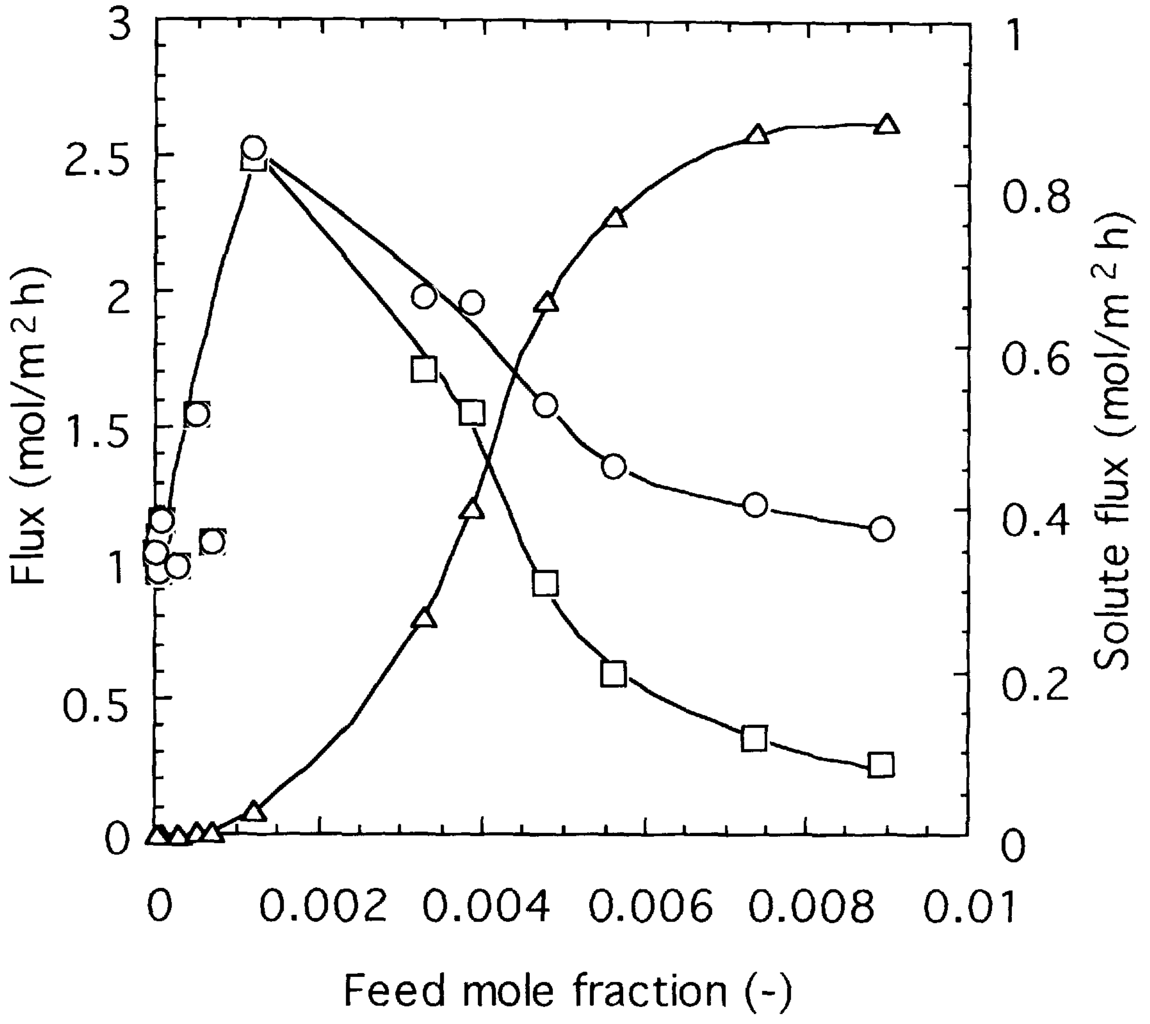

Fig. 3.11 Effect of feed concentration on flux for n-butylamine-water mixtures during pervaporation.: (□) *water flux*, (○) *total flux*, (△) *n-butyl amine flux*.

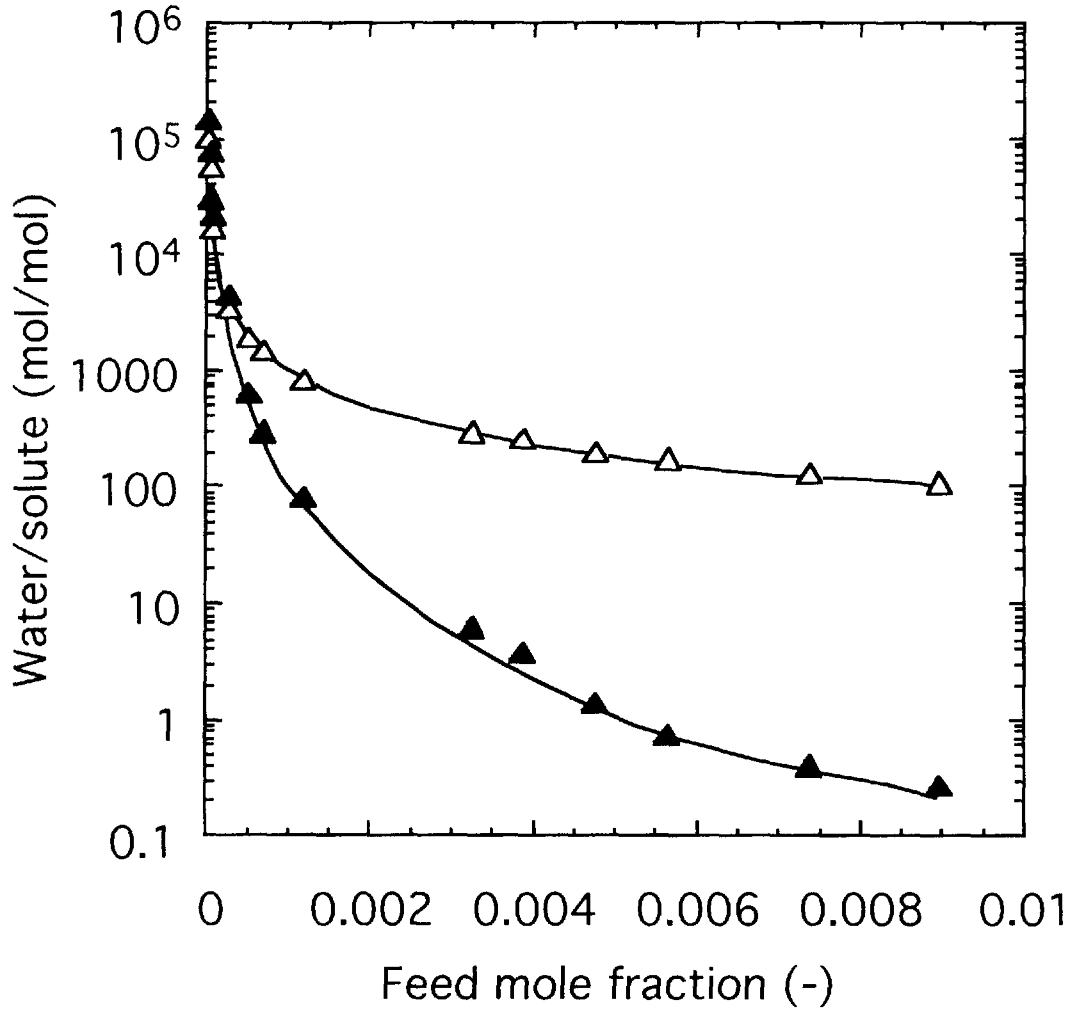

Fig. 3.12 Relationship between feed n-butyl amine concentration and water molecular number/n-butyl amine moleculer numbar in feed or permeate solution: (△) in feed, (▲) in permeate.

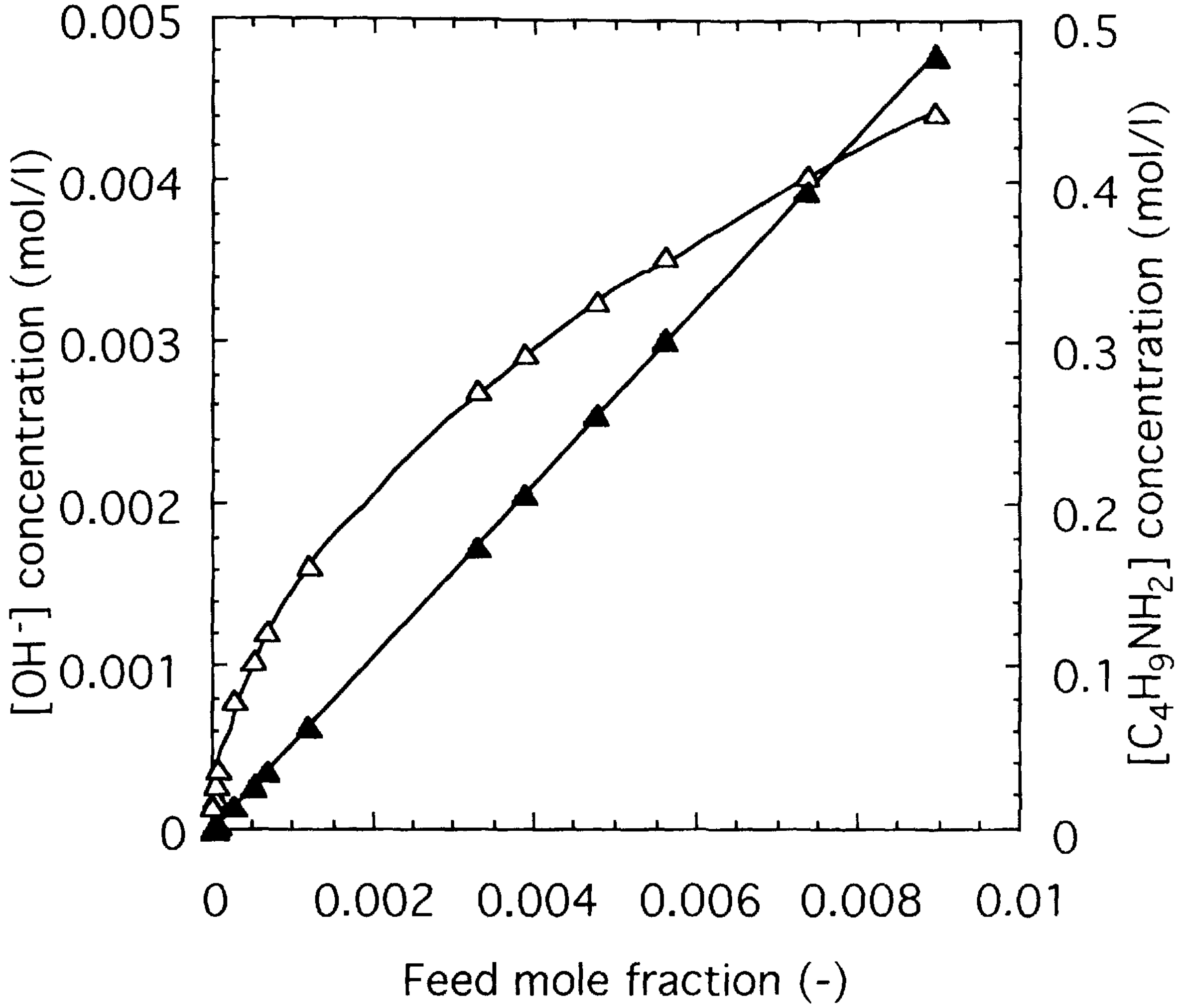

Fig. 3.13 Relationship between feed n-butyl amine concentration and [OH^-] concentration or [$C_4H_9NH_2$] concentration.: (△) [OH^-], (▲) {$C_4H_9NH_2$].

0.01~0.02 feed mole fraction, the concentration of permeate solution was over 0.01 mole fraction and the degree of dissociation is low. The acetic acid flux significantly increased with increasing feed concentration because the permeation of acetic acid was almost the same as the total acetic acid permeation. Over a 0.025 feed mole fraction, the diffusivity of acetic acid was also prevented by hydration. The tentative illustration of the permeation through the PDMS membrane for solute-water mixture is shown in Fig. 3.10. In the feed solution, water molecules are bulk water or hydrate water but when the solution is concentrated in the membrane, bulk water is deceased and hydrate water is included, hence, the diffusivity of molecules is prevented.

The flux as a function of the feed n-butyl amine concentration is shown in Fig.3.11 for the n-butylamine acid solution. The water flux increased until a maximum at the feed n-butylamine mole fraction of 0.0015 and then decreased with increasing feed concentration.

The number of water molecules per one solute in the feed or permeate solution as a function of the feed n-butyl amine concentration is shown in Fig.3.12. The water flux increased until a maximum feed n-butyl amine mole fraction of 0.0015 because the hydration promoted water diffusion. However, at the high feed concentration, mole fraction>0.0015, the n-butyl amine solution was concentrated in the PDMS membrane and the permeate concentration was over 0.05 mole fraction. The hydration numbers for various solutes are shown in Table 3.1. The hydration number of water molecules on n-butyl amine is 20. Almost all water molecules are involved in hydration at the 0.048 mole fraction. When the concentrations are over 0.048 mole fraction, the water molecules hydrate to several solute molecules and the motion of the water molecules are prevented. Hence, it is considered that over a 0.0015 feed mole fraction, the n-butyl amine solution was concentrated in the PDMS membrane and the diffusion of water molecules was prevented.

The total flux increased until a maximum at the feed n-butyl amine mole fraction of 0.0015 and then decreased with increasing feed concentration due to the effect of water flux. The n-butyl amine flux was significantly increased with increasing feed concentration.

For the permeation of an aqueous n-butyl amine solution, n-butyl amine, n-butyl ammonium ion, and water molecules are penetrats. The degree of dissociation as a function of the feed n-butyl amine concentration is shown in Fig.3.8. The hydroxy or n-butyl ammonium ion as a function of the feed n-butyl amine concentration is shown in Fig.3.13. Below a n-butyl amine mole fraction of 0.0015, the concentration of permeate solution was below a 0.02 mole fraction. Hence, the degree of disiccation is high and the permeation of the n-butyl ammonium ion affected the total n-butyl amine permeation.

The solubility of the n-butyl ammonium ion is not very high and the diffusivity of water, which is a small molecule, is high. Therefore, the permselectivity of the n-butyl ammonium ion is not very high. The enrichment factor of n-butyl amine was low at a 0<0.0015 feed mole fraction. At a 0.0015~0.008 feed mole fraction, the n-butylamine flux significantly increased with increasing feed concentration. When the n-butyl amine mole fraction was 0.0015 ~0.008, the concentration of the permeate solution was over 0.02 mole fraction. Hence, the degree of dissociation is low and the permeation of n-butyl amine was almost the same as the total n-butyl amine permeation. Over a 0.008 feed mole fraction, the diffusivity of n-butyl amine was also prevented by hydration.

3.4 Conclusions

In this chapter, the basic permeation behavior for PDMS membrane, the hydration effect on the sorption-diffusion mechanism for various organic compounds which is important like physic and chemical properties of penetrates was investigated.

The water molecule adjacent to the solute becomes less mobile in aqueous solutions of organic compounds than in the pure water due to the hydration. The liquid water has a distribution of hydrogen-bond clusters and space. The organic compounds dissolve in the space of the liquid water. The water molecules hydrate the solute molecules. The motion of the water molecules are prevented in the solute vicinity.

The water flux increased until a maximum at a low feed solute concentration because the hydration promoted water diffusion. However, at the high feed concentration, solute was concentrated in the PDMS membrane and permeate. Almost all water molecules are concerned with hydration when the concentration of (water molecules)/(solute molecules) is the same as the hydration number. When the actual concentration was over this concentration, the water molecules hydrate to several solute molecules and the motion of the water molecules is prevented. During pervaporation, the solute was concentrated in the PDMS membrane and the diffusion of water molecules was prevented. The permeation of the aqueous solution of dissociated solute included more interesting phenomena. For permeate transport, a solution-diffusion mechanism is important. The permselectivity of ions is not very high. Furthermore, the diffusivity of water, which is a small molecule, is high. When the dissociate solute mole fraction was a low, the concentration of permeate solution was a low mole fraction and the degree of dissociation is high. Hence, the permeation of organic ions affected the total dissociate solute permeation. The enrichment factor of dissociated compounds was low in the solution with a high degree of dissociation. At the high feed concentration, the solution was concentrated in the membrane and the degree of dissociation is low. The solute flux significantly increased with increasing feed concentration because the permeation of solute itself became the total solute permeation, until hydration prevents diffusion. The diffusivity of solute and water molecules are prevented by hydration when the concentration of (water molecules)/(solute molecules) is the same as the hydration number.

It was suggested that the enhancement of solubility of PDMS membrane was important to minimize the effect of the selectivity decrease for dissociate penetrates.

3.5 Acknowledgments

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Chapter 4. Characterization of UV Modified PDMS Membranes with Fluoroalkyl Methacrylate and Alkyl Methacrylate and their Permselectivity for Chlorinated Hydrocarbons

4.1 Introduction

Ground water contaminated with chlorinated hydrocarbons (VOC-Cl) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) which are used widely in detergents for metals and cleaning, etc., has been a social problem. Their toxicity has been made clear for several years[1]. Recently, the effluent is regulated, their discharge is regulated and the use of substitutes are considered. The purification of contaminated water has been extensively studied[2]. Pervaporation is an attractive and alternative to traditional methods (e.g., aeration, adsorption on activated carbon, photolysis and ozonization) for removing low concentrations of organic solvents from waste water because of its energy saving features and has been studied[2,3]. In the removal of very low concentrations of VOC-Cl from these contaminated waters (<1000g/m3), the use of pervaporation applications with membranes that permeate VOC-Cl preferentially has been considered[3]. The high selectivity of pervaporation makes it potentially very interesting for continuous recovery of VOC-Cl under compatible conditions[4-9].

Pervaporation performance of a membrane is determined by both the sorption and the diffusion characteristics of the permeating components in the membrane.

Polydimethylsiloxane (PDMS) has been well-known as an excellent polymer membrane material because of its high permeability (diffusivity) to gases and liquids. Fluorinated polymers have also been studied as membranes for organic aqueous mixture separation application and are expected to have excellent affinity for the organic compounds due to their hydrophobicity based on the low surface energy[9-12]. The enhancement of the affinity of PDMS for chlorinated hydrocarbons using fluoroalkyl methacrylates (FALMA) is interesting. For this improvement, the blending of PDMS and poly(FALMA) is difficult due to the low affinity of PDMS for poly(FALMA).

In this chapter, as the first step of improvement, the PDMS membrane was modified using sorbing fluorinated alkyl methacrylates followed by UV irradiation in order to maintain high diffusivity and increase the chlorinated hydrocarbon partition coefficient into the membrane. The effects of the fluoroalkyl side chain on increasing the chlorinated hydrocarbon partition coefficient into the membrane were determined with fluorinated n-alkyl methacrylate (FALMA) and non-fluorinated n-alkyl methacrylate (ALMA).

4.2 Experimental

4.2.1 Materials

Commercial PDMS membranes (Fuji Systems Corporation), 70μm thick, were used throughout this work. 2,2,3,3,3-pentafluoropropyl methacrylate (PFPMA), 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA), 2-(perfluorobutyl)ethyl methacrylate (PFBEMA), 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA) (Daikin Fine Chemical Laboratory Corporation), butyl methacrylate (BMA) and hexyl methacrylate (HMA) (Special grade,Tokyo Kasei Kogyo, Ltd.) were distilled and used. TCE, PCE, 1,1,1-trichloroethane and 2-propanol (Special grade,Waco Pure Chemical Industries, Ltd.) were used as received. The physic chemical properties of FALMA and ALMA used in this study are shown in Table 4.1.

4.2.2 The modification of PDMS Membrane by UV irrdiation

A PDMS membrane (d=7cm) was soaked in methacrylate monomers at room temperature. After reaching an equilibrium, the membrane was taken out of the monomer and excess solution on the surfaces was wiped off with filter paper. The membrane was then irradiated with a high pressure mercury lamp (400W, 365nm) on only one side of the membrane at a distance of 10 cm. After the irradiation, the membrane was placed between filter papers and dried for more than 48 hours in a vacuum oven.

4.2.3 Characterization of the modified PDMS membrane

X-ray photoelectron spectroscopy (XPS) spectra were obtained using an IPS-9000SX (JEOL, Ltd.) with MgKα exciting radiation (1253.6eV).The X-ray gun was operated at 10eV with a sample chamber vacuum of less than 5×10^{-9} Torr. The XPS spectra were recorded at two electron emission angles (J) of 30°and 90°.

Table 4.1 Structure of various FALMA & ALMA used in this study

Compound	Abbreviation	Formula	bp.
	FALMA		
2,2,3,3,3-Pentafluoropropyl methacrylate	PFPMA	$CH_2=C(CH_3)COO-$ $CH_2CF_2CF_3$	55℃/100mmHg
2,2,3,4,4,4-Hexafluorobutyl methacrylate	HFBMA	$CH_2=C(CH_3)COO-$ $CH_2CF_2CHFCF_3$	74℃/100mmHg
2-(Perfluorobutyl)ethyl methacrylate	PFBEMA	$CH_2=C(CH_3)COO-$ $CH_2CH_2(CF_2)_3CF_3$	61℃/5mmHg
1H,1H,9H-Hexadecafluorononyl methacrylate	HDFNMA	$CH_2=C(CH_3)COO-$ $CH_2(CF_2)_8H$	112℃/7mmHg
	ALMA		
Butyl methacrylate	BMA	$CH_2=C(CH_3)COO-$ $(CH_2)_3CH_3$	164℃
Hexyl methacrylate	HMA	$CH_2=C(CH_3)COO-$ $(CH_2)_5CH_3$	70℃/5mmHg

The IR and ATR-IR spectra were obtained using 1800 FT-IR/ATR spectroscopy (Perkin-Elmer Co., Ltd.).The instrument was operated at cycle=30.

The liquid film method was used in IR measurement. For ATR, the KRS-5 (TlBr-T(II)) internal refraction element (IRE) was used at an incident angle of 45°.

The differential scanning calorimeter (DSC) curve was obtained using a DSC7 (Perkin-Elmer Co., Ltd.). The DSC scan started from -150°C and was measured up to 300°C. The rate of temperature increase was usually 10°C/min.

4.2.4 Pervaporation experiment

The pervaporation experiments were performed using the continuous-feed type at

25°C. The apparatus is shown in Fig. 4.1. The feed solution was circulated through the cell and the feed tank. The modified surface of the membrane was kept in contact with the feed solution in the cell. The effective membrane area in the cell was 19.6 cm^2. The pressure on the permeation side was kept below 10 Torr by vacuum pumps. Upon reaching steady state flow conditions, the permeate was collected in traps cooled by liquid nitrogen (-196°C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate, flux(J), was obtained using eq.(4.1)

$$J=Q/At \qquad (4.1)$$

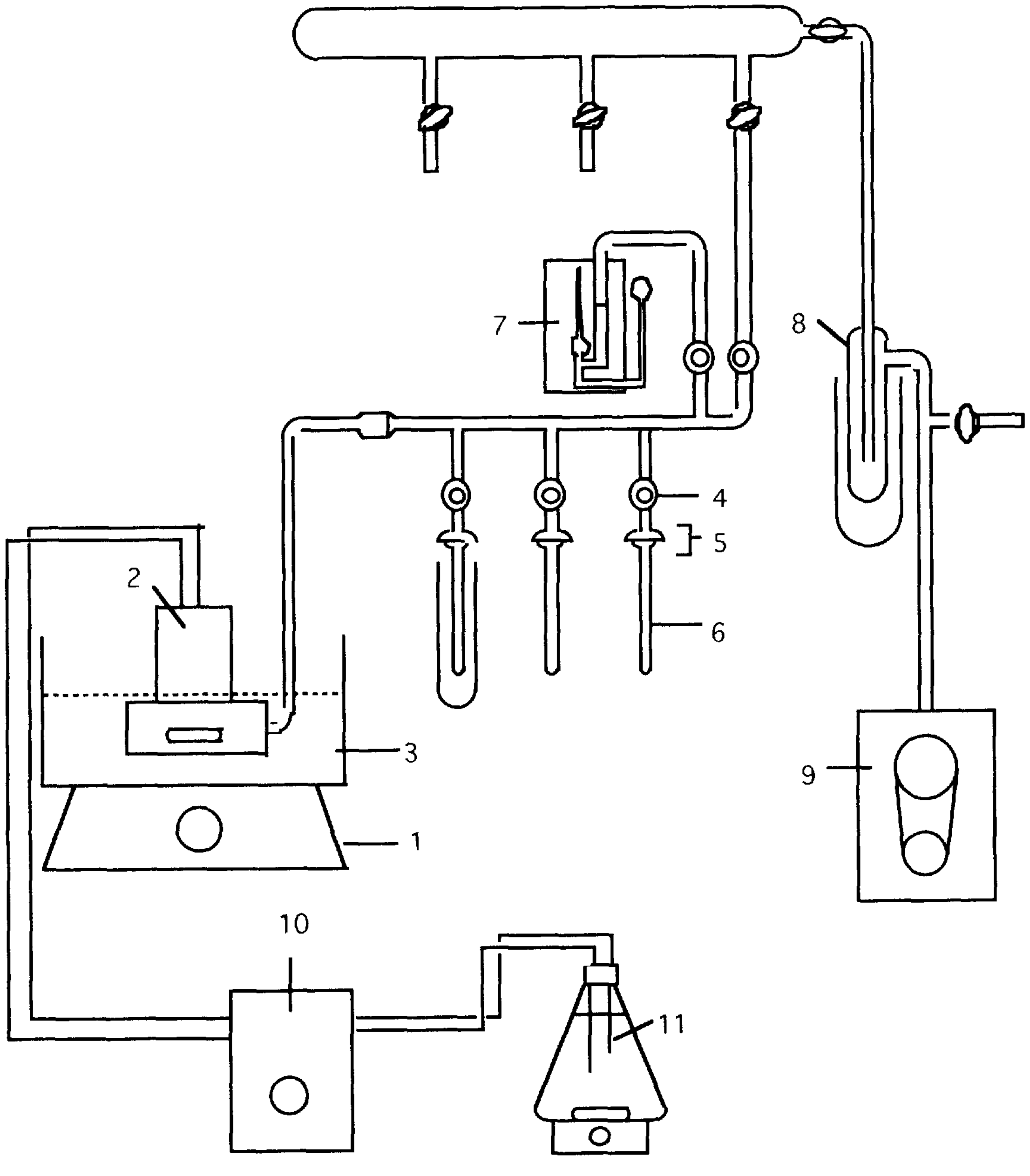
where Q is the amount that permeated during the experimental time interval, t, and A is the effective surface area. The VOC and water flux were calculated from the total flux and the permeate composition. The concentration of TCE in the feed and permeate solution was determined by gas chromatography with an *FID detector (Simazu GC-14A)*. The gas chromatography was operated using a Cromosorb W 60-80 *mesh column with Silicone DC-*200, 20wt% liquid phase. The VOC concentration in the permeate was high, which is far beyond its solubility limit in water. The phase separation took place in the permeate. 2-propanol was added to the permeate solution. The permeate solution was homogenized and analyzed to determine the VOC concentration. The separation factor during pervaporation, α_{pv}, was calculated as

$$\alpha_{pv}=\{Y(1-X)\}/\{(1-Y)X\} \qquad (4.2)$$

where X and Y denote the concentrations of VOC in the feed and permeate solutions, respectively.

4.2.5 Sorption measurement

The dried and weighed membrane was immersed in TCE solution and sealed at 25°C until equilibrium was reached. The membrane was then taken out of the vessel, wiped quickly with filter paper and weighed. The concentration of TCE solution soaked in the membrane was determined using the apparatus in the schematic diagram shown in Fig.4.2. The membrane on reaching equilibrium was taken out of the vessel, wiped quickly with filter



1: magnetic stirrer

2: pervaporation cell

3: constant temperature bath

4: greaseless cocks

5: ground glass joints

6: cold traps for collecting sample

7: vacuum gauge

8: cold trap

9: vacuum pump

10: micro tube pump

11: feed solution

Fig. 4. 1 Pervaporation apparatus.

paper and placed in trap A. The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, cock B was closed and the TCE solution soaked in the membrane and vaporized by heating with a drier was collected in cooled traps. The concentration of TCE solution in the feed and the soaked membrane was determined by gas chromatography.

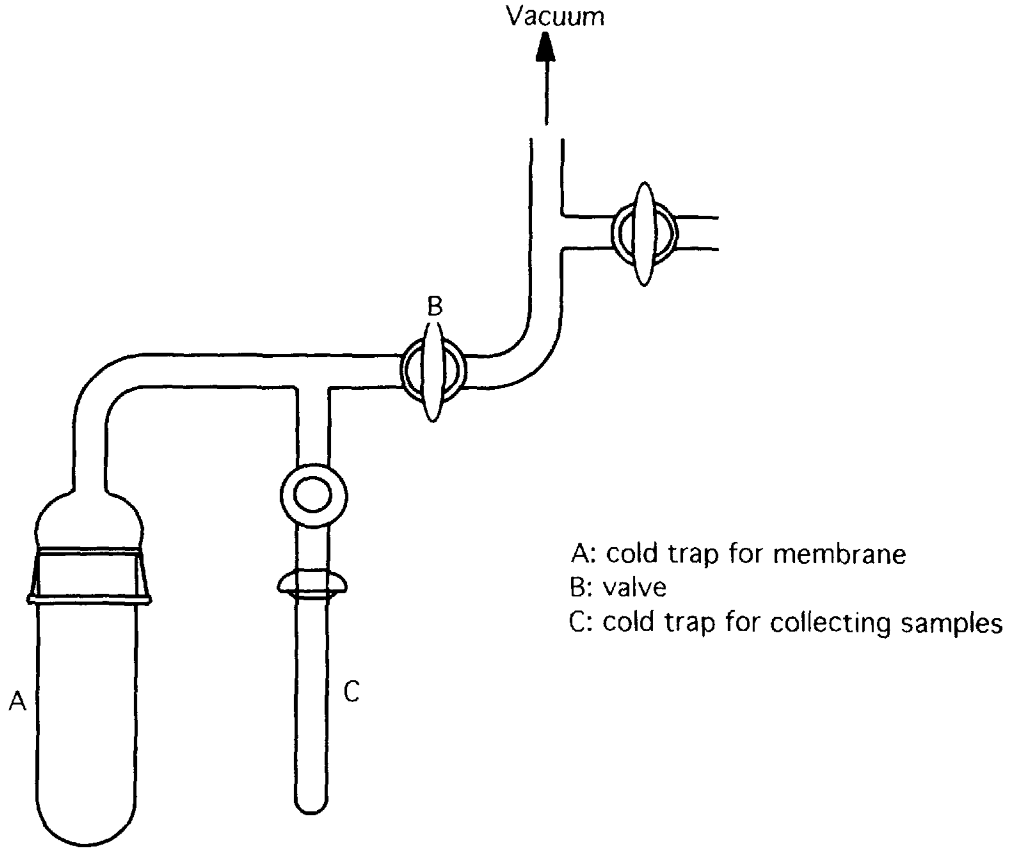


Fig. 4.2 Apparatus for the composition measurement in the membrane.

4.3 Results and discussion

4.3.1 Characterization of the modified PDMS membranes

The time that the membrane was soaked into the monomers was determined from the determination of equilibrium swelling time by weighing the membranes. Dependence of the degree of sorption on immersion time is shown in Fig.4.3 for HFBMA, HDFNMA and BMA. The degree of sorption was increased with increasing immersion time and equilibrium was reached in 1 hour. The immersion time was determined to be 1 hour.

The separation factor was calculated from the pervaporation measurement for each membrane for which the UV-irradiation time was varied by 3, 5, 10, 15, 20, and 30 minutes. Dependence of the selectivity in pervaporation on reaction time (i.e., irradiation time) is shown in Fig.4.4. The selectivity was increased with increasing reaction time and equilibrium in 15 minutes. The reaction time was determined to be 15 minutes. In this study, the PDMS membranes were immersed in FALMA or ALMA for 1 hour and irradiated by UV for 15 minutes to modify them. The modified PDMS membranes were then characterized and ultilized in pervaporation.

The polymerization of FALMA and ALMA by UV irradiation was investigated. HFBMA, HDFNMA and BMA were filled in a flat-bottom dish to a height of 1cm and irradiated for 15 minutes and 2 hours. The FALMA and ALMA irradiated for 15 minutes were highly viscous. The FALMA and ALMA irradiated for 2 hours were hardened. The FALMA and ALMA irradiated for 15 minutes were measured by Infra red (IR) spectra using the liquid film method. The FALMA and ALMA irradiated for 2 hours were measured by ATR. The results are shown in Fig.4.5.

The IR spectra showed a decreasing olefin C=C peak at 1655±5 cm^{-1} for the 15-min irradiated FALMA, but the peak was not found for 2-hour irradiated FALMA. Therefore, the sorbed FALMA and ALMA could be polymerized in the PDMS membranes.

The surface morphologies of the modified membranes were analyzed by ATR. The ATR spectra for the modified PDMS membranes was almost the same as the unmodified PDMS membrane. The FALMA polymer in PDMS was around 1wt%. Because these was

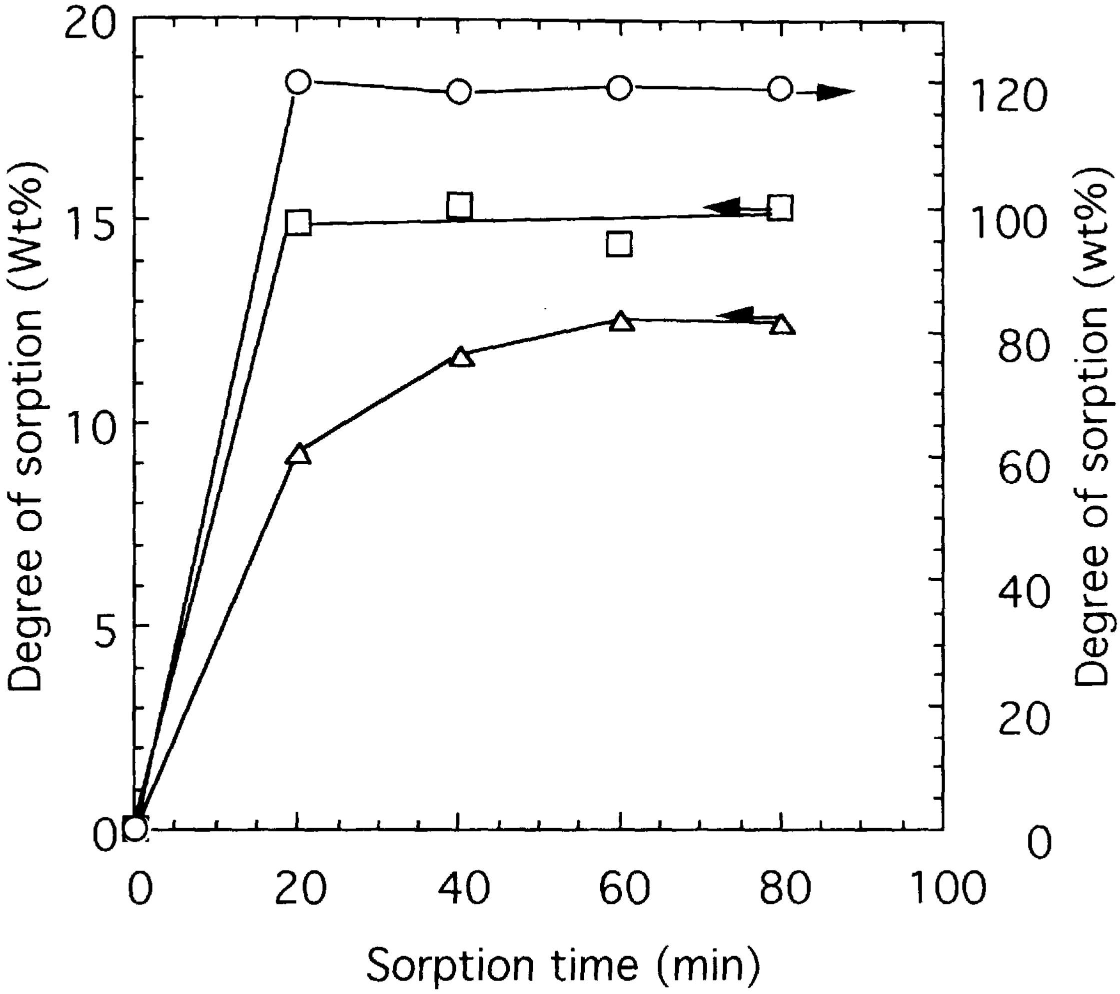


Fig. 4.3 Degree of sorption of methacryrates throughPDMS membrane.: (□) HFBMA, (△) HDFNMA, (○) BMA.

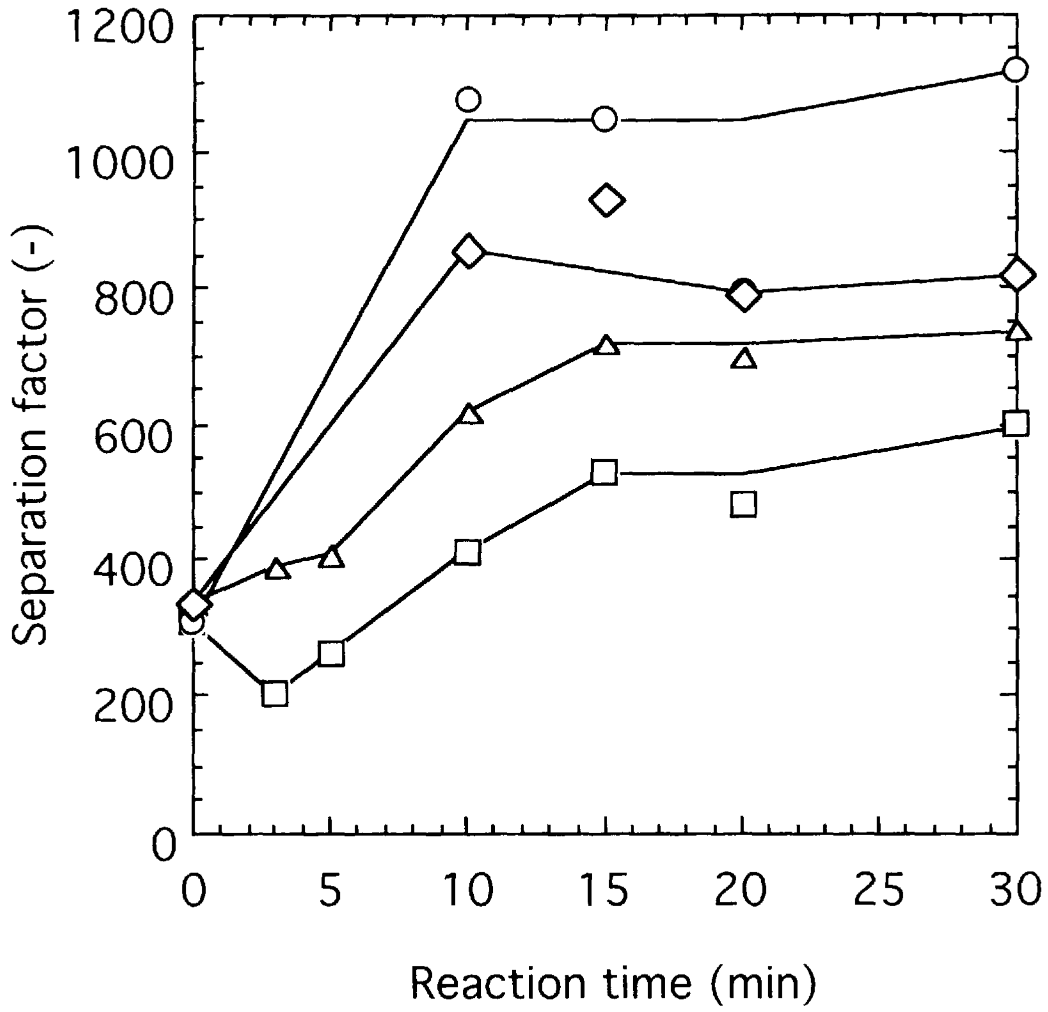


Fig. 4.4 Effect of UV irradiation time on separationfactor of TCE-water mixture through modified PDMS membrane. : (□) 0.01wt% feed solution for HFBMA-modified-PDMS membrane, (△) 0.025wt% feed solution for HFBMA-modified-PDMS membrane, (○) 0.01wt% feed solution for HDFNMA-modified-PDMS membrane, (◇) 0.025wt% feed solution for HDFNMA-modified-PDMS membrane.

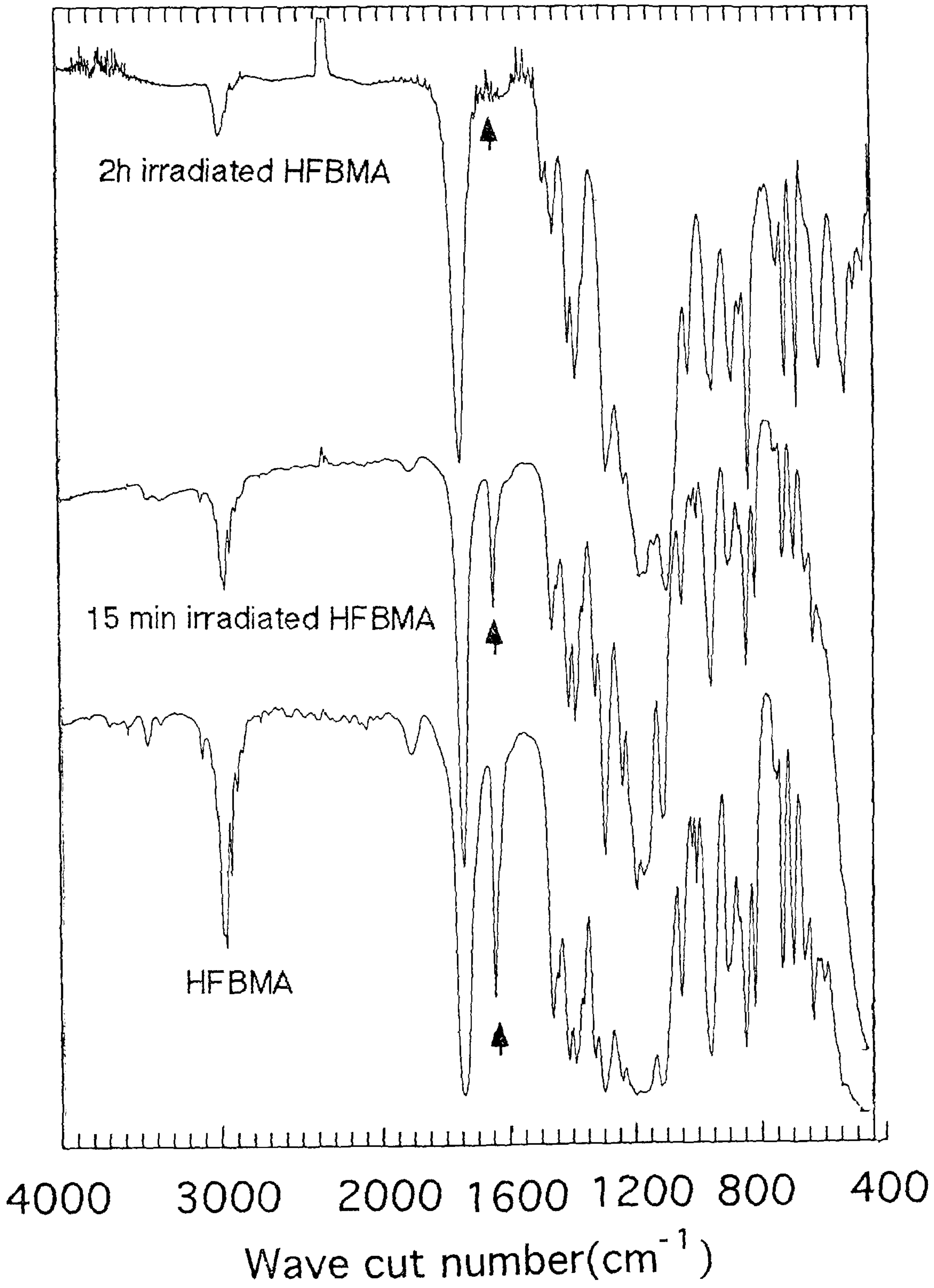


Fig. 4.5 IR spectra of HFBMA and UV irradiated HFBMA.

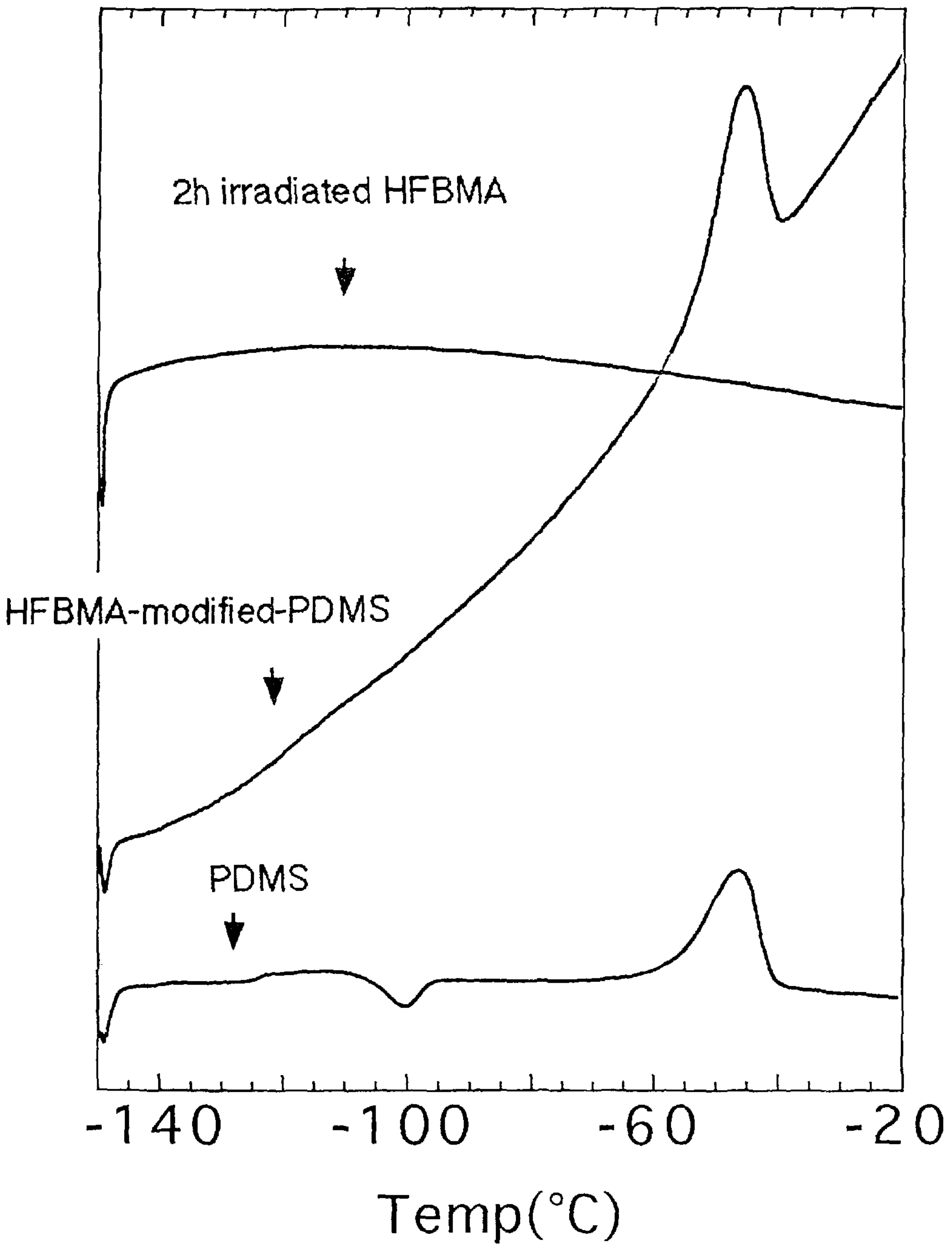


Fig. 4.6 DSC curve of PDMS, and HFBMA-modified-PDMS and UV irradiated HFBMA .

little FALMA polymer in the PDMS membrane, the peak for the polymer was not obtained by low sensitivity ATR[13].

The DSC curves of the modified membranes are shown in Fig.4.6. The glass transition peak at -124°C and a bond energy peak at -100°C were observed for PDMS. The peak for the homopolymer of FALMA polymerized by 2-hour irradiation was not observed in the range of -150°~300°C. The polymer polymerized by UV irradiation has a wide range of polymerization degrees, therefore, these peaks were not obtained. For the membrane after modification by FALMA, the endothermic peaks were not observed. The sorbed FALMA and ALMA were considered to be polymerized in the PDMS membranes.

The surface morphologies of the modified membranes were analyzed by XPS spectra. The ratios of fluorine, oxygen, carbon, and silicon atoms were analyzed and calculated for a few nm beneath the surface on the grafted membrane at 30° and 90° photoelectron emission angles and are characterized in Table 4.2. In this spectra, the composition of atoms are determined up to 4.5 and 9nm depth from the surface at photoelectron emission angles of 30° and 90°, respectively[13]. As the length of the fluorinated side chain of fluoroalkyl methacrylates increased (i.e., number of fluorine atoms increased), the ratio of fluorine atoms was increased at the surface. The ratio of fluorine atoms at 10° was higher than that at 90°; moreover, the results of the UV-irradiated side and non UV-irradiated side were almost the same. In this study, the PDMS membranes were immersed in FALMA or ALMA and irradiated by UV. These composite results suggest that the reaction of the sorbed monomer by UV-irradiation started with the irradiated surface and continued into the membrane[13]. It is considered that the degree of reaction on the inside and the reverse side of the PDMS membranes was lower than that on the surface.

The FALMA polymer in the modified PDMS membrane was extracted using acetone. The surface morphologies of the extracted membranes were then analyzed by XPS spectra. The ratio of fluorine atoms on the extracted membrane were decreased to 60-70% of the un-extracted membranes. It is considered that the polymerized FALMA and ALMA in PDMS did

Table 4.2 Fluorine to silicon atomic ratio for surface of PDMS and modified PDMS membranes by XPSAnalysis[a]

modified membranes	Electron emission angle	Atomic ratio F/Si angle	$CH_2=C(CH_3)COOR$ - R
PFPMA-modified-PDMS	10°	0.0177	$-CH_2CF_2CF_3$
(modified face)	90°	0.0138	
HFBMA-modified-PDMS	10°	0.0445	$-CH_2CF_2CHFCF_3$
(modified face)	90°	0.0086	
(reverse side)	90°	0.0171	
PFBEMA-modified-PDMS	10°	0.0726	$-CH_2CH_2(CF_2)_3CF$
(modified face)	90°	0.0210	
HDFNMA-modified-PDMS	10°	0.241	$-CH_2(CF_2)_8H$
(modified face)	90°	0.173	
(reverse side)	10°	0.127	

a : F/Si:Fluorine atomic ratio(%) / Silicon atomic ratio(%).

not have a sufficiently high degree of polymerization to be extracted. The extraction of the FALMA polymer in the modified PDMS membrane was investigated with 0.1w% aqueous TCE solution. The ratio of fluorine atoms on the immersed membrane was not decreased. The polymerized FALMA and ALMA in PDMS were not extracted by 0.1w% aqueous TCE solution.

4.3.2 The effects of the fluoroalkyl side chain on Sorption and pervaporation

The degree of sorption and the composition of TCE sorbed into the membrane are shown in Table 4.3. The degree of sorption was less than 1 wt% using the 0.035 wt% TCE solution, and the TCE concentration in the sorbed solution could not be measured. The degree of sorption in the modified PDMS membrane and the PDMS membrane was less than 10 wt% for the 0.1 wt% TCE solution. Because the PDMS membrane used in this study was crosslinked and there was little FALMA polymer in the modified PDMS membrane, the

Table 4.3 Sorption selectivity for PDMS and modified PDMS membranes

Membrane	TCE in feed (wt%)	Degree of Swelling (wt%)	TCE in membrane (wt%)	Separation factor α_s
PFPMA-modified-PDMS	0.034	<1	-[a]	-[a]
	0.10	3.2	32	450
HFBMA-modified-PDMS	0.035	<1	-[a]	-[a]
	0.10	7.2	49	980
PFBEMA-modified-PDMS	0.038	<1	-[a]	-[a]
	0.10	5.5	48	960
HDFNMA-modified-PDMS	0.037	<1	-[a]	-[a]
	0.11	4.9	66	1800
BMA-modified-PDMS	0.035	<1	-[a]	-[a]
	0.11	5.8	32	440
HMA-modified-PDMS	0.038	<1	-[a]	-[a]
	0.10	6.2	28	400
UV-modified-PDMS	0.035	<1	-[a]	-[a]
	0.10	7.0	40	640
PDMS	0.040	<1	-[a]	-[a]
	0.11	3.8	31	420

a : Not detected.

degree of sorption was slight. The TCE concentration of the sorbed solution in the modified PDMS membrane was between 32 and 66 wt% for the 0.1 wt% TCE solution, and the separation factor during sorption, α_s, was 400-1800. In FALMA monomers, HDFNMA-modified-PDMS had the highest TCE solubility. The sorbed TCE increased with increasing length of the fluorinated side chain of FALMA, i.e., the number of fluorine atoms. Both modified membranes with non-fluorinated ALMA and only UV-irradiated PDMS membrane were affected much less compared to the membranes modified with FALMA. The solubility of the modified PDMS membrane was attributed to the length of the fluorinated side chain of FALMA.

Table 4.4 Permeation selectivity for TCE-water mixture through PDMS and modified PDMS membranes

	Composition(wt%)		Flux	Separation
Membrane	Feed	Permeate	(10^{-3} kg/m^2/h)	factor α_p
PFPMA-modified-PDMS	0.010	2.4	29	250
	0.027	8.7	34	360
HFBMA-modified-PDMS	0.012	5.8	34	530
	0.026	16	30	720
PFBEMA-modified-PDMS	0.013	8.3	29	690
	0.027	20	33	920
HDFNMA-modified-PDMS	0.011	11	33	1100
	0.024	18	28	930
BMA-modified-PDMS	0.011	3.4	29	330
	0.024	6.0	39	270
HMA-modified-PDMS	0.011	2.2	39	200
	0.025	5.9	41	250
UV-modified-PDMS	0.009	4.9	22	550
	0.024	13	27	610
PDMS	0.011	3.4	27	310
	0.028	8.6	25	340

The pevaporation results of the dilute TCE solution through the modified PDMS membranes are shown in Table 4.4. The selectivity increased with increasing length of the fluorinated side chain of FALMA, i.e., the number of fluorine atoms. In FALMA monomers, HDFNMA-modified-PDMS had highest selectivity. Both modified membranes with non-fluorinated ALMA and only UV-irradiated PDMS membrane were affected much less compared to the membranes modified with FALMA. In the modified PDMS, the best separation performance was shown, due to the introduction of the hydrophobic polymer, poly(FALMA).

The relationship between the separation factor in permeation (α_{pv}), the separation factor in sorption (α_s), and the apparent separation factor in diffusion (α_d) is given by

Eq.(4.3).

$$\alpha_{pv}=\alpha_s \cdot \alpha_d \quad (4.3)$$

$$(P_A/P_B)=(K_A/K_B)\cdot(D_A/D_B) \quad (4.4)$$

where P_A and P_B denote the permeation coefficients of components A and B, K_A and K_B denote the solubility coefficients of components A and B and the diffusion coefficients of A and B, respectively. The solubility coefficient is given as

$$K_i=C_m/C_s \qquad (4.5)$$

where C_m and C_s denote the concentration of component i in the membrane and the solution, respectively. Because the molecular volume of TCE is larger than that of water, the diffusivity of TCE is less than that of water. The solubility of TCE then significantly affects the permselectivity. In this study, the membrane that showed the best separation performance was the membrane having the highest TCE concentration in the sorbed solution.

The flux of the modified PDMS membranes was increased or relatively the same compared to that of a non-modified PDMS membrane. This could be due to the fact that little reaction of the FALMA and ALMA occurred in the membrane and the diffusivity was as high as that of the non-modified PDMS membrane.

Table 4.5 Pervaporation data for chlorinated hydrocarbons-water mixture through PDMS and modified PDMS membranes

Chlorinated hydrocarbon	Membrane	Composition(wt%) Feed	Permeate	Flux (10^{-3} kg/m^2/h)	Separation factor α_p
Tetrachloroethylene	HDFNMA-modified-PDMS	0.0061	3.7	35	640
	PDMS	0.0065	1.3	28	200
1,1,1-trichloroethane	HDFNMA-modified-PDMS	0.0094	5.5	38	620
	PDMS	0.0088	2.4	31	280

The pevaporation results of dilute VOC solutions through the HDFNMA-modified-

PDMS membrane and the PDMS membrane are shown in Table 4.5. The selectivity of the HDFNMA-modified-PDMS membrane was high compared to that of the PDMS membrane. The flux of the modified membrane was not much affected by modification.

4.3.3 The effects of the fluoroalkyl methacrylate on diffusion

The permeate TCE concentration as a function of the feed TCE concentration is shown in Fig.4.7 for the modified PDMS membranes. For all the membranes, The TCE concentration in the permeate increased with increasing feed concentration. For the FALMA-modified-PDMS membranes, a high permeate TCE concentration was obtained.

The TCE flux as a function of the feed TCE concentration is shown in Fig.4.8 for the modified PDMS membranes. For all the membranes, The TCE concentration in the permeate were increased with increasing feed concentration, and for the FALMA-modified-PDMS membranes, the tendency was significant.

In pervaporation through the modified PDMS membrane, a "trade off" of permeability and selectivity was not obtained.

The flux as a function of the feed TCE concentration is shown in Fig.4.9 for the modified PDMS membranes. The flux of the modified PDMS membranes was increased or relatively the same compared to that of the non-modified PDMS membrane. For the FALMA-modified-PDMS membrane, the flux decreased with the feed concentration. The flux increased with increasing feed concentration in pervaporation through the ALMA-modified-PDMS membrane.

The flux as a function of the feed concentration in pervaporation through a non-porous homogeneous membrane is known as Fick's first law and is given by Eq. (4.6).

$$J_i=-D_i(\delta C/\delta x)_i \qquad (4.6)$$

where D_i, C and x denote the diffusion coefficient of component i, the concentration and the membrane thickness, respectively. Fick's first law pertains to any part of the membrane. With increasing feed concentration, the concentration in the membrane increases and the TCE

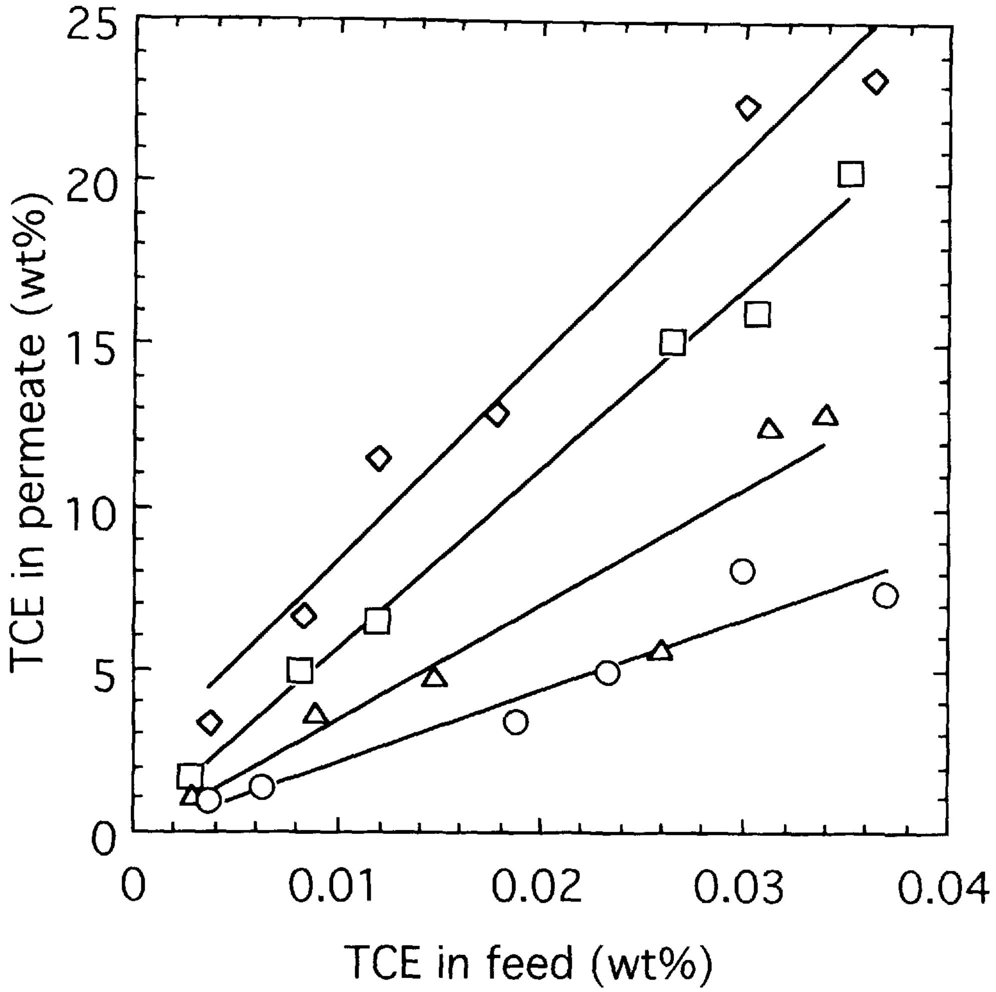


Fig. 4.7 Pervaporation of TCE-water mixtures throughPDMS and modified PDMS membranes. : (□) HFBMA-modified-PDMS membrane, (◇) HDFNMA-modified-PDMS membrane, (○) BMA-modified-PDMS membrane, (△) PDMS membrane.

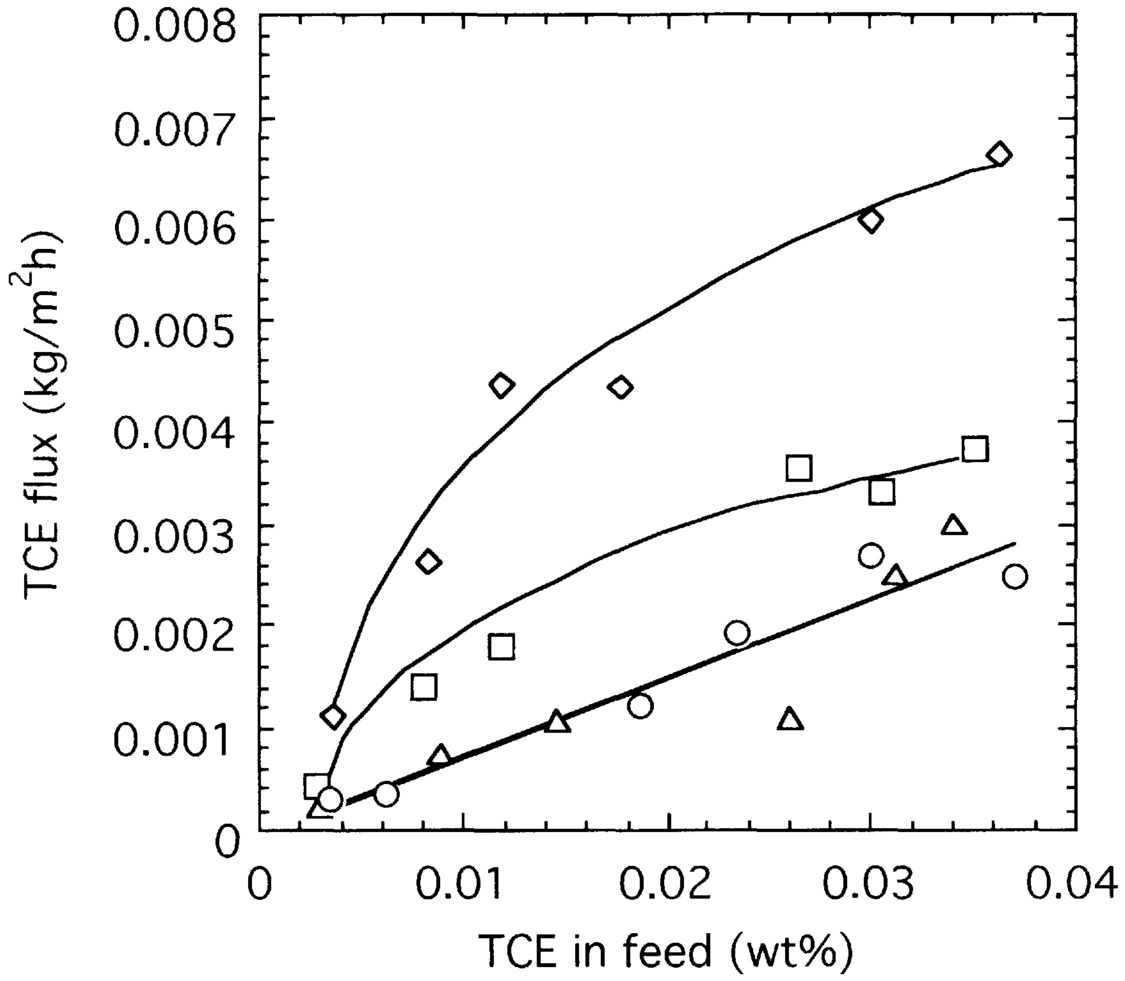


Fig. 4.8 Effect of feed concentration on TCE flux for TCE-water mixture in pervaporation through PDMS and modified PDMS membranes. : (□) HFBMA-modified-PDMS membrane, (◇) HDFNMA-modified-PDMS membrane, (○) BMA-modified-PDMS membrane, (△) PDMS membrane.

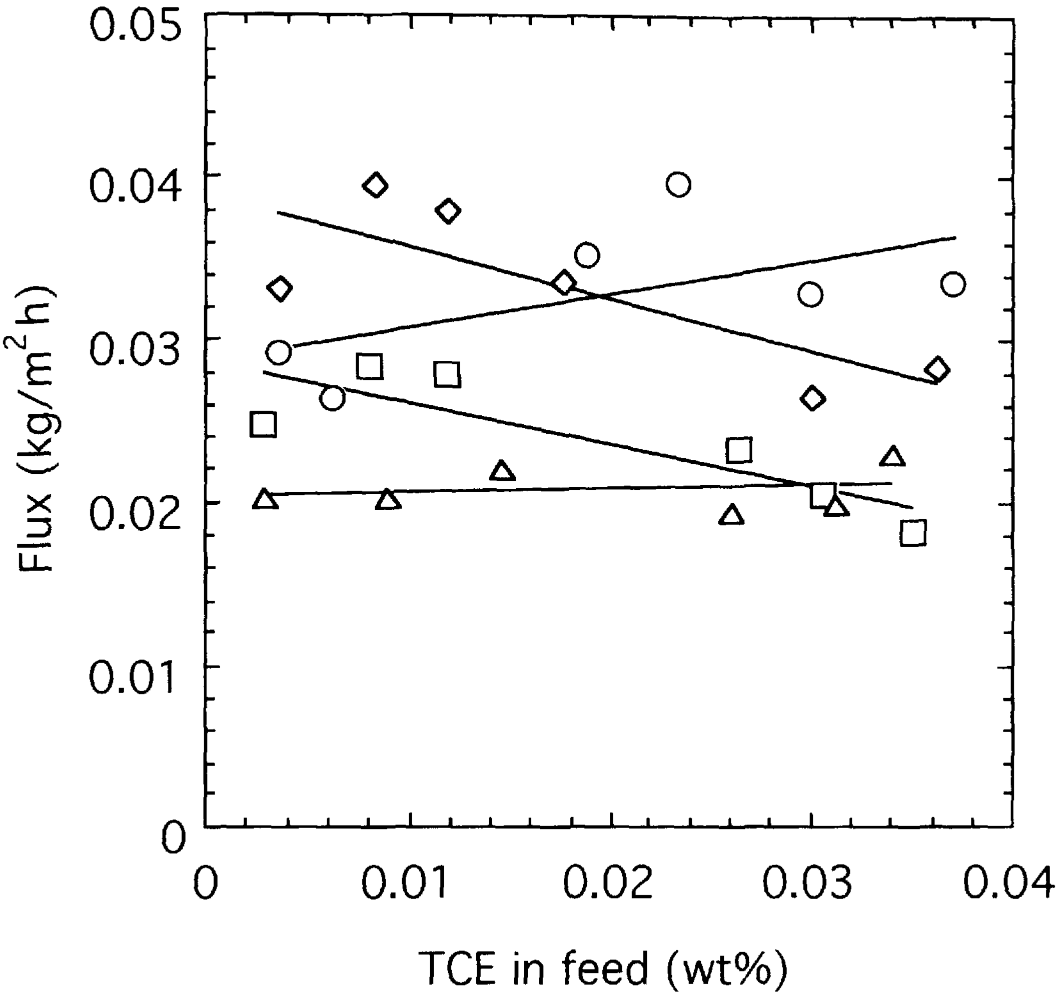


Fig. 4.9 Effect of feed concentration on flux for TCE-water mixture in pervaporation through PDMS and modified PDMS membranes. : (□) HFBMA-modified-PDMS membrane, (◇) HDFNMA-modified-PDMS membrane, (○) BMA-modified-PDMS membrane, (△) PDMS membrane.

flux increases. However, the flux decreased with the feed concentration for the FALMA-modified-PDMS membrane. Due to the introduction of a hydrophobic polymer, FALMA, the TCE quantity sorbed into the membrane was so high that the diffusion of water was prevented[7,14]; in turn, the flux decreased.

4.4 Conclusions

Membrane materials that preferentially permeate chlorinated hydrocarbons in pervaporation were investigated. The PDMS membrane in which FALMA and ALMA were sorbed, was irradiated by UV and ultilized in pervaporation. The polymerized FALMA and ALMA were contained in a modified membrane. The sorbed TCE in the modified membrane increased with increasing length of the fluorinated side chain of FALMA, i.e., the number of fluorine atoms. The membrane that showed the best separation performance was the membrane having the highest TCE concentration in the sorbed solution. The flux of the modified membrane was not much affected by modification. The results of pervaporation and sorption experiments showed that the partition coefficients for chlorinated hydrocarbons increased with the increase in n-fluoroalkyl chain length of the n-fluoroalkyl methacrylates, and, in turn, the permselectivity increased. In the permeation of the modified PDMS membrane, due to the introduction of a hydrophobic polymer, FALMA, the TCE quantity sorbed into the membrane was so high that the diffusion of water was prevented, in turn, the flux decreased.

4.5 Acknowledgments

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Chapter 5. Characterization of Graft Polymerization with Fluoroalkyl Methacrylate and Alkyl Methacrylate onto PDMS Membranes by Electron Beam and their Permselectivity for Chlorinated Hydrocarbons

5.1 Introduction

Recently, the contamination of ground water and soil by volatile organic compounds (VOCs) has become a social problem[1,2]. Pervaporation is attractive and potentially cost-competitive compared to these methods. The pervaporation of VOCs/water solution using organophilic polymers has been studied[1-24].

Polydimethylsiloxane (PDMS) membrane has been the most widely used and studied material to perform VOCs extraction because of its high permeability, ease of preparation into several shapes and relatively slight thickness[10,11,25-27]. To obtain the more useful membrane keeping the properties of the PDMS membrane, the synthesis of copolymers of PDMS and their improvement by the incorporation of fillers such as silicates and zeolites have been expected and studied[15,19]. Fluorinated polymers are recognized as the practical membrane materials just like PDMS and have been studied as organic compounds by their hydrophobicity based on low surface energy[18,28-30]. It is interesting to synthesize a more useful membrane material by combining the PDMS and fluorinated polymer. But, the affinity of PDMS to fluorinated polymer is low. Graft polymerization is a useful method to combine the polymeric materials with incompatible chemical and physical properties. Graft polymerization can be achieved by ionizing radiation, gamma ray, electron beam, ultraviolet light and plasma irradiation, and several papers have been reported on grafting[31-60]. In chapter 4, the PDMS membranes were modified by sorbing fluoroalkylmethacrylates (FALMA) and alkylmethacrylates (ALMA) using UV irradiation in order to increase the partition coefficient of chlorinated hydrocarbons into the membrane. However, in this method, the increase in the membrane weight by poly(FALMA) and poly(ALMA) is about 1wt%. Electron beam has high energy and is able to effectively graft-polymerize in quantity[31,32,38,39,47,48,51]. The growth of the graft chain by polymerization started with reactive radicals caused in the membrane [31,32]. Generally, vinyl monomer has been used in graft polymerization. Preirradiation and simultaneous irradiation have been known as the method of radiation-induced graft polymerization[31,32]. Preirradiation is a method in which a monomer is reacted with a polymer which had been irradiated in advance[41,42]. In simultaneous irradiation, monomer and polymer are irradiated simultaneously[31,32]. In this study, the improvement PDMS membranes by graft-polymerization of FALMA to enhance the affinity of PDMS to VOCs was studied [3-5,7].The grafted membranes increased the selectivity for VOCs and showed effective separation performance.

The solubility and diffusibility of the monomer for the membrane are important for the preirradiation method. The solubility is affected by the chemical affinity of the monomer for the membrane. Also, the molecular volume is closely concerned with the diffusibility of organic compounds. Hence, for the preirradiation method, the solubility parameter, the octanol-water partition coefficient (Pow) and the molecular volume are important. The solubility parameter (δ) by Hansen[61] can be described as:

$$\delta^2=\delta_d^2+\delta_p^2+\delta_h^2 \qquad (5.1)$$

$$\delta_d=(\Delta E_d/V)^{1/2} \qquad (5.1\text{-a})$$

$$\delta_p=(\Delta E_p/V)^{1/2} \qquad (5.1\text{-b})$$

$$\delta_h=(\Delta E_h/V)^{1/2} \qquad (5.1\text{-c})$$

where δ_d, δ_p and δ_h represent the solubility parameter of dispersion, polarization and hydrogen bonding, and $\Delta E_d/V$, $\Delta E_p/V$ and $\Delta E_h/V$ represent the energy density of dispersion, polarization and hydrogen bonding, respectively. Total heat of mixing of solvent and polymer (ΔH_m) is described using the solubility parameter as follows[61]:

$$\Delta Hm=V_m\cdot(\delta_{solvent}-\delta_{polymer})^2\cdot\phi_{solvent}\cdot\phi_{polymer} \qquad (5.2)$$

where V_m and ϕ represent the total molecular volume of the polymer solution and the volume fraction in the polymer solution, respectively. When ΔH_m is lower, that is, the difference of $\delta_{solvent}$ and $\delta_{polymer}$ is smaller, solvent and polymer are mixed more homogeneously. The hydrophobicity is used to indicate the physical property of the molecule which governs its partitioning into the nonaqueous partner of an immiscible or partially immiscible solvent pair[62]. According to Nernst[62], the partition coefficient can be simply described as:

$$P=C_O/C_W \text{ or } \log P=\log C_O-\log C_W \quad (5.3)$$

where C_O and C_W represent molar concentrations of the partitioned compound in the organic and aqueous phase, respectively. The octanol-water partition coefficient (P_{OW}) has been generally used in expressing hydrophobicity[62,63]. In hydrophobicity, Pow is closely concerned with the solubility of organic compounds[62,63].

In this chapter, we grafted PDMS membranes with FALMA and ALMA by the electron beam preirradiation method. We then investigated the effect of solubility and diffusibility of the monomer on graft polymerization and applied the grafted membrane to pervaporation.

5.2 Experimental

5.2.1 Graft polymerization of fluoroalkyl methacrylate by electron beam

Commercial PDMS membranes (Fuji Systems Corporation), 50 μm thick, were used throughout this work. 2,2,3,3,3-pentafluoropropyl methacrylate (PFPMA), 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA), 2-(perfluorobutyl)ethyl methacrylate (PFBEMA), 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA) (Daikin Fine Chemical Laboratory Corporation), butyl methacrylate (BMA) and hexyl methacrylate (HMA) (Special grade,Tokyo Kasei Kogyo, Ltd.) were used as received to avoid homopolymerization. Trichloroethylene (TCE), 2-propanol and acetone (Special grade,Waco Pure Chemical Industries, Ltd.) were used as received. The abbreviation and physico-chemical properties of FALMA and ALMA used in this study are given in Table 5.1.

The graft polymerization was performed as reported by Ishigaki et al.[47,48]. The schematic diagram of the apparatus is shown in Fig.5.1

Preirradiation:

A PDMS membrane of 7×7 cm evacuated in advance was placed in a polyethylene bag under nitrogen. The bag was then placed on dry ice and irradiated by an electron beam of a total dose of 150 kGy. The membranes were then placed in contact with degassed FALMA or ALMA monomer in the liquid phase under vaccum. After the polymerization was ended, the membranes were rinsed in acetone overnight to remove the homopolymers and the nonreacted monomers and dried for 48 hours in an evacuated vessel.

Table 5.1 Composition and properties of various FALMA and ALMA used in this study

Compound	Abbreviation	Formula	MW	bp.
	FALMA			
2,2,3,3,3-Pentafluoropropyl methacrylate	PFPMA	$CH_2=C(CH_3)COO-CH_2CF_2CF_3$	218.11	55°C/100mmHg
2,2,3,4,4,4-Hexafluorobutyl methacrylate	HFBMA	$CH_2=C(CH_3)COO-CH_2CF_2CHFCF_3$	250.13	74°C/100mmHg
2-(Perfluorobutyl)ethyl methacrylate	PFBEMA	$CH_2=C(CH_3)COO-CH_2CH_2(CF_2)_3CF_3$	332.15	61°C/5mmHg
1H,1H,9H-Hexadecafluorononyl methacrylate	HDFNMA	$CH_2=C(CH_3)COO-CH_2(CF_2)_8H$	500.16	112°C/7mmHg
	ALMA			
Butyl methacrylate	BMA	$CH_2=C(CH_3)COO-(CH_2)_3CH_3$	142.20	164°C
Hexyl methacrylate	HMA	$CH_2=C(CH_3)COO-(CH_2)_5CH_3$	170.25	70°C/5mmHg

Simultaneous irradiation:

A PDMS membrane of 7x7 cm and a FALMA or ALMA monomer were simultaneously degassed. After reaching equilibrium, the membrane was taken off the monomer, the excess solution on the surfaces was wiped off with a filter paper and placed in a polyethylene bag under nitrogen. The membrane was then grafted by the same method as preirradiation. The degree of grafting was calculated as:

$$\text{Degree of grafting}(\%)=(W_1-W_0)/W_0\times 100 \quad (5.4)$$

where W_0 and W_1 denote the weight of the PDMS membrane and the grafted PDMS membrane, respectively.

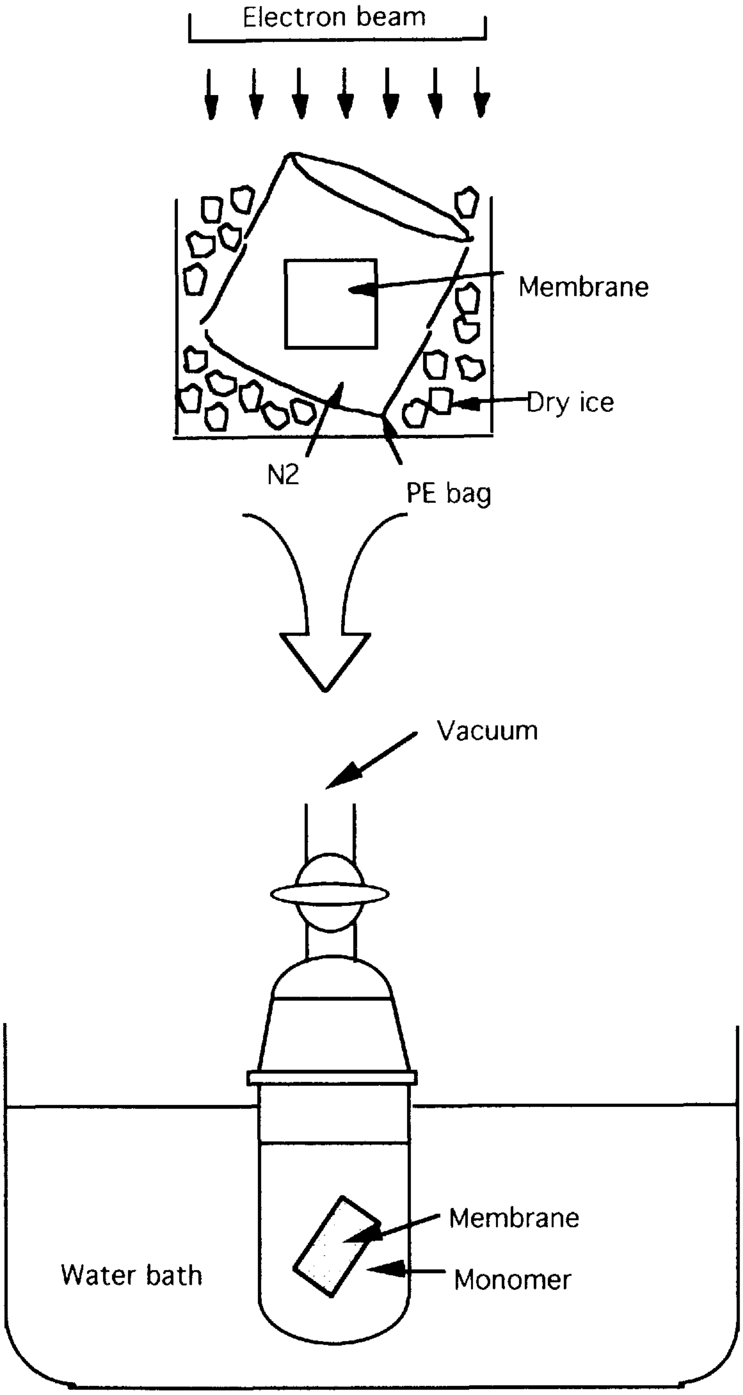

Fig. 5.1 Apparatus for the graft polymerization by Electron beam.

5.2.2 Characterization of the grafted PDMS membrane

X-ray photoelectron spectroscopy (XPS) spectra were obtained using an IPS-9000SX (JEOL, Ltd.) with MgKα exciting radiation (1253.6 eV). The X-ray gun was operated at 10 eV with a sample chamber vacuum of less than 5×10^{-9} Torr. The XPS spectra were recorded at two electron emission angles (ϑ) of 30°and 90°.

5.2.3 Pervaporation experiment and sorption measurement

The pervaporation experiments were performed in a previous study[3-5,7] using the continuous-feed type at 25 °C. The feed solution was circulated through the cell and the feed tank. The grafted surface of the membrane was kept in touch with the feed solution in the cell. The effective membrane area in the cell was 19.6 cm^2. The pressure on the permeation side was kept below 10 Torr by vacuum pumps. Upon reaching steady-state flow conditions, the permeate was collected in traps cooled by liquid nitrogen (-196 °C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate of solution, total flux (J), was obtained using eq.5.5

$$J=Q/At \qquad (5.5)$$

where Q is the amount that permeated during the experimental time interval, t, and A is the effective surface area. The TCE and water flux were calculated from the total flux which is the permeation rate of solution (J) and the permeate composition.

The concentration of TCE in the feed and permeate solution was determined by gas chromatography using an FID detector. The TCE concentration in the permeate was high, which is far beyond its solubility limit in water. The phase separation took place in the permeate. 2-propanol was added to the permeate solution. The permeate solution was homogenized and analyzed to determine the TCE concentration. The separation factor during pervaporation, α_{pv}, was calculated as:

$$\alpha_{pv}=\{Y(1-X)\}/\{(1-Y)X\} \qquad (5.6)$$

where X and Y denote the concentrations of TCE in the feed and permeate solutions, respectively and their concentration unit is weight per cent (wt%).

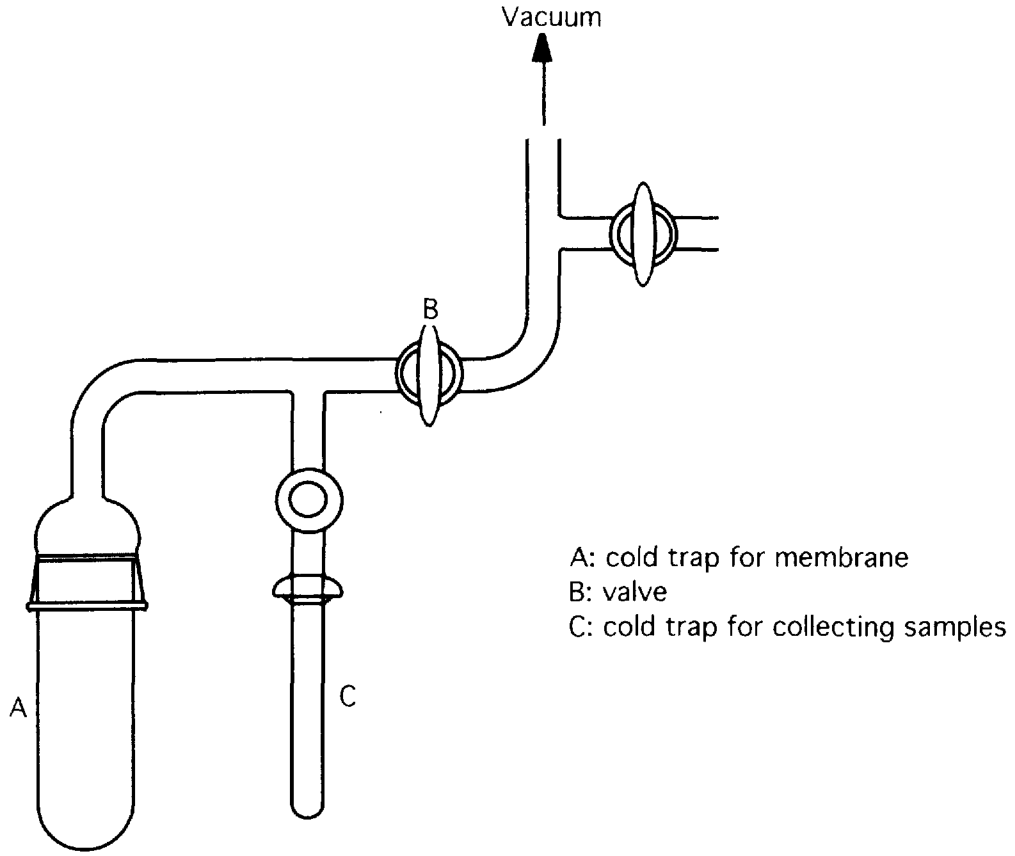

Fig. 5.2 Apparatus for the composition measurement in the membrane.

The dried and weighed membrane was immersed in TCE solution or TCE liquid and sealed at 25 °C until equilibrium was reached. The membrane was then removed from the vessel, quickly wiped with filter paper and weighed. The degree of sorption of the TCE liquid of the TCE solution into the membranes was measured as:

$$\text{Degree of sorption}(\%)=(W_3-W_2)/W_2\times 100 \quad (5.7)$$

where W_2 and W_3 denote the weights of the dried membrane and the swollen membrane, respectively.

The concentration of the TCE solution soaked into the membrane was determined using the apparatus shown in Fig.5.2. Upon reaching equilibrium, the membrane was removed from the vessel, quickly wiped with filter paper and placed in cold trap A. The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, valve B was closed, and the TCE solution soaked in the membrane was vaporized by heating with a drier and collected in cold trap C.

The concentration of TCE solution in the feed and the soaked membrane was determined by gas chromatography the same as in the pervaporation experiment. The separation factor during sorption, α_S, was calculated as:

$$\alpha_S=\{Y'(1-X)\}/\{(1-Y')X\} \quad (5.8)$$

where X and Y' denote the concentrations of TCE in the feed solution and the swollen membranes, respectively and their concentration unit is weight per cent (wt%).

5.3 Results and discussion

5.3.1 Graft-polymerization of Fluoroalkyl methacrylate by Electron beam

Dependence of the degree of grafting on polymerization time (i.e. immersion time) for HDFNMA grafted PDMS membrane by preirradiation is shown in Fig.5.3. The degree of grafting was increased with increasing polymerization time and achieved equilibrium in 2 hours. Therefore, the polymerization time was determined to be 2 hours. The degree of grafting obtained was around 4.4 wt% for HDFNMA. The degree of sorption for PDMS with HDFNMA is 12.6 wt%. The grafted amount of HDFNMA was less than the sorpted amount. One part of the HDFNMA sorpted into the PDMS membrane was grafted onto the PDMS membrane.

5.3.2 Characterization of the grafted PDMS membrane

The surface morphologies of the grafted membranes were analyzed by XPS spectra. The ratios of fluorine, oxygen, carbon, and silicon atoms were analyzed and calculated for a few nm beneath the surface on the grafted membrane at 30° and 90° photoelectron emission angle and characterized in Table 5.2. In this spectra, the composition of the atoms is determined up to 4.5- and 9-nm depth from the surface at the photoelectron emission angle of

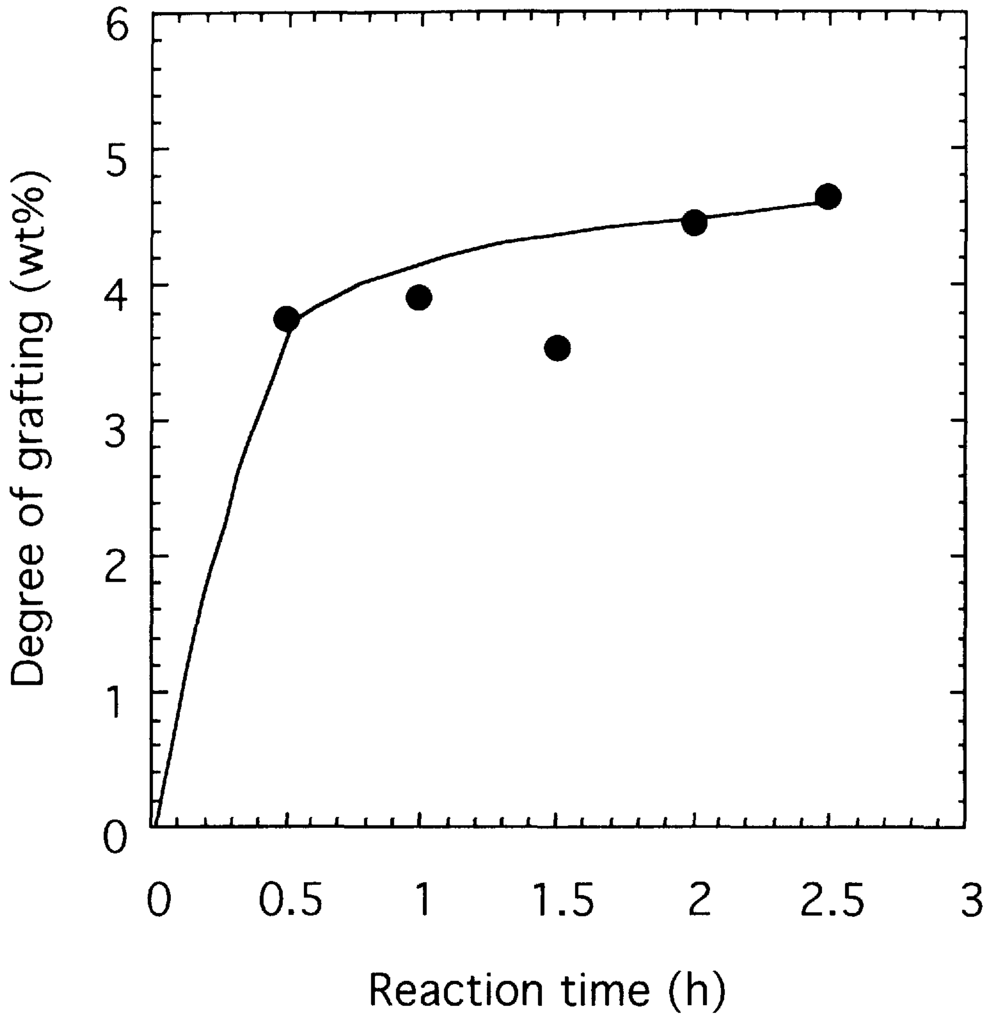

Fig. 5.3 Dependence of the degree of grafting on polymerization time for HDFNMA grafted PDMS membrane by preirradiation.

Table 5.2 Fluorine to silicon atomic ratio for surface of PDMS and grafted PDMS membranes by XPS analysis

Grafted membranes	Electron emission angle (°)	F/Si by XPS	Degree of grafting (wt%)	F/Si calculated by degree of grafting
PFPMA-grafted-PDMS	30	0.463	10.1	0.1716
(pre-irradiation)	90	0.456		
HFBMA-grafted-PDMS	30	0.057	5.6	0.09957
(pre-irradiation)	90	0.011		
PFBEMA-grafted-PDMS	30	0.07	5.9	0.1185
(pre-irradiation)	90	0.113		
HDFNMA-grafted-PDMS	30	0.226	4.4	0.1067
(pre-irradiation)	90	0.347		
(reverse side)	30	0.106		
	90	0.142		
HDFNMA-grafted-PDMS	30	0.355	4.5	0.1091
(simultaneous irradiation)	90	0.260		
(reverse side)	30	0.381		
	90	0.167		

30° and 90°, respectively[64]. As the ratio of the fluorine atom calculated by the degree of grafting increased, the ratio of the fluorine atom by XPS increased at the surface. The F/Si ratio on the reverse side of the grafted PDMS membranes was lower than the F/Si on the grafted surface by preirradiation. After the irradiation, the degassed FALMA was placed in the reactor, and the PDMS membranes were soaked and grafted. The graft polymerization was promoted in the grafted PDMS membrane[64]. The quantity of the radicals on the inside and reverse side of the grafted PDMS membrane was lower than that on the surface. Hence, the degree of grafting on the inside and reverse side of the grafted PDMS membrane was lower than that on the surface. By a simultaneous irradiation method that irradiates a membrane swollen by a monomer, the F/Si ratio on the reverse side of the grafted PDMS membranes was not so low compared to the F/Si on the grafted surface.

5.3.3 The diffusivity of fluoroalkyl methacrylate through PDMS membrane

We investigated the effect of solubility and diffusibility of the monomer on graft polymerization according to solubility parameter, octanol- water partition coefficient (P_{ow}) and the molecular volume of the monomer.

Table 5.3 Sorption and solubility data of various FALMAs and ALMAs for PDMS membrane

Compound	Degree of sorption in PDMS membrane (mol / PDMS-100g)	Degree of grafting in PDMS membrane (mol / PDMS-100g)	Molecular volume (cm^3 / mol)	Solubility parameter ($[J / m^3]^{1/2}\ 10^{-3}$)	logPow
PFPMA	0.152	0.046	170	16.18	2.74
HFBMA	0.062	0.022	187	16.70	2.82
PFBEMA	0.055	0.018	240	15.84	2.84
HDFNMA	0.025	0.0089	325	16.25	3.61
BMA	0.840	0.017	158	18.04	2.88
HMA	0.649	0.013	193	17.95	3.75
PDMS				15.11	

The sorption amount and grafted amount are shown in Table 5.3. The sorption amount of ALMA in the PDMS membrane was 10 times as much as the sorpted FALMA amount. The grafted amount of ALMA was about the same as the grafted FALMA amount. The grafted amount/ sorpted amount for each FALMA and ALMA is shown in Fig.5.4. Around 33% of FALMA sorpted in PDMS membrane was grafted, and around 2% of ALMA sorpted in PDMS membrane was grafted. The ratio of the grafted amount to the sorpted amount of monomer in the same group of FALMA or ALMA was almost the same. The relationships

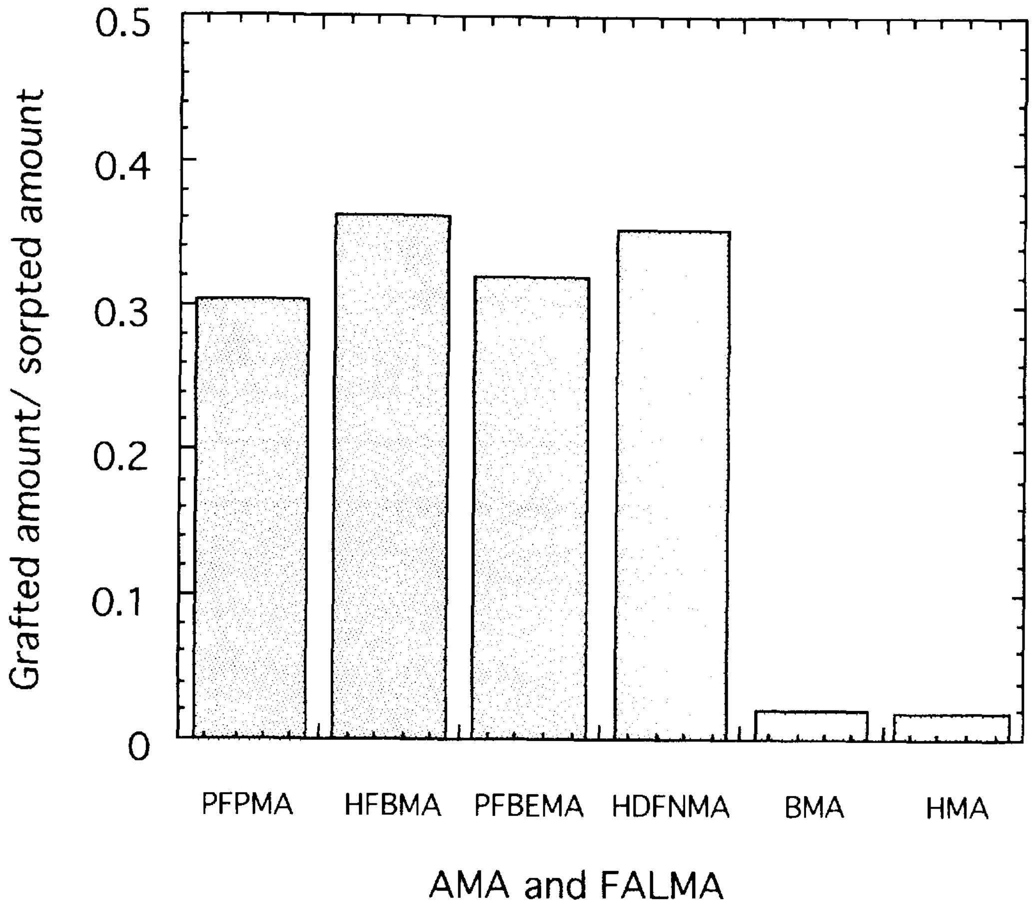

Fig. 5.4 The grafted amount/ sorpted amount for each FALMA and ALMA in PDMS membrane.

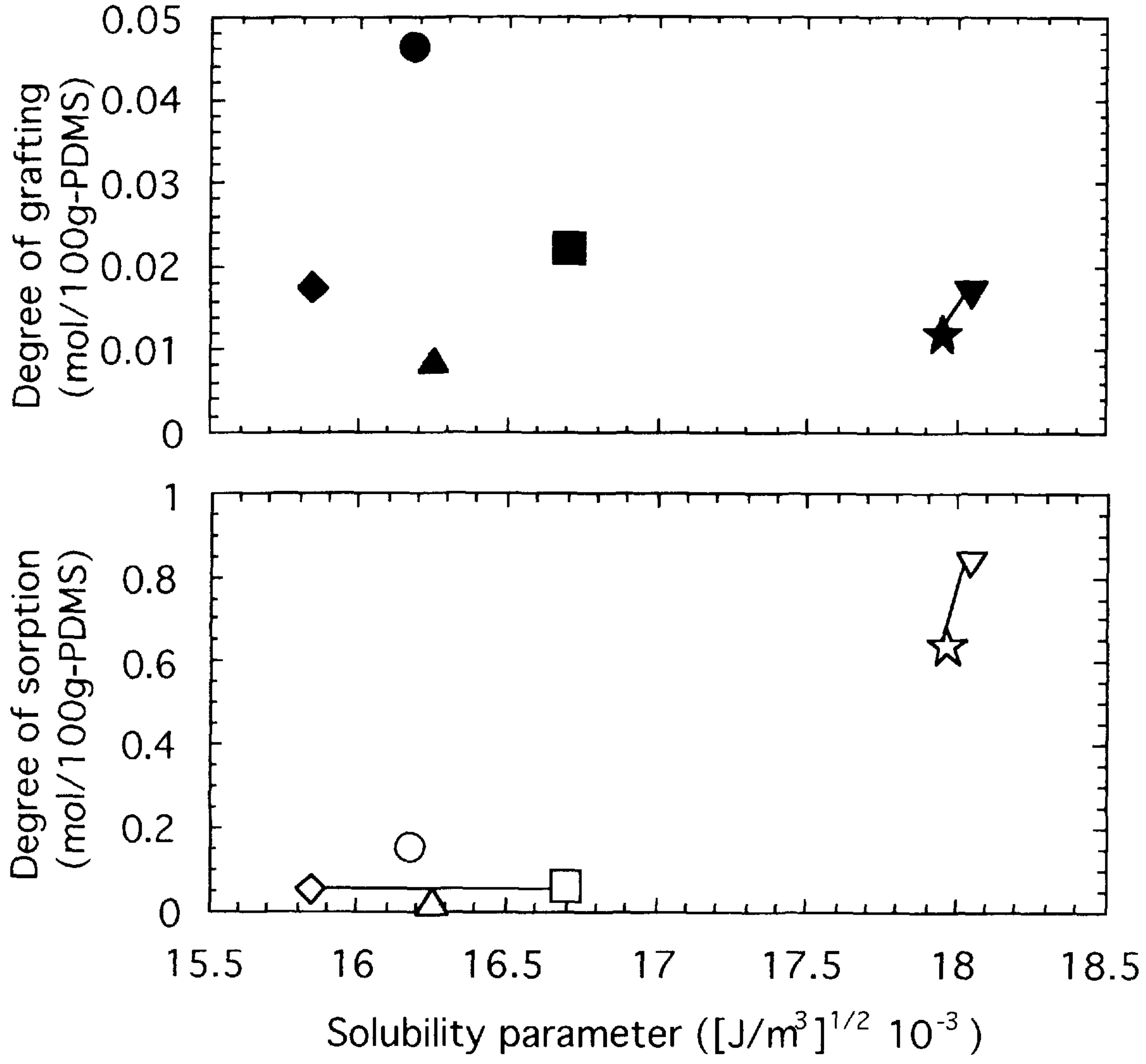

Fig. 5.5 Relationship between the solubility parameter of monomer and the grafted amount or the sorpted amount in PDMS membrane.: (○) PFPMA, (□) HFBMA, (◇) PFBEMA, (△) HDFNMA, (▽) BMA, (☆) HMA, closed: grafted amount, open: sorpted amount.

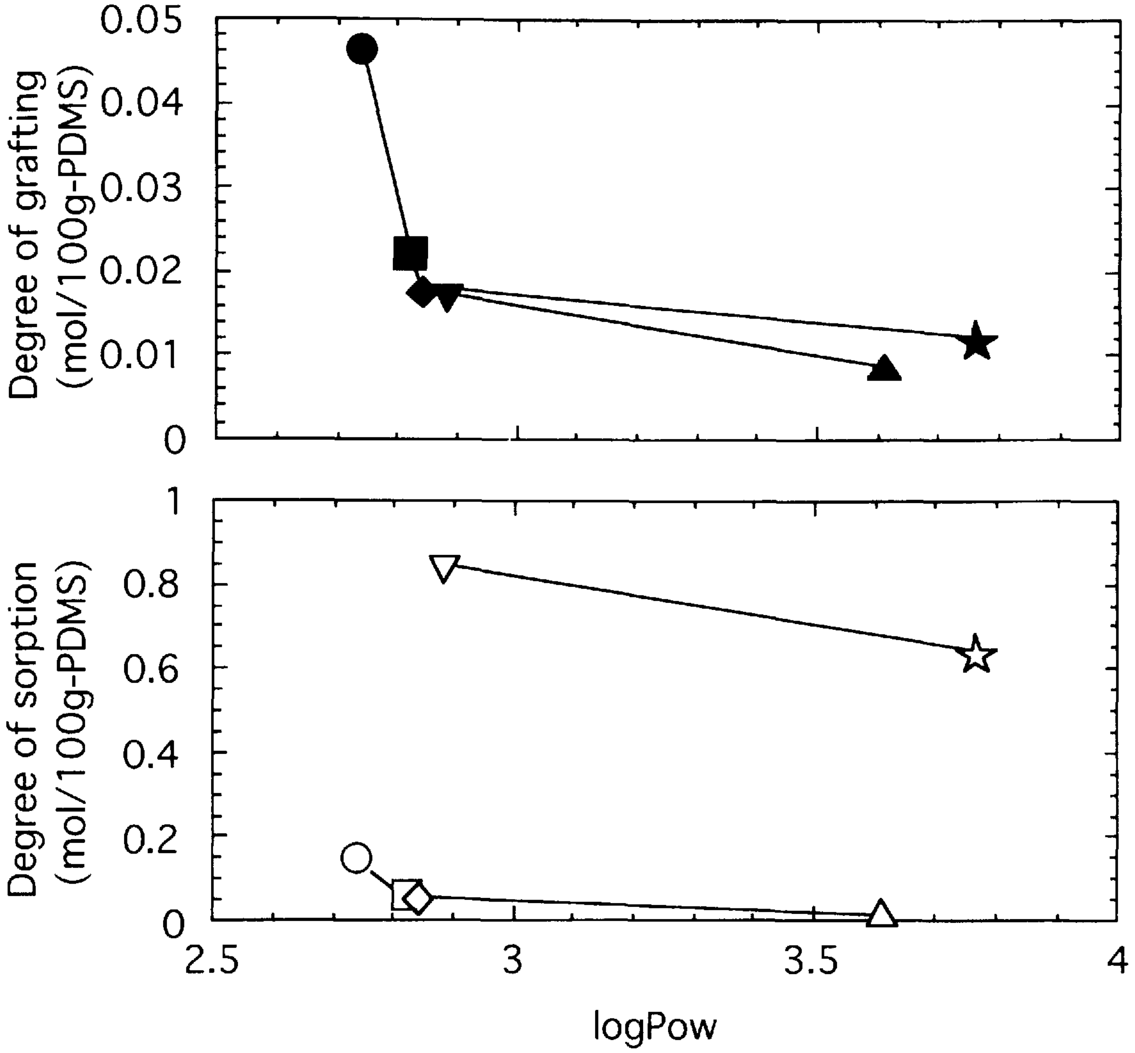

Fig. 5.6 Relationship between the logPow of monomer and the grafted amount or the sorpted amount in PDMS membrane.: (○) PFPMA, (□) HFBMA, (◇) PFBEMA, (△) HDFNMA, (▽) BMA, (☆) HMA, closed: grafted amount, open: sorpted amount.

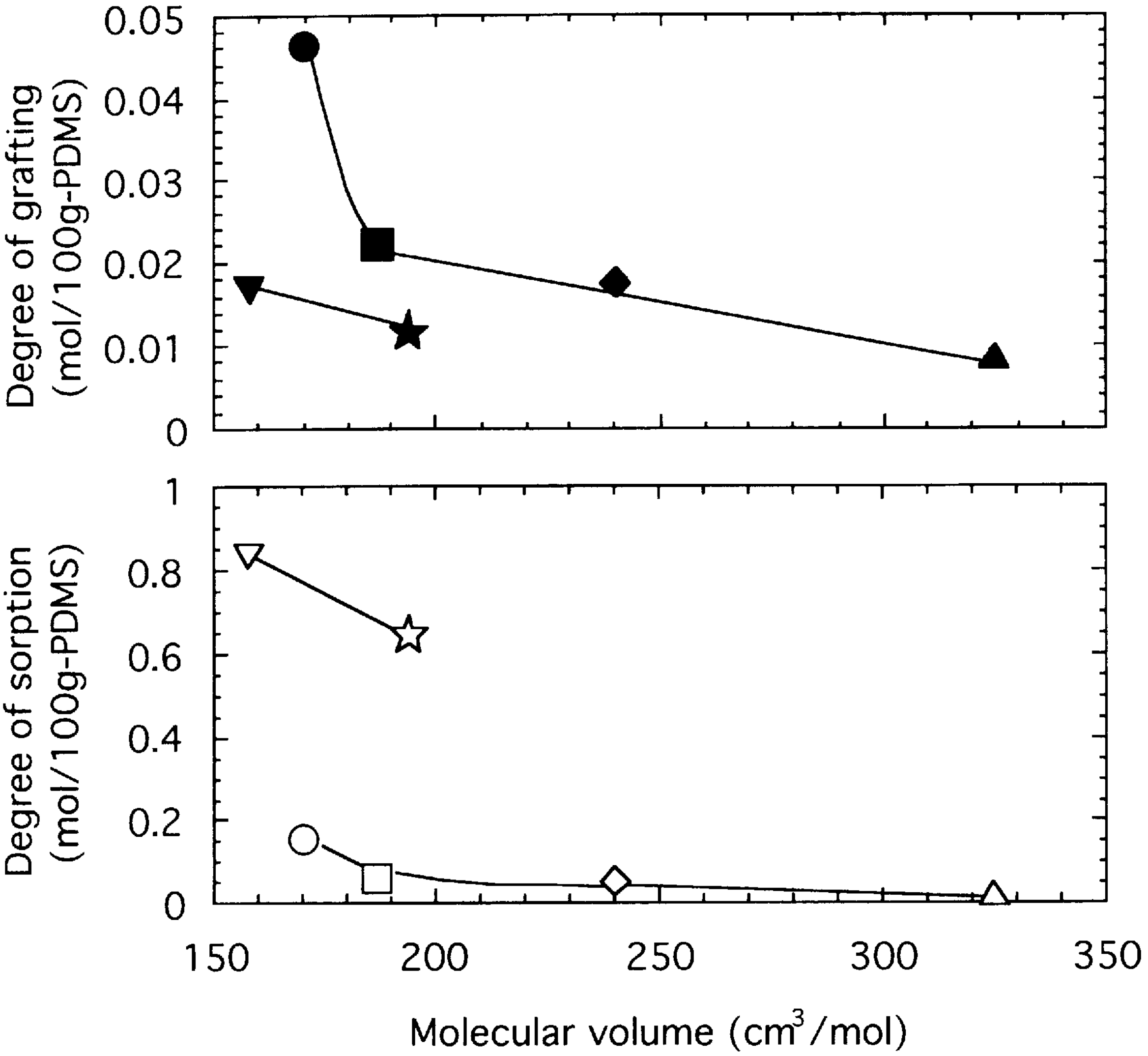

Fig. 5.7 Relationship between the moleculer volume of monomer and the grafted amount or the sorpted amount in PDMS membrane.: (○) PFPMA, (□) HFBMA, (◇) PFBEMA, (△) HDFNMA, (▽) BMA, (☆) HMA, closed: grafted amount, open: sorpted amount.

between the solubility parameter and the grafted amount or sorpted amount are shown in Fig.5.5. The solubility parameter of PDMS is 15.11, low value compared to FALMA and ALMA. The sorpted amount for ALMA that has a high solubility parameter was high. The sorpted amount for FALMA that has a low solubility parameter was low. The difference of δ_{FALMA} and δ_{PDMS} is small but the sorpted FALMA amount in PDMS membrane was low. The grafted amount was not so affected by the difference in the solubility parameter. The relationships between the $\log P_{OW}$ and grafted amount or sorpted amount are shown in Fig.5.6. The sorpted amount and the grafted amount was not so affected by the difference in the $\log P_{OW}$. The relationships between the molecular volume and the grafted amount or sorpted amount are shown in Fig.5.7. The sorpted amount for ALMA was high because of the low molecular volume. The sorpted amount for FALMA was low because of the high molecular volume. In this chapter, the PDMS membrane was grafted with FALMA and ALMA. Comparing monomers in the same group of FALMA or ALMA, the sorpted and grafted amount was high for the monomer which has low molecular volume, and the sorpted and grafted amount was low for the monomer which has high molecular volume.

5.3.4 The effects of the grafted fluorine amount on sorption and pervaporation

The pervaporation results of dilute TCE solution through the grafted PDMS membranes are shown in Table 5.4. The pervaporation for the PDMS membrane, PDMS membrane irradiated by electron beam, grafted PDMS membranes by the preirradiation method and simultaneous irradiation was investigated. The total flux for the PDMS membranes irradiated by electron beam was high compared to the un-irradiated PDMS membrane. It is thought that the PDMS membranes were made brittle by electron beam irradiation. By the preirradiation method, FALMA grafted PDMS membranes exhibited excellent separation performance. Among them, PFPMA grafted PDMS membrane which had a high grafted amount and a high F/Si ratio had high selectivity for TCE. By the simultaneous irradiation method, the PDMS membrane swollen by HDFNMA was irradiated. The PDMS membrane was grafted and made brittle simultaneously. The

HDFNMA grafted PDMS membrane by the simultaneous irradiation method did not have high permselectivity for TCE.

Table 5.4 Permeation selectivity for TCE-water mixture through PDMS membrane and grafted PDMS membrane

	Composition(wt%)		Total flux	Separation
Membranes	Feed	Permeate	(10^{-3}kg/m^2/h)	factor α_{pv}
PFPMA-grafted-PDMS	0.011	11	86	1100
(pre-irradiation)	0.023	20	120	1100
HFBMA-grafted-PDMS	0.012	5.0	120	450
(pre-irradiation)	0.024	9.1	130	410
PFBEMA-grafted-PDMS	0.0089	5.1	160	600
(pre-irradiation)	0.026	10	200	450
HDFNMA-grafted-PDMS	0.0083	3.2	210	400
(pre-irradiation)	0.024	11	100	520
HDFNMA-grafted-PDMS	0.010	1.5	190	150
(simultaneous irradiation)	0.023	2.9	130	130
BMA-grafted-PDMS	0.0099	3.7	140	390
(pre-irradiation)	0.025	8.3	140	350
HMA-grafted-PDMS	0.0091	2.2	140	240
(pre-irradiation)	0.025	6.1	140	260
EB irradiated-PDMS	0.011	0.53	490	51
(not grafted)	0.025	1.3	540	52
PDMS	0.010	4.8	63	500
	0.026	9.6	60	400

The water and TCE flux as a function of the TCE concentration in the feed solution are shown in Fig.5.8 for the HDFNMA grafted PDMS membranes by the preirradiation method and simultaneous irradiation method. For the PDMS membranes, the water flux was almost constant with increasing feed concentration. For the grafted PDMS membranes by the pre-irradiation method, the water flux decreased with increasing feed concentration. For all the membranes, the TCE flux was increased with increasing feed concentration, and for the grafted PDMS membranes by the preirradiation method, the tendency was significant.

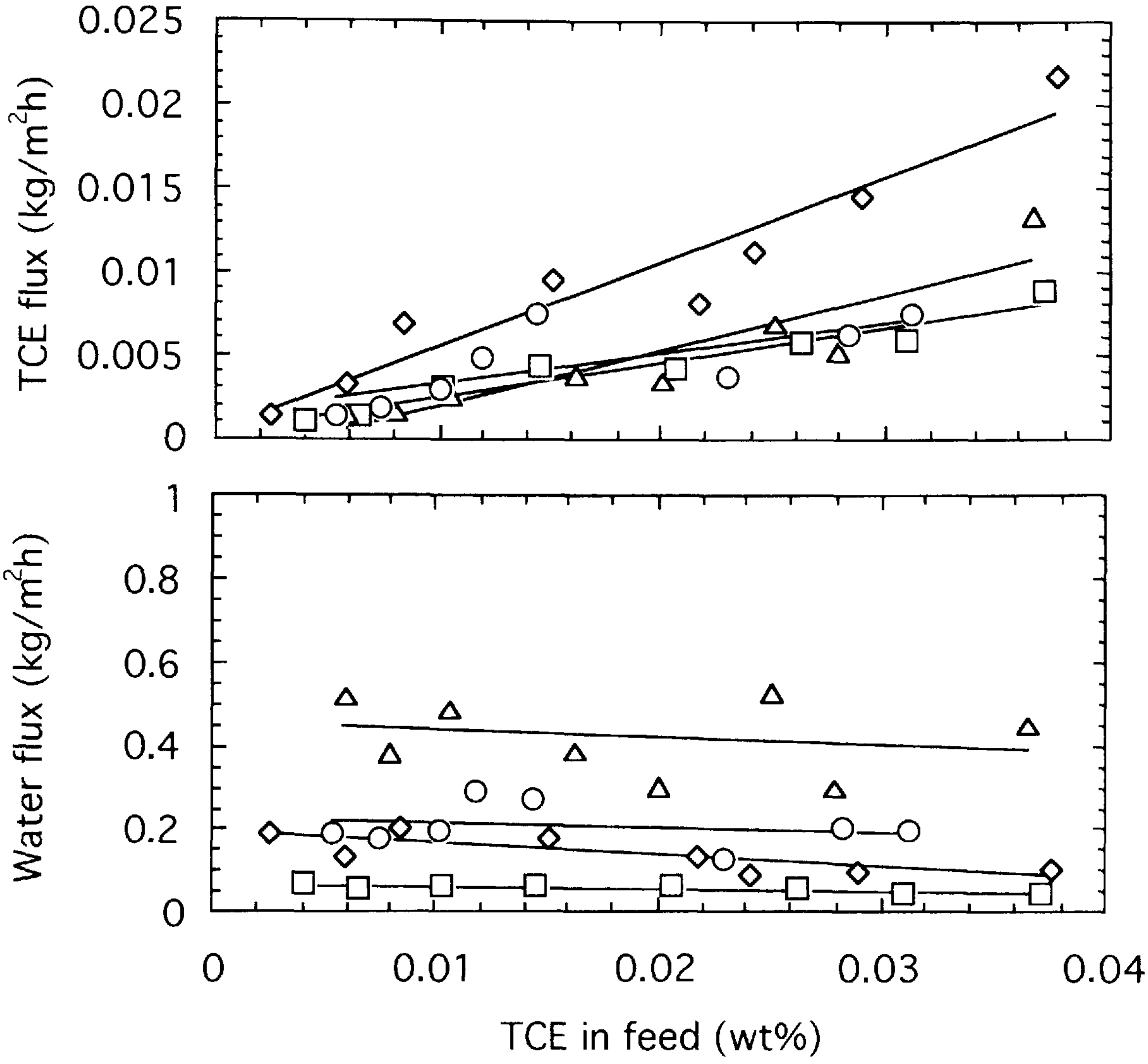

Fig. 5.8 Effect of feed concentration on Water and TCE flux for TCE-water mixture in pervaporation through PDMS membrane and grafted PDMS membrane by Electron beam.: (◇) grafted PDMS membrane by pre-irradiation method, (○) grafted PDMS membrane by simultaneous irradiation method, (△)PDMS membrane irradiated by Electron beam , (□) PDMS.

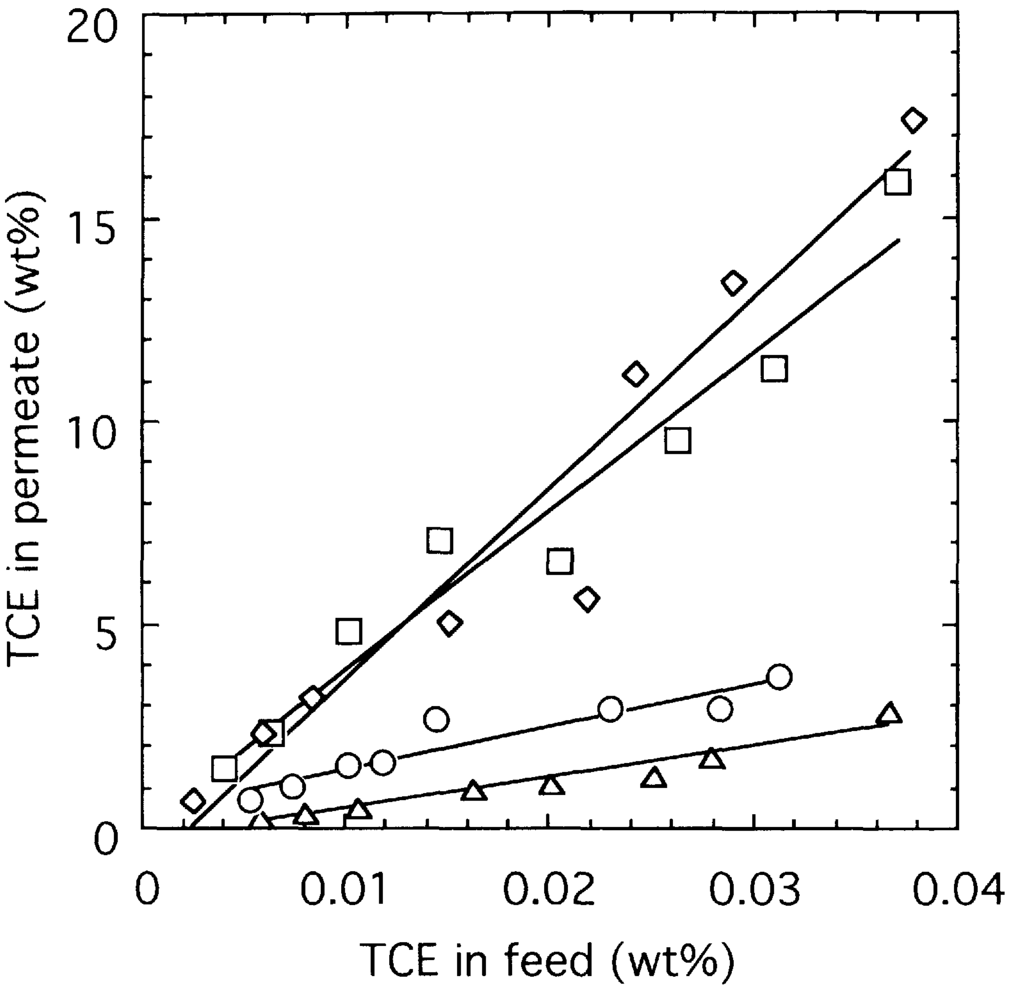

Fig. 5.9 Relationship between TCE concentration in feed and permeation in pervaporation through PDMS and grafted PDMS membranes by Electron beam : (◇) grafted PDMS membrane by pre-irradiation method, (○) grafted PDMS membrane by simultaneous irradiation method, (△)PDMS membrane irradiated by Electron beam , (□) PDMS.

The relationships between the TCE concentration in the feed and the permeate are shown in Fig.5.9 for the HDFNMA grafted PDMS membranes by the pre-irradiation method and simultaneous irradiation method. For all the membranes, the TCE concentration in the permeate increased with increasing feed concentration, and for the grafted PDMS membranes by the pre-irradiation method, the tendency was significant.

In the FALMA grafted PDMS membrane by the preirradiation method, the high separation performance was exhibited, due to the introduction of hydrophobic polymer, poly(FALMA).

Table 5.5 Sorption selectivity for PDMS membrane and grafted PDMS membrane

Membranes	TCE in feed(wt%)	Degree of swelling(wt%)	TCE in membrane(wt%)	Separation factor α
PFPMA-grafted-PDMS	0.011	2.6	13	1300
(pre-irradiation)	0.026	2.1	27	1400
HFBMA-grafted-PDMS	0.011	4.0	8.2	830
(pre-irradiation)	0.028	6.6	16	640
PFBEMA-grafted-PDMS	0.012	1.4	9.3	860
(pre-irradiation)	0.030	9.3	17	660
HDFNMA-grafted-PDMS	0.011	1.0	14	1500
(pre-irradiation)	0.026	1.1	18	840
HDFNMA-grafted-PDMS	0.011	1.2	3.9	360
(simultaneous irradiation)	0.028	2.5	21	930
BMA-grafted-PDMS	0.012	3.7	5.1	460
(pre-irradiation)	0.029	4.8	11	450
HMA-grafted-PDMS	0.012	1.3	3.9	340
(pre-irradiation)	0.028	4.5	11	430
EB irradiated-PDMS	0.01	3.3	4.2	460
(not grafted)	0.029	1.0	14	550
PDMS	0.012	1.0	8.9	770
	0.032	1.8	14	530

The sorption results of dilute TCE solution through the grafted PDMS membranes are shown in Table 5.5. The sorption for the PDMS membrane, PDMS membrane irradiated by electron beam, grafted PDMS membranes by the preirradiation method and simultaneous irradiation was investigated. The solubility of TCE for the FALMA grafted PDMS membranes by the preirradiation method was great compared with the PDMS membranes. Among them, PFPMA grafted PDMS membrane which had a high grafted amount and a high F/Si ratio had high sorption selectivity for TCE. The FALMA grafted PDMS membranes that had the high TCE concentrations in the sorbed solution exhibited high permselectivity for TCE.

5.4 Conclusions

In this chapter, the effect of solubility and diffusibility of a monomer on graft polymerization according to solubility parameter, octanol-water partition coefficient (Pow) and the molecular volume of the monomer was investigated. Around 33% of FALMA sorpted in PDMS was grafted, and around 2% of ALMA sorpted in PDMS was grafted. The difference of δ_{FALMA} and δ_{PDMS} is small but the sorpted FALMA amount in PDMS membrane was low. The difference in the grafted amount was little when considering the difference of the solubility parameter. The difference in the sorpted amount or grafted amount was little when considering the difference of the logPow. The sorpted amount for ALMA that have low molecular volume was high. The sorpted amount for FALMA that have high molecular volume was low. Compared to each other in the same group of FALMA or ALMA, the sorpted and grafted amount for the monomer which has low molecular volume was high, and the sorpted and grafted amount for monomer which has high molecular volume was low.

The pervaporation for the PDMS membrane, PDMS membrane irradiated by electron beam, grafted PDMS membranes was investigated. The total flux for the irradiated PDMS membranes by electron beam was high compared to the un-irradiated PDMS membrane. It is thought that the PDMS membranes were made brittle by electron beam irradiation. FALMA grafted PDMS membranes showed excellent separation performance. Among them, PFPMA grafted PDMS membrane which had a high grafted amount and F/Si ratio had high permselectivity for TCE. In pervaporation through the PDMS and grafted PDMS membrane, the TCE concentration in the permeate were increased with increasing feed concentration, and for the grafted PDMS membranes by the preirradiation method, the tendency was significant. The TCE flux significantly increased with increasing feed concentration for the grafted PDMS membranes by the preirradiation method.

FALMA grafted PDMS membranes exhibited high sorption performance. Among them, PFPMA grafted PDMS membrane which had a high grafted amount and F/Si ratio had high sorption selectivity for TCE. In the grafted PDMS membranes, the high permselectivity was shown, due to the introduction of the hydrophobic polymer, poly(FALMA).

5.5 Acknowledgments

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Chapter 6. Plasma-Grafting of Fluoroalkyl Methacrylate onto PDMS Membranes and their Permselectivity for Volatile Organic Compounds

6.1 Introduction

Pervaporation with organophilic membranes is an interesting alternative process to distillation or solvent extraction for the separation and the concentration of diluted organic compounds in the water treatment, recovery and quantitative analysis[1-6] and has been widely studied[5-23].

The dilute solution can be concentrated by pervaporation to be detected. When the relationship between the feed concentration and the permeate concentration is observed to be linear, the relationship is used as calibration curve and the pervaporation is used as analytical method. The concentration of feed solution can be calculated from the concentration of permeate solution.

The study of the pervaporation separation of VOCs from water has focused on the use of organophilic and elastomeric (rubbery) polymers, including polydimethylsiloxane (PDMS) and its copolymers[24-27]. The hydrophobic nature of fluorinated polymers was exploited to promote the selective adsorption and transport of the organic component of an organic/water feed solution[28-32]. The improvement PDMS usimg fluorinated compounds is expected for the permselectivity. In graft polymerization, the irradiation by gamma rays, electron beams, ultraviolet light and plasma are well known as radical formation methods [33,34].

In chapter 4, we modified the PDMS membrane with fluoroalkyl methacrylate (FALMA). The modified PDMS membrane showed the best separation performance due to introduce hydrophobic polymer, poly(FALMA). In chapter 5, we grafted PDMS membranes with FALMA and alkylmethacrylates (ALMA) by the electron beam preirradiation method. When we modified the PDMS membrane with FALMA by UV irradiation, the partition coefficient of chlorinated hydrocarbons into the membrane increased. However, in this method, the increase in the membrane weight by poly(FALMA) was low. For the pervaporation through the modified PDMS membrane, the relationship between the feed concentration and the permeate concentration was observed to be linear as well as for the PDMS membrane. By electron beam irradiation which neeeds high cost, the degree of grafting was over 4wt% but the PDMS membranes were made brittle due to high irradiation power. The plasma technique does not require a high installation cost for the energy source. The radical formation is easily performed on the surface of the polymer. The treatment time is short, within a few minutes.

In this chapter, the PDMS membrane was improved by graft polymerization with 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA) using plasma preirradiation method, which had a long n-fluoroalkyl chain and the effect on increasing the selectivity for chlorinated hydrocarbons with low reacted amount (in chapter 4). The grafted PDMS membranes were expected to be remained the advantage of rubbery PDMS membrane and their application to the analytical pervaporation.

6.2 Experimental

6.2.1 Graft polymerization of fluoroalkyl methacrylate by plasma

Commercial PDMS membranes (Fuji Systems Corporation), 50μm thick, were used throughout this work. HDFNMA (Daikin Fine Chemical Laboratory Corporation) was used as received to avoid homopolymerization. Trichloroethylene (TCE), tetrachloroethylene (PCE), benzene, toluene, 2-propanol and acetone (Special grade,Waco Pure Chemical Industries, Ltd,.) were used as received.

The plasma graft polymerization was performed as reported by Hiritsu et al.[35,36] and a schematic diagram of the apparatus is shown in Fig.6.1. PDMS membranes with 7x7cm dimensions were placed in a flask under vacuum overnight. Ar gas was then introduced into the flask. The flask was next evacuated. The introduction of Ar gas and evacuation was repeated several times. The membrane was treated by 13.56MHz plasma and fixed powers (W), for fixed time intervals. The membranes were then contacted with HDFNMA in the liquid phase at 60°C. After the polymerization stopped, the membranes were rinsed in acetone overnight to remove the homopolymers and any nonreacted monomers, then dried for 48 hours in an evacuated vessel. The degree of grafting was calculated as

$$\text{Degree of grafting}(\%)=(W_1-W_0)/W_0\times 100 \quad (6.1)$$

where W_0 and W_1 denote the weight of the PDMS membrane and the grafted PDMS membrane, respectively.

6.2.2 Characterization of the grafted PDMS membrane

X-ray photoelectron spectroscopy (XPS) spectra were obtained using an IPS-9000SX (JEOL, Ltd.) with MgKα exciting radiation (1253.6eV). The X-ray gun was operated at 10eV with a sample chamber vacuum of less than 5×10^{-9} Torr. The XPS spectra were recorded at two electron emission angles (ϑ) of 30°and 90°.

6.2.3 Pervaporation experiment and sorption musurement

The pervaporation experiments were performed in a previous study[33,34] using the continuous-feed type at 25°C. The feed solution was circulated through the cell and the feed tank. The effective membrane area in the cell was 19.6 cm^2. The pressure on the permeation side was kept below 10 Torr by vacuum pumps. Upon reaching steady state flow conditions, the permeate was collected in traps cooled by liquid nitrogen (-196°C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate, flux(J), was obtained using eq.(1)

$$J=Q/At \quad (1)$$

where Q is the amount that permeated during the experimental time interval, t, and A is the effective surface area. The VOC and water flux were calculated from the total flux and the permeate composition.The concentration of VOC in the feed and permeate solution was determined by gas chromatography using an FID detector. The VOC concentration in the permeate was high, which is far beyond its solubility limit in water. The phase separation took place in the permeate. 2-propanol was added to the permeate solution. The permeate solution was homogenized and analyzed to determine the VOC concentration.

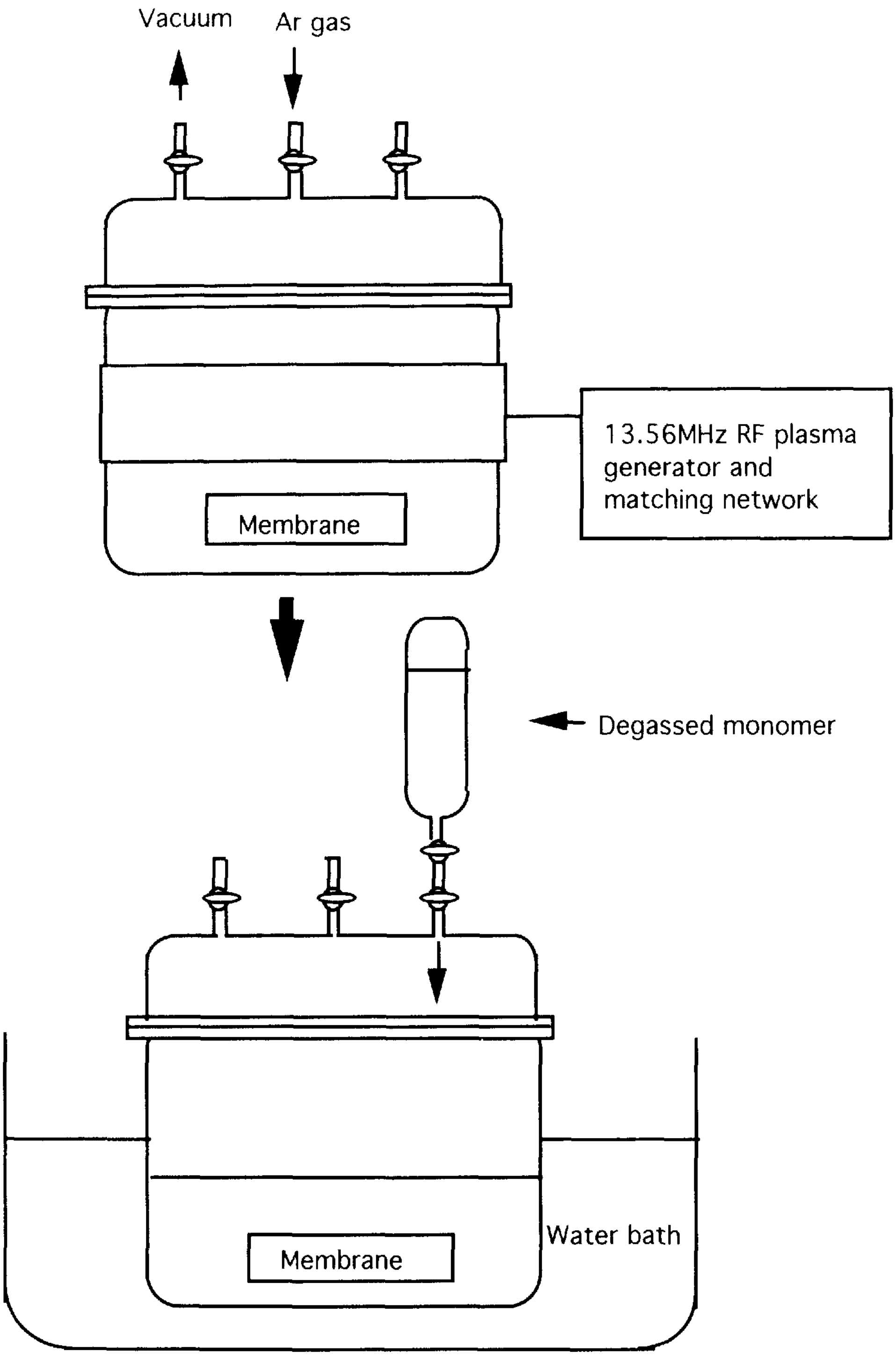
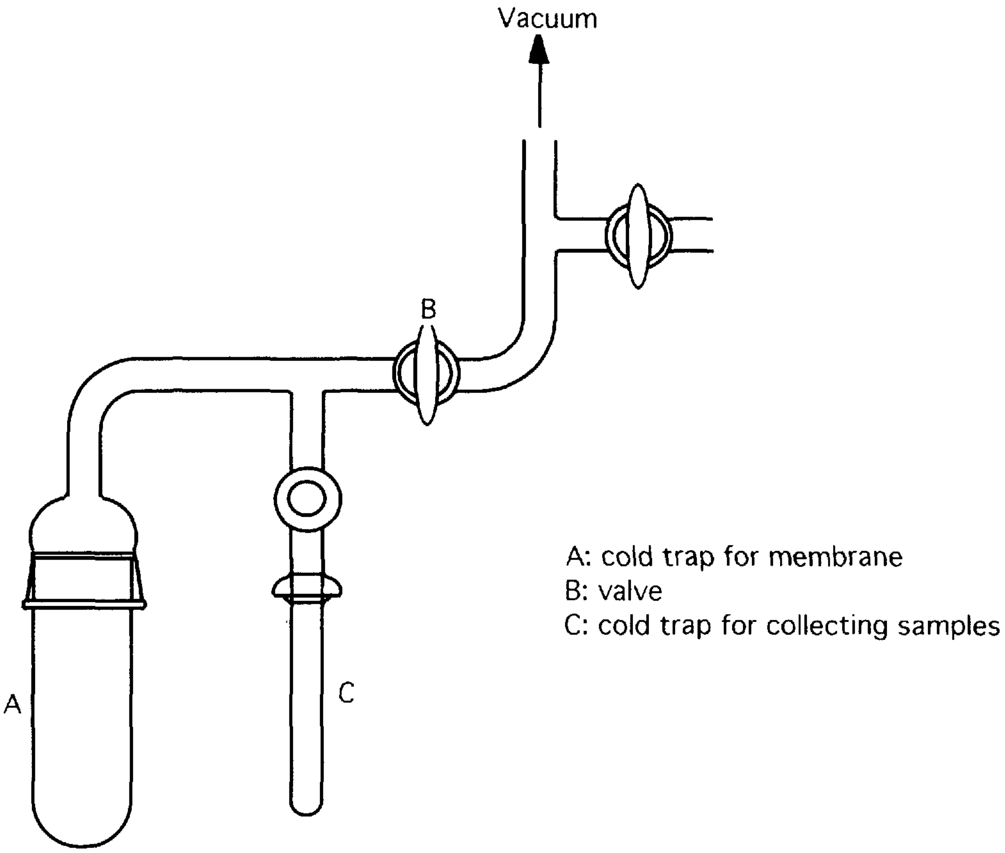


Fig. 6.1 Apparatus for the graft polymerization by plasma.



A: cold trap for membrane
B: valve
C: cold trap for collecting samples

Fig. 6.2 Apparatus for the composition measurement in the membrane.

The separation factor, α_{pv}, was calculated as

$$\alpha_{pv}=\{Y(1-X)\}/\{(1-Y)X\} \quad (6.2)$$

where X and Y denote the concentrations of VOC in the feed and permeate solutions, respectively.

The dried and weighed membrane was immersed in VOC solution and sealed at 25°C until equilibrium was reached. The membrane was then taken out of the vessel, wiped quickly with filter paper and weighed. The degree of sorption of the VOC solution into the membranes was measured as

$$\text{Degree of sorption}(\%)=(W_1-W_0)/W_0\times 100 \quad (6.3)$$

where W_0 and W_1 denote the weights of the dried membrane and the swollen membrane, respectively. The concentration of VOC solution soaked into the membrane was determined using the apparatus shown in Fig.6.2. The membrane upon reaching equilibrium was taken out of the vessel, quickly wiped with filter paper and placed in the cold trap A. The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, valve B was closed and the VOC solution soaked in the membrane was vaporized by heating with a drier and collected in the cold trap C. The concentration of VOC solution in the feed and the soaked membrane was determined by gas chromatography. The separation factor, α_s, was calculated as

$$\alpha_s=\{Y'(1-X)\}/\{(1-Y')X\} \quad (6.4)$$

where X and Y' denote the concentrations of VOC in the feed solution and the swollen membranes, respectively.

6.3 Results and discussion

6.3.1 Graft-polymerization of fluoroalkyl methacrylate by plasma

The dependence of the degree of grafting on polymerization time, i.e., immersion time is shown in Fig.6.3 for plasma preirradiation at 50W for 180s. The degree of grafting

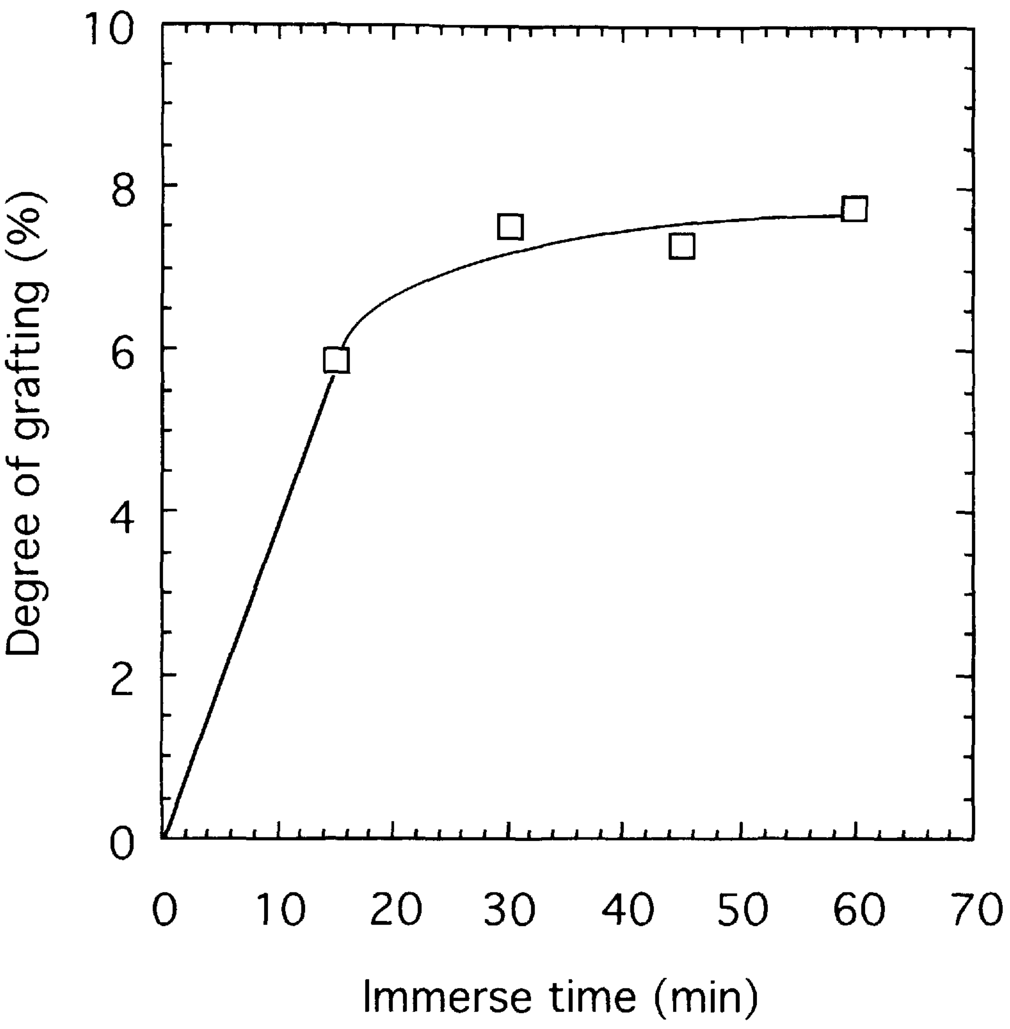


Fig. 6.3 Dependence of the degree of grafting on polymerization time for plasma preirradiation at 50W for 180s.

increased with increasing polymerization time and leveled off in 60 minutes. The polymerization time was determined to be 60 minutes. The obtained degree of grafting was around 7.5 wt%. The degree of sorption of HDFNMA in PDMS is 13 wt%. Only a part of the HDFNMA sorbed into the PDMS membrane was grafted on the PDMS membrane.

6.3.2 Characterization of the grafted PDMS membrane

The surface morphologies of the grafted PDMS membranes were analyzed using their XPS spectra. The ratio of fluorine, oxygen, carbon, and silicon atoms were analyzed and calculated for ~ 9 nm beneath the surface on the grafted PDMS membrane at 30° and 90° photoelectron emission angles and are characterized in Table 6.1. In this spectra, the composition of atoms are determined up to a depth of 4.5 and 9nm from the surface at the photoelectron emission angles of 30° and 90° , respectively[37]. On the surface of the PDMS membrane exposed to the air after irradiation, the O/Si and C/Si ratios increased. The surface of the membrane was oxidized by oxygen or water vapor in the air.

Fig.6.4 shows the effect of the plasma power on the F/Si, O/Si, C/Si ratios for the 180s plasma graft polymerization. The F/Si and C/Si ratios on the surface of the grafted PDMS membrane increased with increasing plasma power, due to the graft polymerization of HDFNMA by the plasma. The radical produced on the surface significantly increased with increasing plasma power. Hence, the degree of grafting increased with increasing plasma power. After graft polymerization, the residual radicals on the surface of the membrane reacted with oxygen or water vapor in the air.

Fig.6.5 shows the effect of the plasma irradiation time on the F/Si and C/Si ratios for the 10W plasma graft polymerization. The F/Si and C/Si ratios on the surface of the grafted PDMS membrane increased with increasing plasma irradiation time due to the graft polymerization of HDFNMA by the plasma. The O/Si ratio on the surface of the grafted PDMS membranes leveled off in the irradiation time of 60s. For a long irradiation time, the probability of radical bonding reciprocally increased[37]. The radical produced on the surface gradually increased with increasing plasma irradiation time. The degree of grafting and

Table 6.1 Fluorine to silicon, oxgen to silicon and carbon to silicon atomic ratios for the surface of PDMS and grafted PDMS membranes by XPS analysis

Plasma graft condition		Electron	Atomic ratio[a]		
Power (W)	Exposure time (s)	emission angle (°)	F/Si	O/Si	C/Si
10	30	30	0.0584	1.18	1.63
		90	0.0174	1.36	1.74
	60	30	0.0355	1.80	2.86
		90	0.0512	2.61	4.39
	(Reverse side)	30	0.0109	1.19	1.78
		90	0.0106	1.35	1.86
	180	30	0.110	1.80	3.34
		90	0.101	2.15	4.82
	(Reverse side)	30	0.0288	1.29	1.83
		90	0.0268	1.36	1.80
	300	30	0.0590	1.71	2.88
		90	0.0869	3.00	5.07
10	180	30	0.110	1.80	3.34
		90	0.101	2.15	4.82
30		30	0.136	1.88	3.37
		90	0.102	2.93	6.20
50		30	0.0958	2.02	3.29
		90	0.154	3.69	6.97
10	180	90	-[b]	1.60	1.21
under air after plasma exposure : not grafted					
PDMS		90	-[b]	1.42	1.85

a : F/Si:Fluorine atomic ratio(%)/Silicon atomic ratio(%)
O/Si:Oxgen atomic ratio(%)/Silicon atomic ratio(%)
C/Si:Carbon atomic ratio(%)/Silicon atomic ratio(%).

b: not detected.

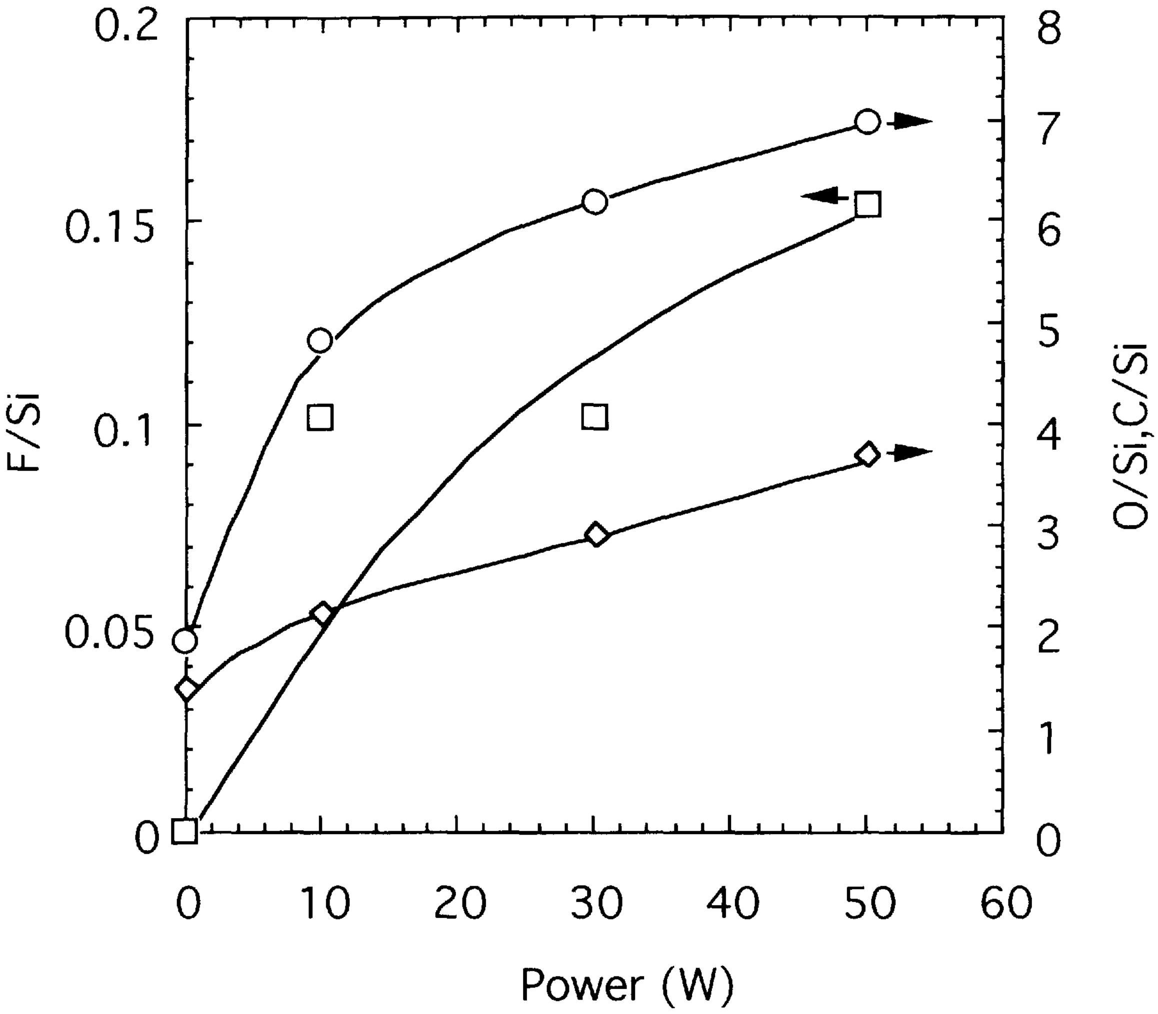


Fig. 6.4 Effect of plasma power on F/Si, O/Si, C/Si of the membrane surface grafted for 180s plasma preirradiation: (□) F/Si; (◇) O/Si; (○)C/Si at electron emission angle of 90°.

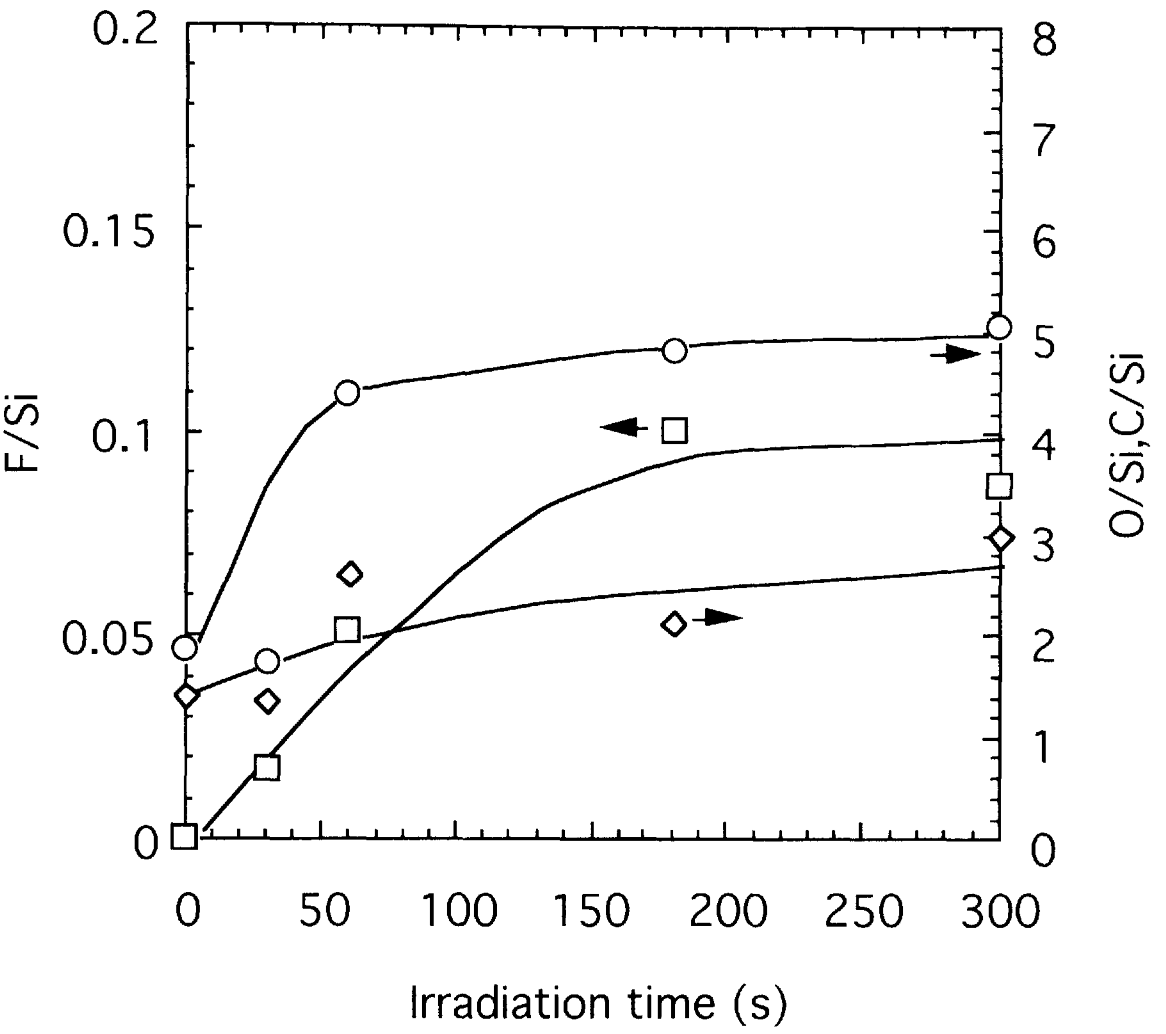


Fig. 6.5 Effect of plasma irradiation time on F/Si, O/Si, C/Si of the membrane surface grafted at 10W plasma preirradiation.: (□) F/Si; (◇) O/Si; (○)C/Si at electron emission angle of 90°.

hydrophobicity then gradually increased with increasing plasma irradiation time. The residual radicals after graft polymerization did not exist for a long time. The residual radicals on the surface of the membrane did not significantly react with oxygen or water vapor in the air.

The F/Si, O/Si and C/Si ratios on the reverse side of grafted PDMS membranes were lower than on the grafted surface. After the irradiation, the degassed HDFNMA was placed in the reactor, and the PDMS membranes were soaked and grafted. The graft polymerization was promoted in the grafted PDMS membrane[37]. The quantity of the radicals on the inside and reverse side of the grafted PDMS membrane was lower than that on the surface. Hence, the degree of grafting on the inside and reverse side of the grafted PDMS membrane was lower than that on the surface.

6.3.3 The effects of the graft condition on sorption and pervaporation

We shows the effect of the plasma power on the flux and separation factor for the TCE solution during pervaporation through the PDMS membrane for a 180s plasma treatment in Fig.6.6. The flux of the grafted PDMS increased with increasing plasma power. The separation factor showed a maximum at 10W and then decreased with increasing plasma power. The radical produced on the surface was significantly increased with increasing plasma power. The degree of grafting and oxidation were simultaneously increased. The membrane grafted at a weak power, 10W, was not significantly oxidized very much. The hydrophobicity of the grafted membrane was a maximum when the membrane was irradiated at 10W and grafted.

We shows the effect of the plasma irradiation time on the flux and separation factor for the TCE solution during pervaporation through the PDMS membrane at 10W plasma power in Fig.6.7. The flux of grafted PDMS membrane was constant regardless of the plasma irradiation time. The surface of the grafted PDMS membrane was not significantly oxidized. The separation factor of the grafted PDMS membranes increased with increasing irradiation time and the maximum was for the 180s plasma treatment. The degree of grafting increased

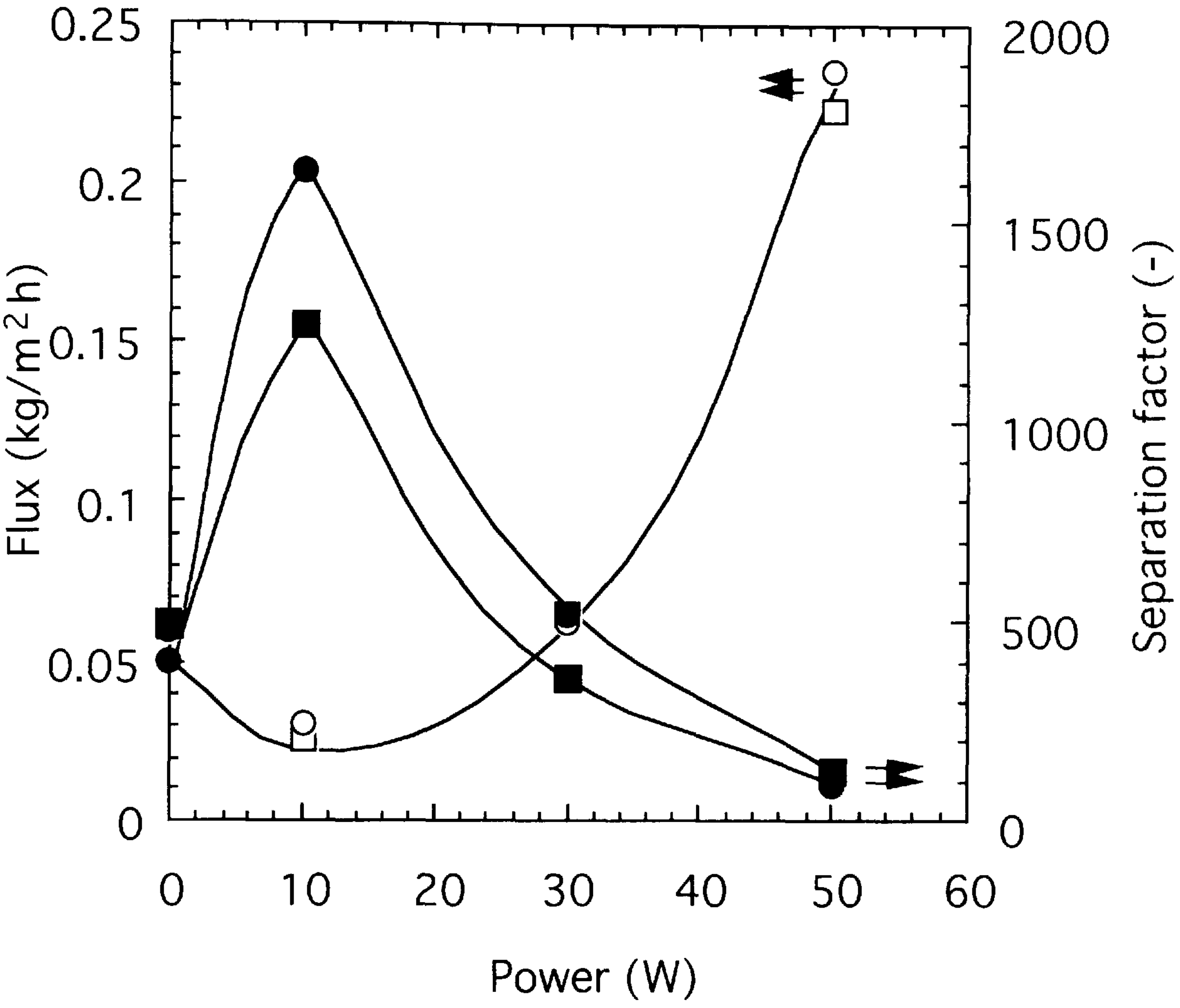


Fig. 6.6 Effect of plasma power on the flux and separation factor (α_{pv}) for TCE-water mixtures in pervaporation through grafted PDMS membrane for 180s plasma preirradiation.: (□) 0.005wt% feed concentration; (○) 0.01wt%, open: flux, closed: separation factor.

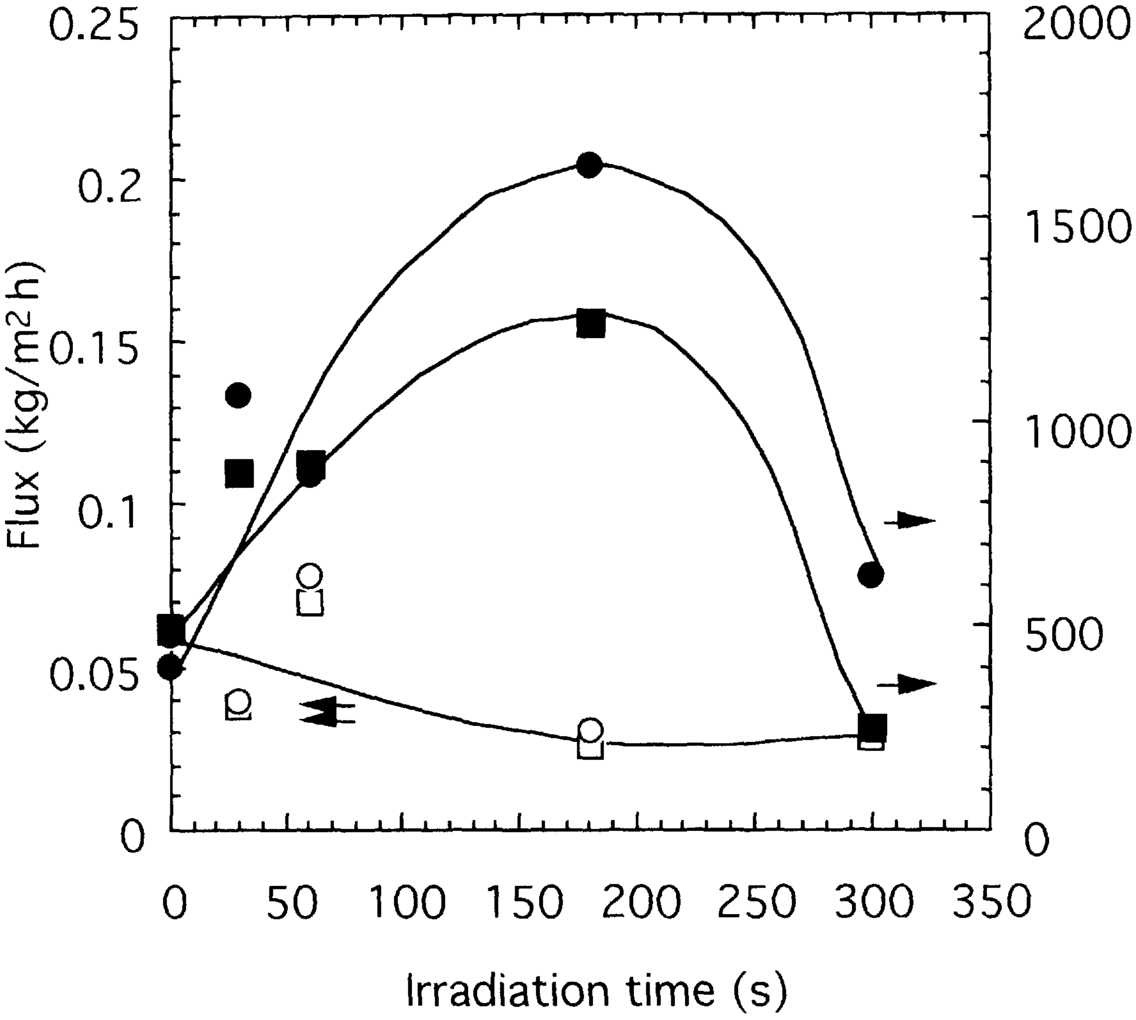


Fig. 6.7 Effect of plasma irradiation time on the flux and separation factor (α_{pv}) for TCE-water mixtures in pervaporation through grafted PDMS membrane at 10W plasma preirradiation.: (□) 0.005wt% feed concentration; (○) 0.01wt%, open: flux, closed: separation factor.

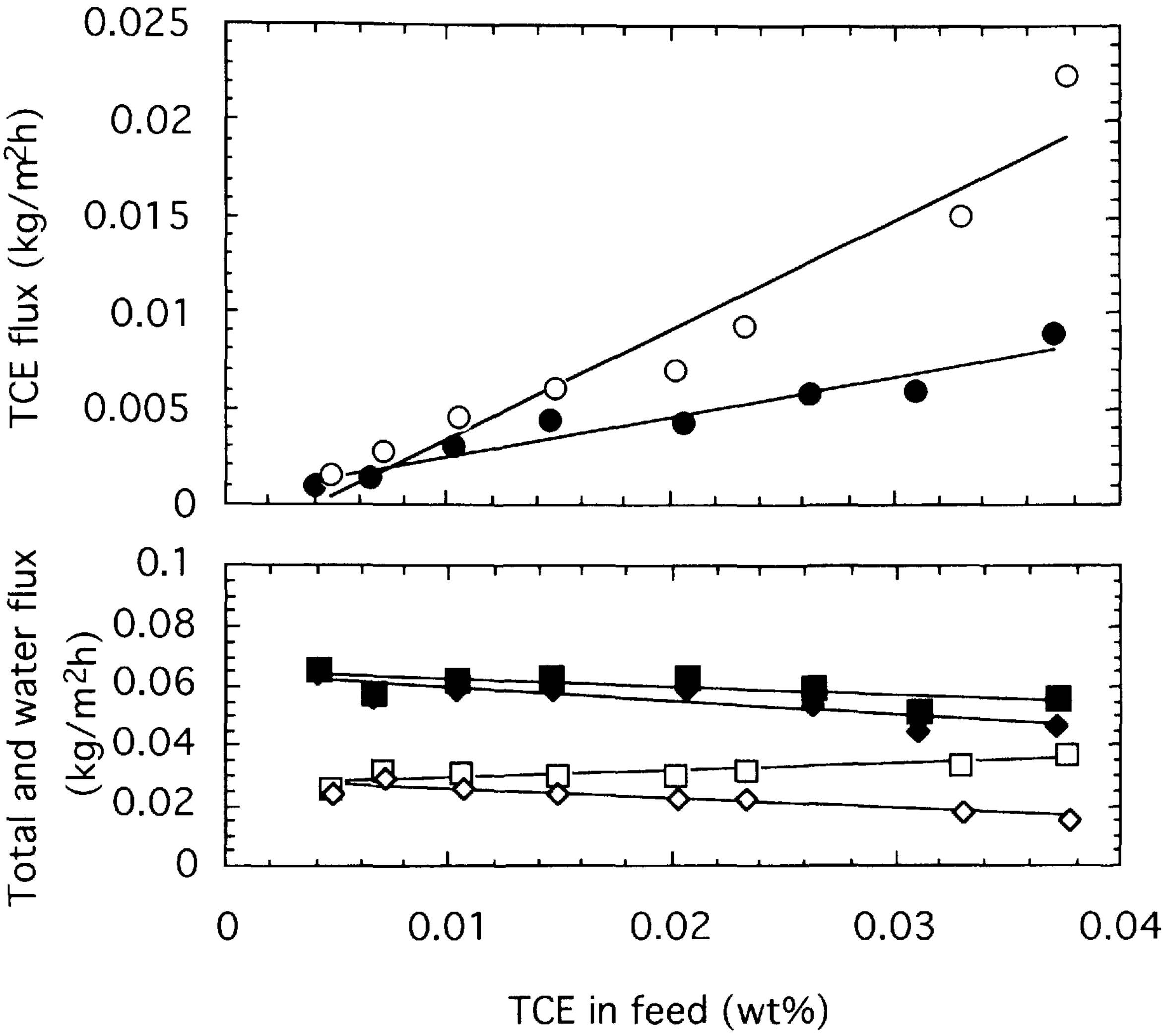


Fig. 6.8 Effect of feed concentration on the flux for TCE-water mixtures in pervaporation through PDMS membrane and plasma grafted PDMS membrane at 10W for 180s.: (□) total flux; (◇) water flux; (○) TCE flux, open: grafted membrane, closed: PDMS membrane.

with increasing plasma irradiation. The hydrophobicity of the grafted PDMS membranes was effectively increased due to introducing the hydrophobic polymer, poly(HDFNMA).

The flux as a function of the TCE concentration in the feed solution are shown in Fig.6.8 for the grafted PDMS membranes. For the PDMS and the grafted PDMS membranes, the water flux decreased with increasing feed TCE concentration. In a previous study, for the PDMS membranes grafted using HDFNMA by ^{60}Co irradiation, the water flux decreased with increasing feed concentration. In this study, the similar phenomena was observed. The TCE flux increased with increasing feed concentration. For the grafted PDMS membranes, this tendency was significant. The total flux consisted of TCE and water for the grafted PDMS membrane increased with increasing feed concentration while the total flux for PDMS membrane decreased with increasing feed concentration. The PDMS membranes that grafted with HDFNMA and simultaneously oxidized by plasma-graft polymerization, had a high selectivity for TCE.

The relationships between the TCE concentration in the feed and permeate are shown in Fig.6.9 for the grafted PDMS membranes. For all the membranes, the TCE concentration in the permeate increased with increasing feed concentration, and for the grafted PDMS membranes, the tendency was significant. The relationship between the feed concentration and the permeate concentration was observed to be linear. The pervaporation through the grafted PDMS could be used for easy quantitative analysis. The feed concentration can be known by the measurement of the permeate concentration. The grafted PDMS membrane had a high selectivity for VOCs. It is important to concentrate the VOC solutions for quantitative analysis.

The separation factor, α_{pv} , as a function of the TCE concentration in the feed solution is shown in Fig.6.10 for the grafted PDMS membranes. α_{pv} was significantly increased with increasing feed concentration for the grafted membranes.

In the grafted PDMS membrane, the best separation performance was, due to introducing the hydrophobic polymer, poly(HDFNMA).

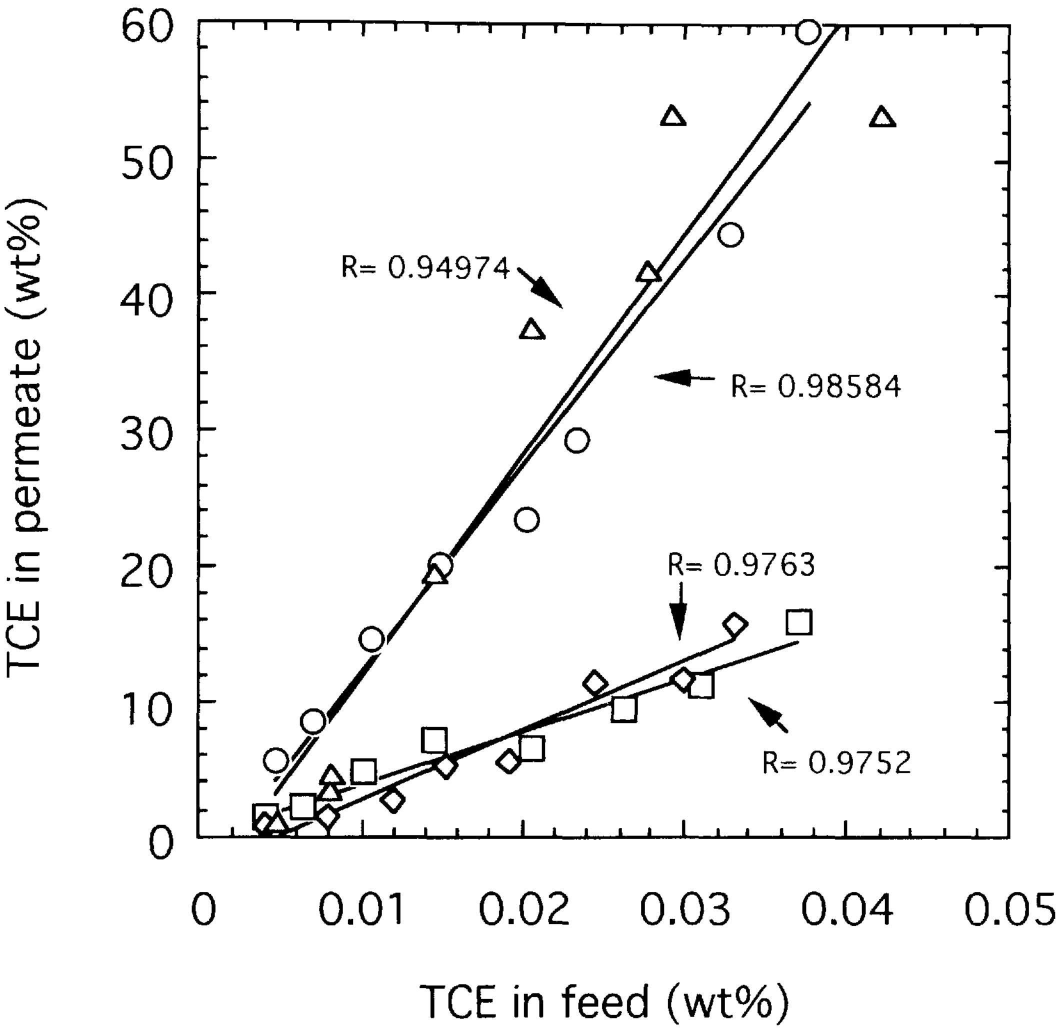


Fig. 6.9 Relationship between TCE concentration in feed and permeation in pervaporation through PDMS and grafted PDMS membranes : (○) membrane irradiated at 10W for 180s and grafted, (△) membrane irradiated at 10W for 300s and grafted; (◇)membrane irradiated at 10W for 180s and exposured in the air; (□) PDMS.

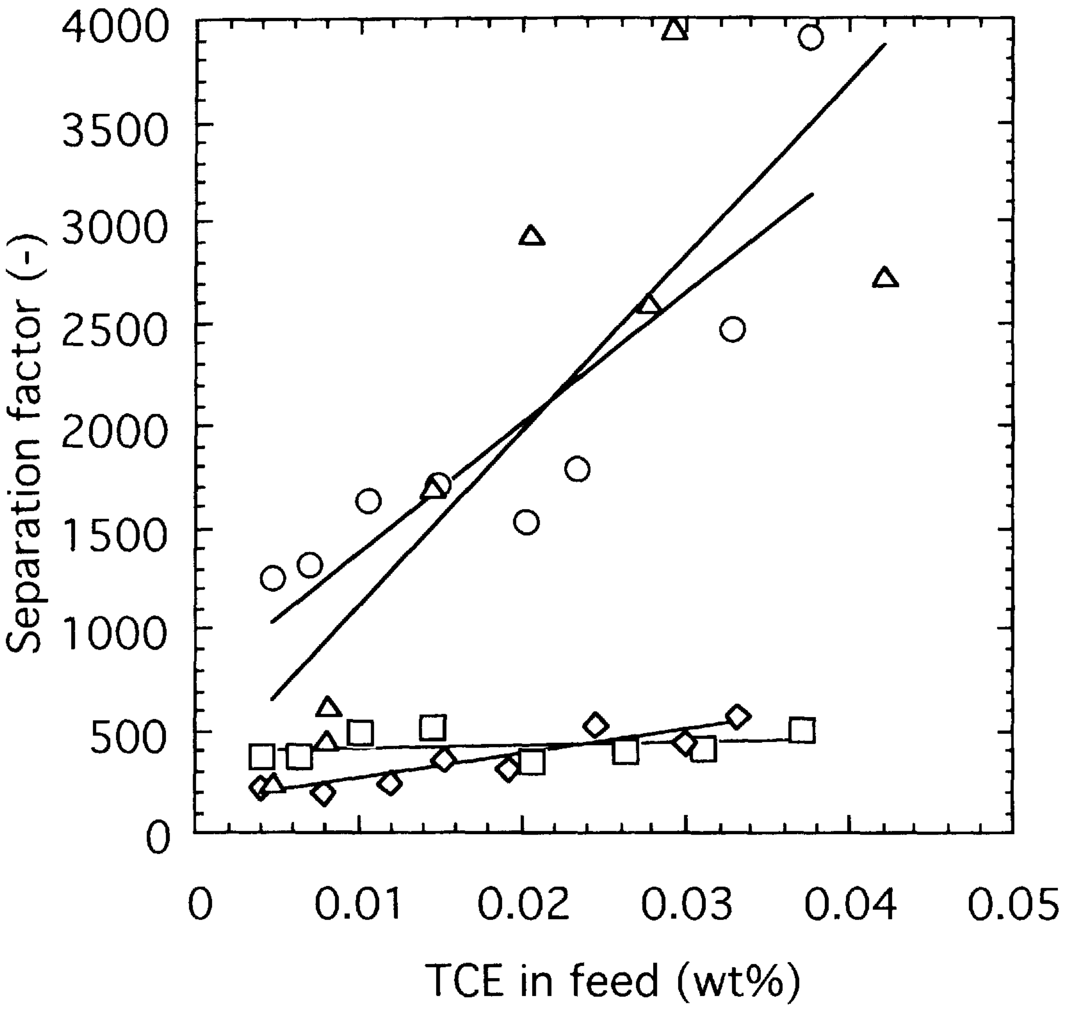


Fig. 6.10 Separation factor (α_{pv}) as a function of feed concentration in pervaporation through PDMS and grafted PDMS membranes : (○) membrane irradiated at 10W for 180s and grafted, (△) membrane irradiated at 10W for 300s and grafted; (◇)membrane irradiated at 10W for 180s and exposured in the air; (□) PDMS.

Table 6.2 Pervaporation data for various VOCs through PDMS membrane and plasma grafted PDMS membrane at 10W for 180s

VOC	Membrane	Composition(wt%) Feed	Permeate	Flux ($gm^{-2}h^{-1}$)	Separation factor α_{pv}
TCE	Grafted membrane	0.015	20	30	1700
	PDMS	0.015	7.0	64	520
PCE	Grafted membrane	0.0070	14	40	2300
	PDMS	0.0079	5.6	37	740
Benzene	Grafted membrane	0.017	31	31	2600
	PDMS	0.016	7.5	65	500
Toluene	Grafted membrane	0.014	22	28	2000
	PDMS	0.014	6.8	57	530

The pervaporation results of dilute TCE, PCE, benzene and toluene solutions through the grafted PDMS membranes are shown in Table 6.2. The permselevtivity for VOCs through the grafted PDMS membrane at 10W for 180s were high when compared with the PDMS membrane.

The degree of sorption of the VOC-water mixtures for the grafted PDMS membranes are shown in Table 6.3.

Table 6.3 Sorption data for various VOCs in PDMS membrane and plasma grafted PDMS membrane at 10W for 180s

VOC	Membrane	VOC in feed (wt%)	Degree of swelling (wt%)	VOC in membrane (wt%)	Separation factor α_s
TCE	Grafted membrane	0.017	5	20	1500
	PDMS	0.018	1	12	720
PCE	Grafted membrane	0.010	3	68	20300
	PDMS	0.0085	2	25	4000
Benzene	Grafted membrane	0.013	4	34	4000
	PDMS	0.014	4	8.0	630
Toluene	Grafted membrane	0.017	8	33	2900
	PDMS	0.016	1	27	2400

The solubility of VOCs for the grafted PDMS membrane at 10W for 180s was high when compared with the PDMS membrane. The grafted PDMS membrane that had the high VOC concentrations in the sorbed solution showed the best separation performance.

6.4 Conclusions

The PDMS membrane was improved by the graft polymerization with HDFNMA by plasma, which had the effect on increasing the selectivity for VOCs. When the pervaporation is used as analytical method, it is expected that the relationship between the feed concentration and the permeate concentration is observed to be linear as well as for PDMS. The application to the analytical pervaporation through plasma-grafted PDMS membranes was expected.

The degree of grafting was around 7.5wt%. The degree of sorption for the PDMS with HDFNMA is 13wt%. Only a part of the HDFNMA sorbed into PDMS membrane was grafted onto the PDMS membrane. The radicals on the surface were significantly increased with increasing plasma power. Hence, the degree of grafting increased with increasing plasma power and oxidation was also increased. The radical on the surface was gradually increased with increasing plasma irradiation time. Hence, the degree of grafting and hydrophobicity increased with increasing plasma irradiation. After the irradiation, the degassed HDFNMA was introduced into the reactor, the PDMS membranes were soaked in HDFNMA and then grafted. The graft polymerization was promoted in the PDMS membrane. The degree of grafting on the inside and reverse side of the PDMS membranes was lower than on the surface.

The flux of the grafted PDMS membrane increased with increasing plasma power. The radical produced on the surface significantly increased with increasing plasma power. The degree of grafting and oxidation simultaneously increased. The flux of the grafted PDMS membrane was constant regardless of the plasma irradiation time. The degree of grafting increased with increasing plasma irradiation. The hydrophobicity of the grafted PDMS membranes was effectively increased due to introducing the hydrophobic polymer, poly(HDFNMA). The solubility of VOCs represented by TCE, PCE, benzene and toluene for the grafted PDMS membrane at 10W for 180s was significant when compared with the PDMS membrane. The grafted PDMS membrane that had the high VOC concentrations in the sorbed solution showed the best separation performance. The permeselectivity for VOCs of the membrane was enhanced by the introduction of the hydrophobic polymer, poly(HDFNMA).

The relationship between the feed concentration and the permeate concentration was observed to be linear. Because the grafted amount of the plasma grafted PDMS membrane was little and the advantage of rubbery PDMS membrane remained, the relationship between the feed concentration and the permeate concentration was observed to be linear. The feed concentration is able to be introduced from the permeate concentration. The pervaporation through the grafted PDMS membrane could to be used for easy quantitative analysis.

6.5 Acknowledgments

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Chapter 7. Sorption and Diffusion of Volatile Organic Compounds in Fluoroalkyl Methacrylate Grafted PDMS Membranes

7.1 Introduction

Volatile organic compounds have been considered toxic in the human body. Recently, it was found to a social problem that ground water and soil are contaminated with volatile organic compounds (VOCs)[1,2].

Pervaporation has been is known as the superior method when applied to the purification of contaminated water and the extraction of aroma compounds, etc., and has been widely studied[1~13]. The prediction of permeation is important for the treatment, extraction and quantitative analysis by pervaporation. To account for the permeation through the non-porous membrane, a sorption-diffusion mechanism is important factor. For predicting permeation, a sorption-diffusion mechanism is proposed and has been studied[14~19].

The need for hydrophobicity data in the studies of organic compounds can be traced back at least to the turn of the century. The hydrophobicity is used to indicate the physical property of the molecule which governs its partitioning into the non aqueous portion of an immiscible or partially immiscible solvent pair[20]. According to Nernst[20], the partition coefficient can be simply described as:

$$P=Co/Cw \quad \text{or } \log P=\log Co-\log Cw \qquad (7.1)$$

where Co and Cw represent the molar concentrations of the partitioned compound in the organic and aqueous phases, respectively.

The octanol-water partition coefficient (Pow) has been generally used in expressing hydrophobicity. The hydrophobicity, Pow, is closely related to the solubility of organic compounds[21].

Also, the molecular volume is closely related to the diffusivity of organic compounds. The molecular volume is important for the diffusivity of the permeability.

Polydimethylsiloxane (PDMS) is well known as an excellent polymer membrane material based on its high permeability to gases and liquids[22]. It is desirable to enhance the selectivity of PDMS for VOCs and has been studied[23~28]. Fluorinated polymers have been studied as organic compounds due to its hydrophobicity based on the low surface energy[29~31]. It is expected to synthesize a more useful membrane material by combining the PDMS and fluorinated polymer using graft polymerization and investigated in this study.

In chapter 3, the result was obtained that the solute properties and interaction effected on the permeation behavior. In this chapter, the PDMS membranes were improved by the plasma-grafting of fluoroalkyl methacrylates (FALMA) to enhance the affinity of PDMS to VOCs. Furthermore, the pervaporation through the plasma-grafted PDMS membrane and the solution-diffusion mechanism for various VOCs based on their properties were investigated.

7.2 Experimental

7.2.1 Graft polymerization of fluoroalkyl methacrylate by plasma

Table 7.1 Phisico-chemical properties of volatile organic compounds (VOCs)

Compound	Abbreviation	Formula	Molecular weight	Solubility in water at 20℃ (wt%)
Trichloroethylene	TCE	$CHCl=CCl_2$	131.89	0.11
Tetrachloroethylene	PCE[a]	$CCl_2=CCl_2$	165.83	0.015
Benzene		C_6H_6	78.11	0.181
Toluene		$C_6H_5CH_3$	92.13	0.047
Ethyl butanoate	EBU	$CH_3(CH_2)_2COOCH_2CH_3$	116.16	0.68
Ethyl benzoate	EBZ	$C_6H_5COOCH_2CH_3$	150.2	0.08

a : The another name of Tetrachloroethylene is Perchloroethylene.

Commercial PDMS membranes (Fuji Systems Corporation), 50μm thick, were used throughout this work. 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA) (Daikin Fine Chemical Laboratory Corporation) were used as received to avoid homopolymerization. trichloroethylene (TCE), tetrachloroethylene (PCE), benzene, toluene, ethyl butanoate (EBU), ethyl benzene (EBZ), 2-propanol and acetone (Special grade,Wako Pure Chemical Industries, Ltd,.) were used as received. The phisico-chemical properties of VOCs used in this study were shown in Table 7.1.

The plasma graft polymerization was performed as reported by C. Ihm et al.[32] and T. Hiritsu [33]. and a schematic diagram of the apparatus is shown in Fig.7.1. The PDMS membranes used in this study had stick to glass. To treat one surface, PDMS membranes of 7x7cm were placed in a flask without any spaces between the surface and the glass of bottom not to introduce air. The PDMS membranes in a flask were under vacuum overnight. Ar gas was then introduced into the flask. The flask was next evacuated. The introduction of Ar gas and evacuation was repeated several times. The membrane was treated by 13.56MHz plasma and at 10 W for 180s. The membranes were then contacted with HDFNMA in the liquid phase at 60°C for 1h. After the polymerization stopped, the membranes were rinsed in acetone overnight to remove the homopolymers and any nonreacted monomers, then dried for 48 hours in an evacuated vessel.

In this chapter, seven sheets of membranes were subjected to the treatment. The degree of grafting was calculated as

$$\text{Degree of grafting}(\%)=(W_1-W_0)/W_0\times 100 \quad (7.2)$$

where W_0 and W_1 denote the weight of the PDMS membrane and the grafted PDMS membrane, respectively. The coefficient of standard deviation (Vs) for their degree of grafting was 0.32. Among them, the Vs of three samples was 0.10. Therefore, the three samples were provided to the subsequent investigation. The average of the degree of grafting for the three samples was 7.0wt%.

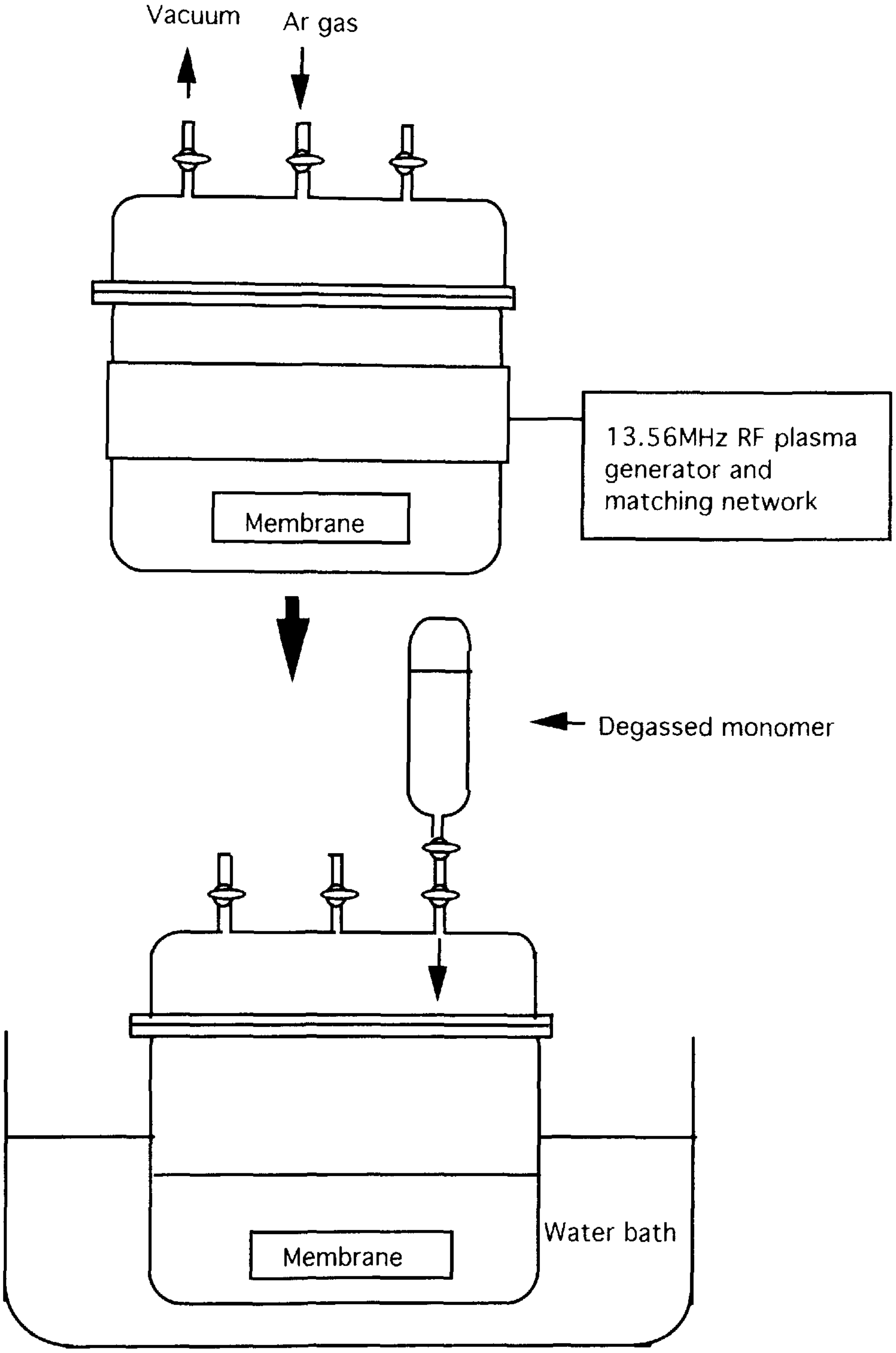

Fig. 7.1 Apparatus for the graft polymerization by plasma.

7.2.2 Characterization of the grafted PDMS membrane

X-ray photoelectron spectroscopy (XPS) spectra were obtained using an IPS-9000SX (JEOL, Ltd.) with MgKα exciting radiation (1253.6eV).The X-ray gun was operated at 10eV with a sample chamber vacuum of less than 5×10^{-9} Torr. The XPS spectra were recorded at two electron emission angles (ϑ) of 30°and 90°.

7.2.3 Pervaporation experiment and sorption musurement

The pervaporation experiments were performed in a previous study[23~25] using the continuous-feed type at 25°C. The feed solution was circulated through the cell and the feed tank. The grafted surface of the membrane was keeping in touch with the feed solution in the cell. The effective membrane area in the cell was 19.6 cm^2. The pressure an the permeation side was kept below 10 Torr by vacuum pumps. Upon reaching steady state flow conditions, the permeate was collected in traps cooled by liquid nitrogen (-196°C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate, flux(J), was obtained using eq.(7.3)

$$J=Q/At \qquad (7.3)$$

where Q is the amount that permeated during the experimental time interval, t, and A is the effective surface area. The VOC and water flux were calculated from the total flux and the permeate composition. The concentration of VOC in the feed and permeate solution was determined by gas chromatography using an FID detector. The VOC concentration in the permeate was high, which is far beyond its solubility limit in water. The phase separation took place in the permeate. 2-propanol was added to the permeate solution. The permeate solution was homogenized and analyzed to determine the VOC concentration. The separation factor, α_{pv}, was calculated as

$$\alpha_{pv}=\{Y(1-X)\}/\{(1-Y)X\} \qquad (7.4)$$

where X and Y denote the concentrations of VOC in the feed and permeate solutions, respectively.

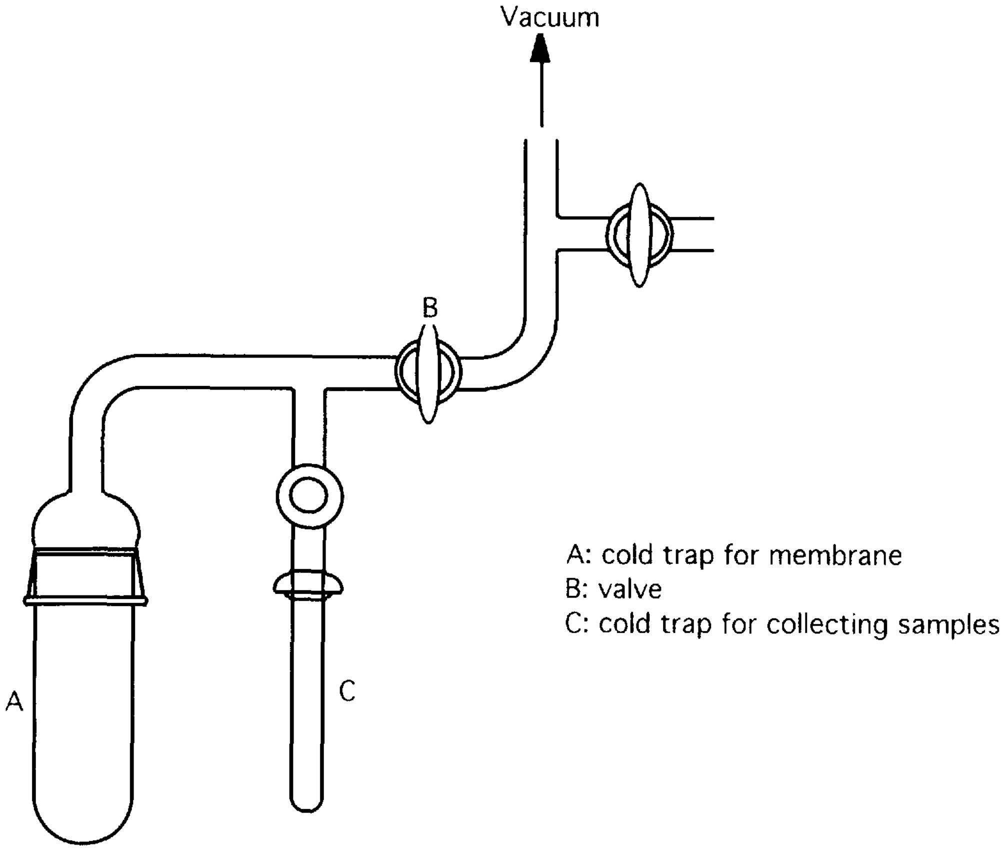

Fig. 7.2 Apparatus for the composition measurement in the membrane.

The dried and weighed membrane was immersed in VOC solution or VOC liquid and sealed at 25°C until equilibrium was reached. The membrane was then taken out of the vessel, wiped quickly with filter paper and weighed. The degree of sorption or VOC liquid of the VOC solution into the membranes was measured as

$$\text{Degree of sorption}(\%)=(W_1-W_0)/W_0\times 100 \qquad (7.5)$$

where W_0 and W_1 denote the weights of the dried membrane and the swollen membrane, respectively. The concentration of VOC solution soaked into the membrane was determined using the apparatus shown in Fig.7.2. The membrane upon reaching equilibrium was taken out of the vessel, quickly wiped with filter paper and placed in the cold trap A. The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, valve B was closed and the VOC solution soaked in the membrane was vaporized by heating with a drier and collected in the cold trap C. The concentration of VOC solution in the feed and the soaked membrane was determined by gas chromatography same as pervaporation experiment. The solubility coefficient (K) and the separation factor during sorption, α_S, were calculated as

$$K = Y'/X \qquad (7.6)$$

$$\alpha_S = \{Y'(1-X)\}/\{(1-Y')X\} \qquad (7.7)$$

where X and Y' denote the concentrations of VOC in the feed solution and the swollen membranes, respectively.

7.3 Results and discussion

7.3.1 Characterization of the grafted PDMS membrane

The surface morphologies of the grafted membranes were analyzed using the XPS spectra. The ratio of fluorine, oxygen, carbon, and silicon atoms were analyzed and calculated for ~9 nm beneath the surface of the grafted membrane at 30° and 90° photoelectron emission angles and characterized in Table 7.2. In these spectra, the composition of atoms are determined up to 4.5 and 9nm deep from the surface at the photoelectron emission angles of 30° and 90°, respectively[34]. The F/Si ratio on the reverse side of the grafted membranes was lower than on the grafted surface. The O/Si and C/Si ratios on the reverse side of grafted membranes were almost same as on the grafted surface. The degree of grafting for whole membrane was 7.0wt%. The thickness of grafted PDMS membrane was almost the same as untreated PDMS membrane. After the irradiation, the

Table 7.2 Fluorine to silicon, oxgen to silicon and carbon to silicon atomic ratios for the surface of PDMS and grafted PDMS membranes by XPS analysis

Plasma graft condition Power (W)	 Exposure time (s)	Electron emission angle (°)	Atomic ratio[a] F/Si	 O/Si	 C/Si
10	180	30	0.110	1.80	3.34
		90	0.101	2.15	4.82
(Reverse side)		30	0.0288	1.29	1.83
		90	0.0268	1.36	1.80
10 under air after plasma exposure : not grafted	180	90	-[b]	1.60	1.21
PDMS		90	-[b]	1.42	1.85

a : F/Si:Fluorine atomic ratio(%)/Silicon atomic ratio(%)
O/Si:Oxgen atomic ratio(%)/Silicon atomic ratio(%)
C/Si:Carbon atomic ratio(%)/Silicon atomic ratio(%).
b: not detected.

degassed HDFNMA was introduced into the reactor, the PDMS membranes were soaked in HDFNMA and grafted. The graft polymerization started with the surface of membrane and was caused in the PDMS membrane. Hence, the degree of grafting on the inside and reverse side of the PDMS membranes was lower than on the surface.

7.3.2 Effect of the VOC properties on the pervaporation

The pervaporation properties of various VOC aqueous solutions were determined in this study. The total flux as a function of the VOC concentration in the feed solution are shown in Fig.7.3 for the PDMS membrane and the grafted PDMS membrane. Except for benzene, when feed VOC concentration increased, the total flux was almost constant in the PDMS membrane. For benzene, the total flux increased with the feed concentration in the PDMS

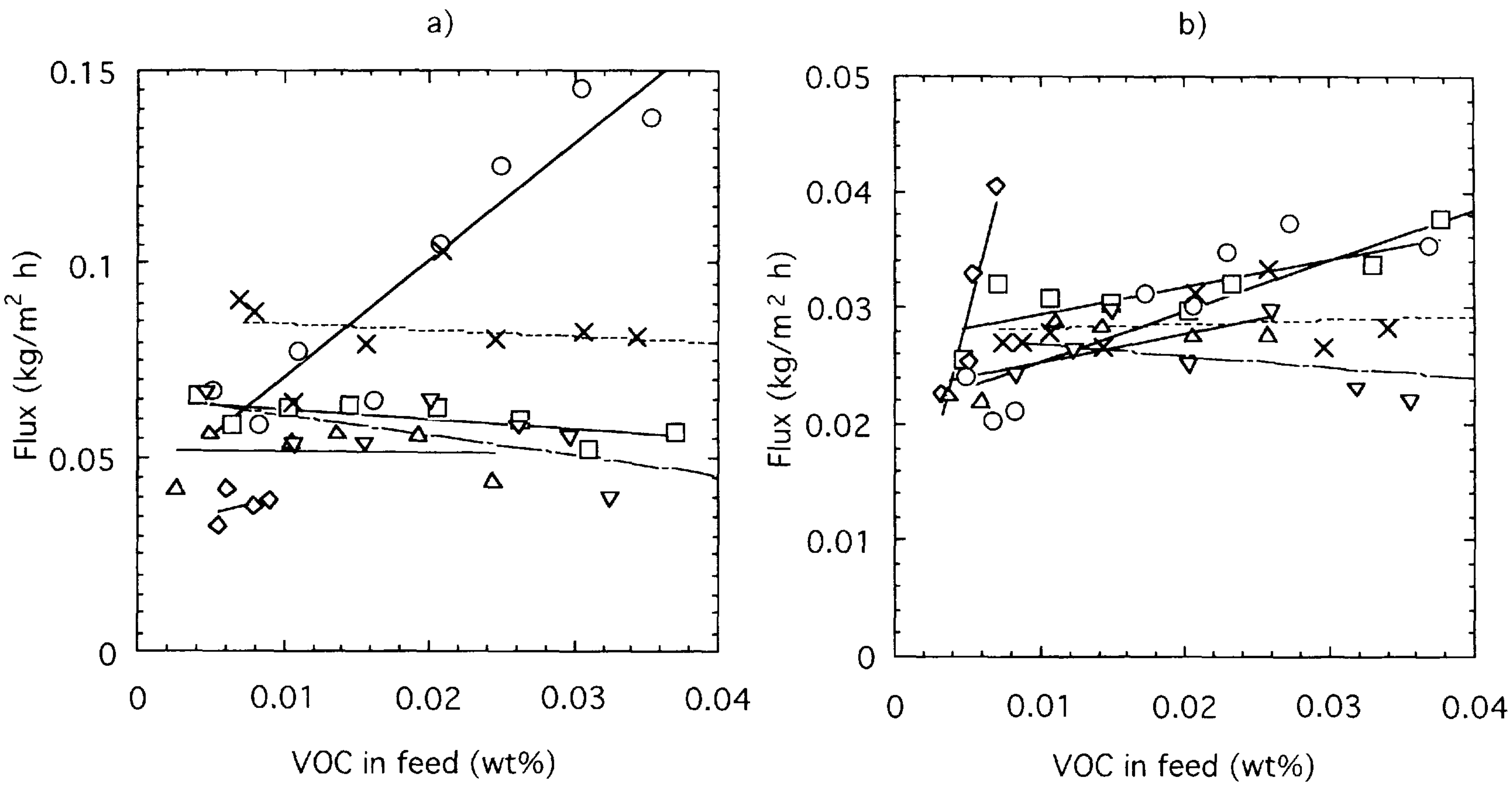

Fig. 7.3 Effect of feed concentration on total flux for VOC-water mixtures during pervaporation through a) PDMS membrane, and b) grafted PDMS membrane.: (□) TCE, (◇) PCE, (○) Benzene, (△) Toluene, (×) EBU, (▽) EBZ.

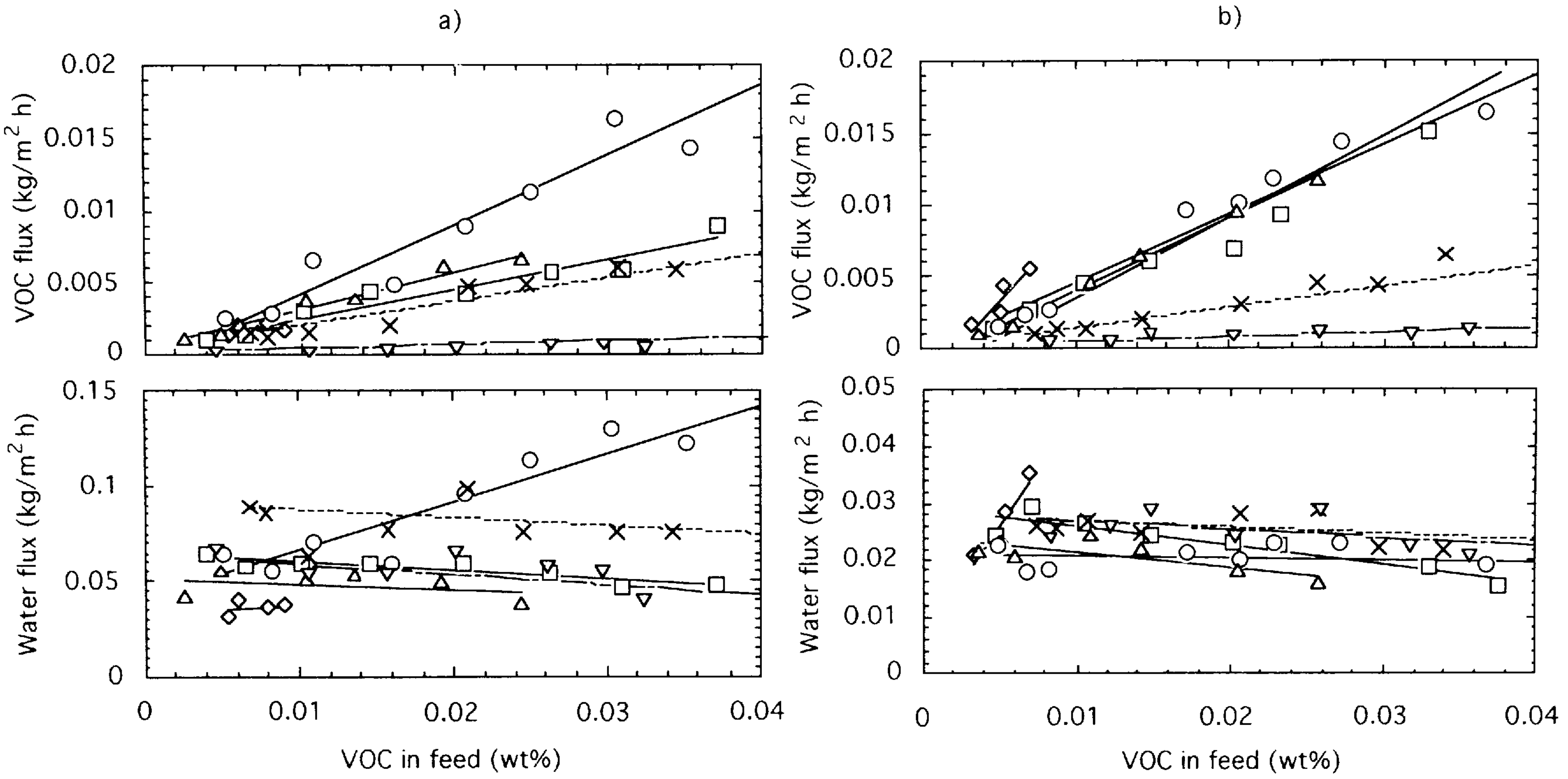

Fig. 7.4 Effect of feed concentration on water and VOC flux for VOC-water mixtures during pervaporation through a) PDMS membrane, and b) grafted PDMS membrane.: (□) TCE, (◇) PCE, (○) Benzene, (△) Toluene, (×) EBU, (▽) EBZ.

membrane. For the HDFNMA grafted membranes, the total flux was almost constant when the feed VOC concentration increased.

The water flux and VOC flux as a function of the VOC concentration in the feed solution are shown in Fig.7.4 for the PDMS membrane and the grafted PDMS membrane. Except for benzene, when the feed VOC concentration increased, the water flux was almost constant in the PDMS membrane. For benzene, the water flux increased with feed concentration in the PDMS membrane. This results in the total flux being increased with feed benzene concentration in the PDMS membrane.

To account for the permeation of the mixture, the penetrates and membrane interact each others and one component affects the transport of the other component[19]. The diffusion of molecules are promoted, or inhibited by another component. Huang et. al.[35,36] proposed permeation ratio (ϑ) which represent the ratio of actual flux to ideal flux, that is, the interaction of one component with the other component or the membrane. ϑ is described as

$$\vartheta = J / J^{o} \qquad (7.8)$$

Where J and J_o represent the actual flux and the ideal flux, respectively. when $\vartheta > 1$, the transport of the component is promoted. when $\vartheta < 1$, the transport of the component is inhibited. In pervaporation, the membrane can be swollen by the penetration of components and the diffusion is promoted. In this case, the water flux was affected by benzene and increased with feed benzene concentration. While the feed benzene solution used in this study was dilute aqueous solution, it may be considered that the swelling effect by benzene affected the permeation of water. In the HDFNMA grafted membranes, the water flux was almost constant with increasing feed concentration of the VOCs. The promotion of the water transport was not observed. In our previous studies[24,25], for the membranes grafted with fluoroalkyl methacrylate, the diffusion of water was prevented and the water flux decreased with increasing feed concentration. In this chapter, the diffusion of water in benzene solution was not promoted in the HDFNMA grafted PDMS membranes, while the diffusion of water in benzene solution was promoted in the PDMS membranes. Grafted HDFNMA inhibited the increase of water flux.

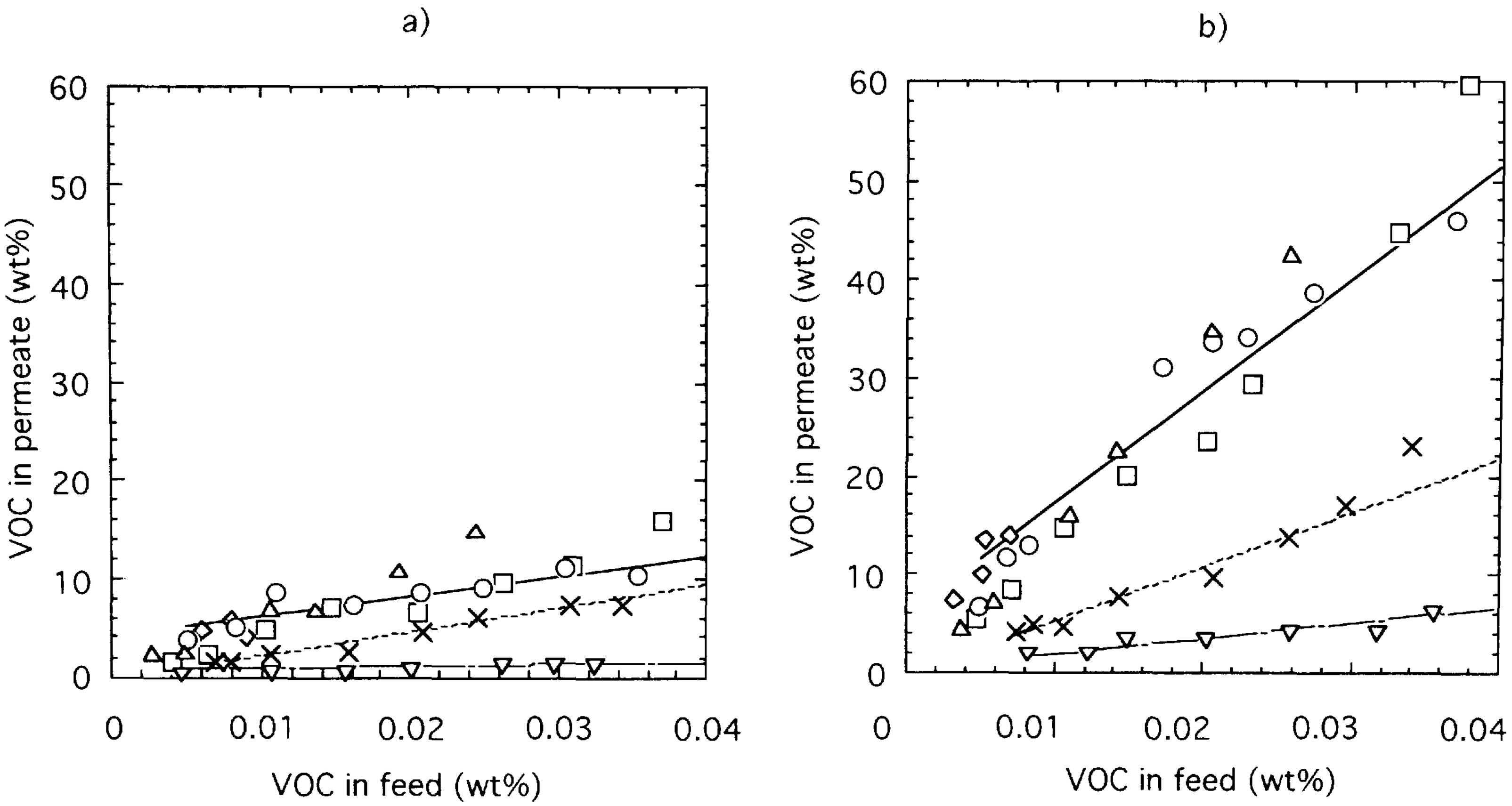

Fig. 7.5 Relationship between VOC concentration in feed and permeation during pervaporation through a) PDMS membrane, and b) grafted PDMS membrane.: (□) TCE, (◇) PCE, (○) Benzene, (△) Toluene, (×) EBU, (▽) EBZ.

The VOCs flux was increased with the feed concentration in both the PDMS membrane and the grafted PDMS membrane.

The relationships between the feed concentration and the permeate concentration are shown in Fig.7.5 for the PDMS membrane and the grafted PDMS membrane. The VOC flux increased with the feed concentration in both the PDMS membrane and the grafted PDMS membrane. In the grafted PDMS membrane, the best separation performance was due to introducing the hydrophobic polymer, poly(HDFNMA). The permselectivity for PCE and toluene was high in both the PDMS membrane and the grafted PDMS membrane. The permselectivity for EBU and EBZ was low in both the PDMS membrane and the grafted PDMS membrane.

The pervaporation properties of TCE and benzene mixed aqueous solutions were studied. The flux as a function of the TCE concentration in the feed solution is shown in Fig.7.6 for the PDMS membrane and the grafted PDMS membrane. The feed benzene concentration was fixed at 0.015wt%. For the PDMS membrane, when the feed TCE concentration increased, the water flux and the benzene flux were almost constant. The TCE flux increased with feed concentration. Hence, the total flux increased with feed concentration. The relationship between the TCE flux and feed TCE concentration of this TCE-benzene-water mixture was almost same as the relationship between the TCE flux and feed TCE concentration of the TCE-water mixture. Benzene did not affect the permeation of TCE in the PDMS membrane. For the grafted membrane, the pervaporation property of TCE and benzene mixed aqueous solutions was different from the PDMS membrane. The water flux decreased with increasing feed TCE concentration over TCE=0.02wt%. The TCE flux increased with feed concentration, and the the increase was keep down at a high feed concentration, in the grafted PDMS membrane. The benzene flux decreased with increasing feed concentration. The total flux decreased with increasing feed TCE concentration over TCE=0.02wt%. For the pervaporation property in the grafted PDMS membrane, TCE

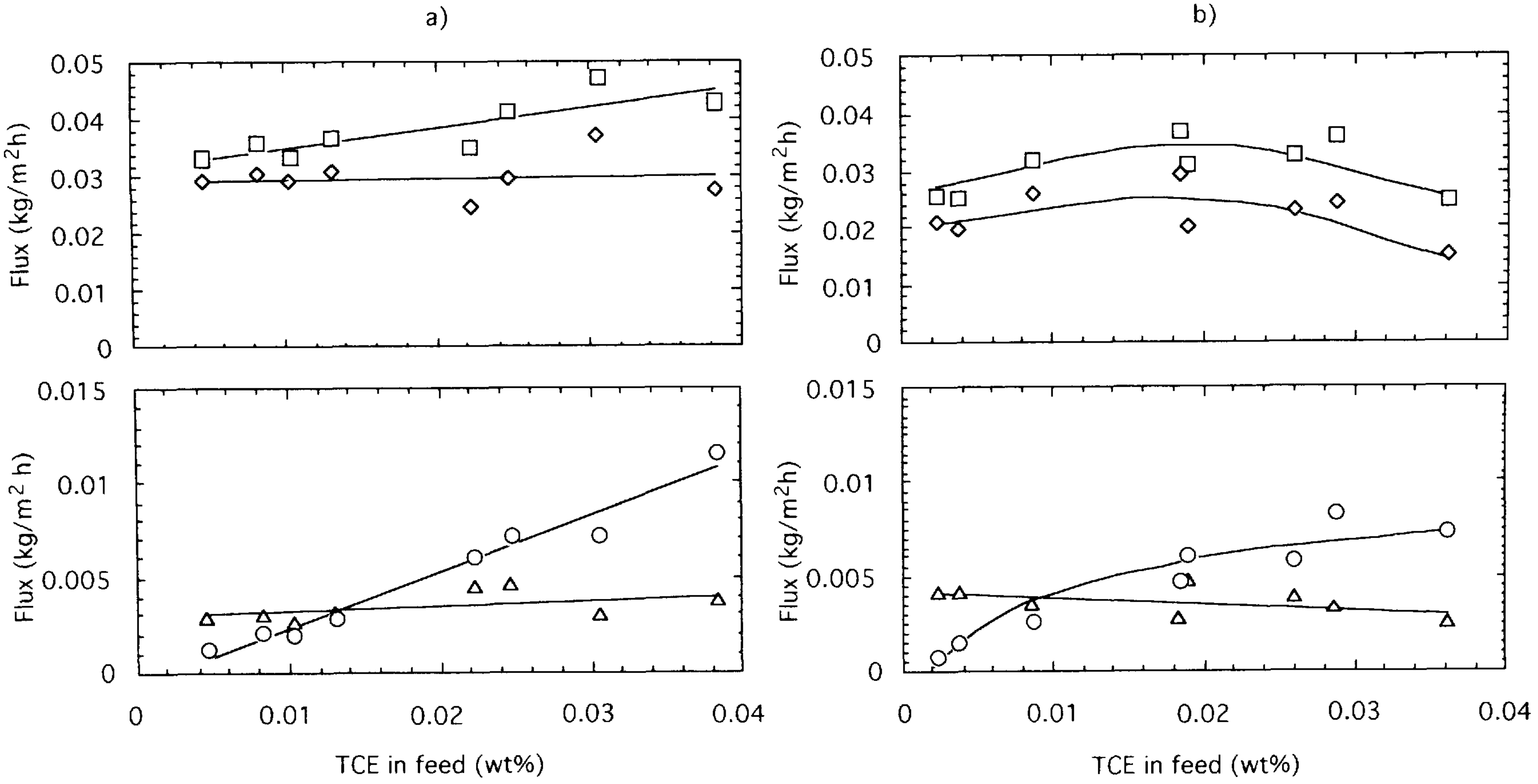

Fig. 7.6 Effect of feed TCE concentration on flux for TCE-Benzene-water mixture during pervaporation through a) PDMS membrane, and b) grafted PDMS membrane at 0.015wt% feed benzene concentration.: (□) Total, (◇) water, (○) TCE, (△) Benzene.

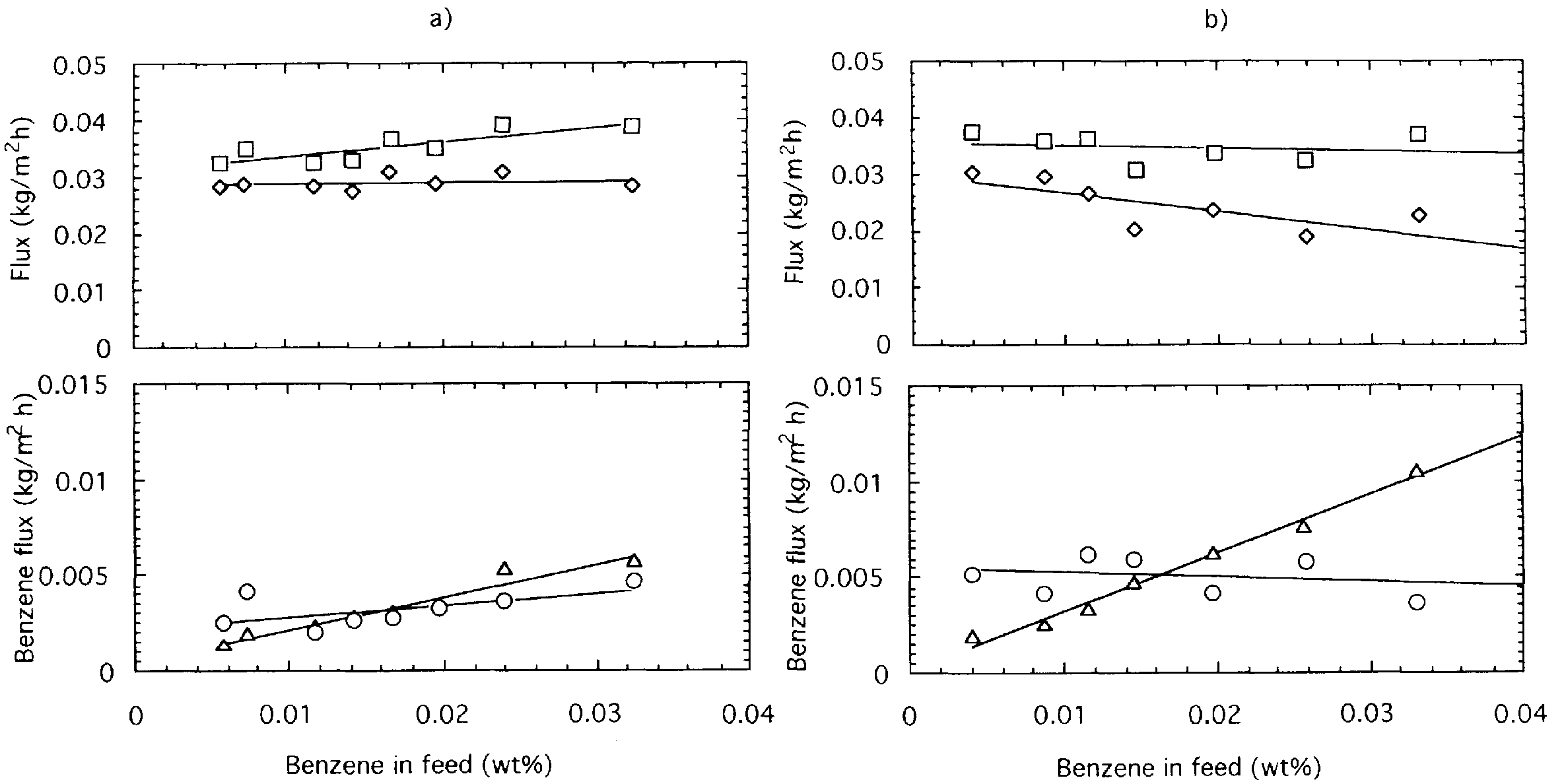

Fig. 7.7 Effect of feed benzene concentration on flux for TCE-Benzene-water mixture during pervaporation through a) PDMS membrane, and b) grafted PDMS membrane at 0.015wt% feed TCE concentration.: (□) Total, (◇) water, (○) TCE, (△) Benzene.

quantity sorbed into the membrane was very high due to introducing the hydrophobic polymer, HDFNMA, so that the diffusion of water and benzene was prevented, in turn, the flux decreased. Compared with the pervaporation for the TCE-water mixture, the TCE flux for the TCE-benzene-water mixture was low. The TCE flux was prevented by benzene during pervaporation of the TCE-benzene-water mixture. During pervaporation for TCE-benzene-water mixture through the grafted PDMS membrane, the compounds which permeate interfere each other.

Next, the feed TCE concentration was fixed at 0.015wt% and the feed benzene concentration was varied. The flux as a function of the benzene concentration in the feed solution is shown in Fig.7.7 for the PDMS membrane and the grafted PDMS membrane. For PDMS membrane, the water flux and the TCE flux were almost constant when the feed TCE concentration increased. The benzene flux increased with feed concentration. The Total flux were almost constant when the feed TCE concentration increased. While the water flux increased with feed benzene concentration during pervaporation of benzene-water mixtures, the phenomenon was not observed for benzene-TCE-water mixture through PDMS membrane. TCE molecules prevented the rise of water flux.

For grafted PDMS membrane, the water flux decreased with increasing feed concentration. The TCE flux were almost constant when the feed TCE concentration increased. The benzene flux increased with feed concentration. The total flux were almost constant when the feed TCE concentration increased. For the pervaporation of benzene-water mixture through the grafted PDMS membrane, the promote of water permeation was prevented. In addition to that, TCE molecules inhibited the rise of water flux during pervaporation of benzene-TCE-water mixture through the PDMS membrane. It is considered that during pervaporation of benzene-TCE-water mixture through the grafted PDMS membrane, both of grafted HDFNMA and TCE molecules prevented the permeation of water molecules.

7.3.3 Effect of the VOC properties on the sorption

The sorption isotherms for the VOCs are presented in Fig.7.8 for the PDMS membrane and the grafted PDMS membrane, respectively. The relationship between the feed concentration and the concentration in PDMS membranes was observed to be linear. For the grafted PDMS membranes, the concentration of VOC solution soaked into the membrane was significantly increased with increasing feed concentration. The sorption selectivity for VOCs was higher in the grafted PDMS membrane than in the PDMS membrane. As the consideration of characterization, the grafting started with the surface of membrane and was caused into the PDMS membrane. It is considered that the introducing hydrophobic HDFNMA to the PDMS membrane make the sorption selectivity enhanced. The grafted PDMS membrane that had the high VOC concentrations in the sorbed solution showed an excellent separation performance. The solubility for PCE and toluene was high in both the PDMS membrane and the grafted PDMS membrane. The solubility for EBU and EBZ was low in both the PDMS membrane and the grafted PDMS membrane.

The need for hydrophobicity data in the studies of organic compounds can be traced back at least to the turn of the century. The hydrophobicity is used to indicate the physical property of the molecule which governs its partitioning into the non aqueous portion of an immiscible or partially immiscible solvent pair. Pow, the partition coefficient between water and n-octanol, expressed the hydrophobicity of the compounds.

T.Lamer et. al.[21], considered the relationship between the logPow of aroma compounds and their solubility for PDMS membrane. The hydrophobicity, Pow, is closely related to the solubility of organic compounds[21]. The solubility coefficient (K) represent the solubility of organic compounds for membrane. The decimal logarithms of the solubility coefficient (K) as a function of the logPow are shown in Fig. 7.9 for the PDMS membrane and the grafted PDMS membrane. The solubilitiy (logK) for PCE and toluene which have a high logPow, were high in both the PDMS membrane and the grafted PDMS membrane. The solubility (logK) for EBU which have low logPow was low in both the PDMS membrane and the grafted PDMS membrane.

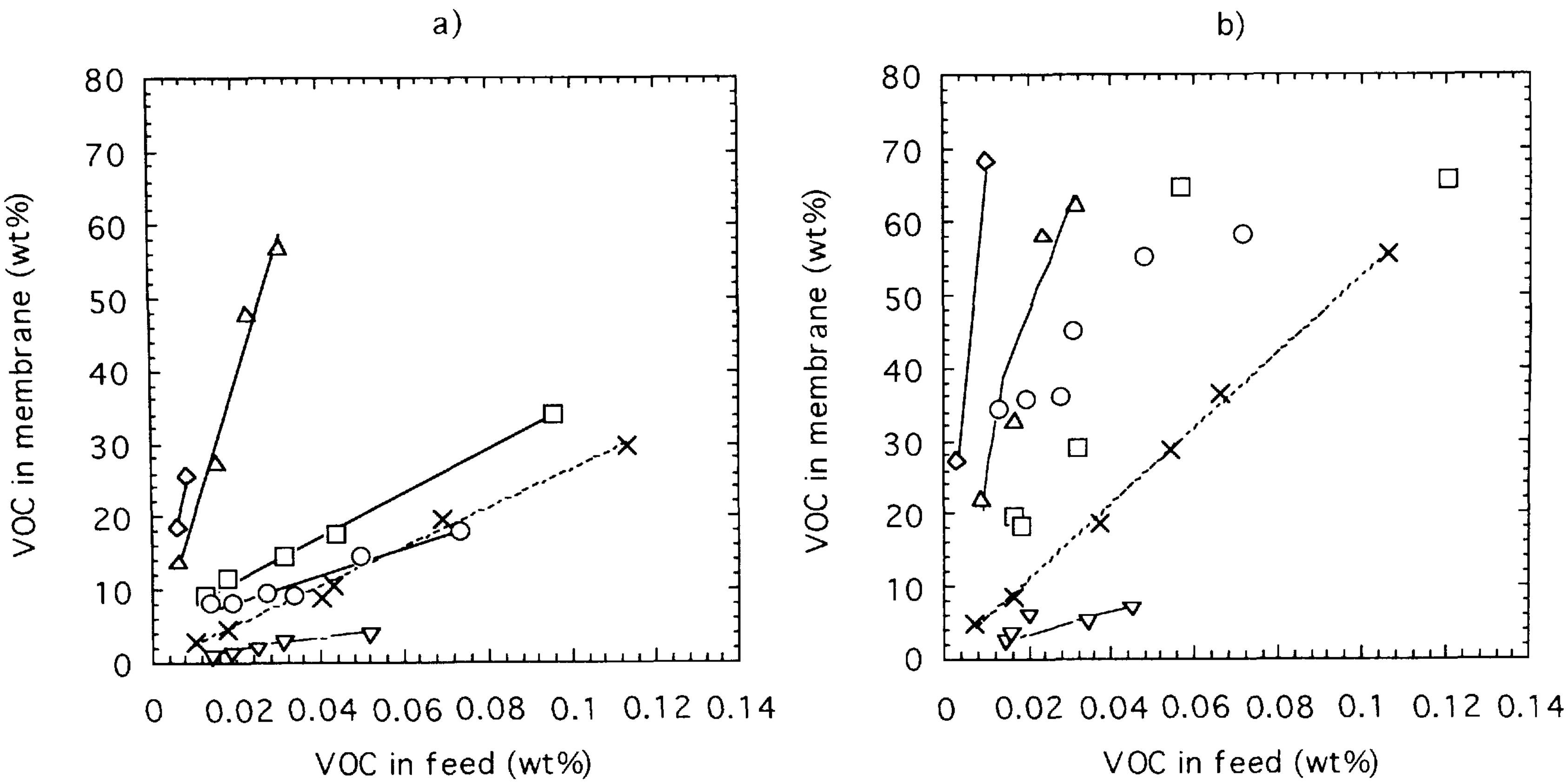

Fig. 7.8 Sorption of VOC on PDMS membrane as a function of the feed concentration at equilibrium for a) PDMS membrane, and b) grafted PDMS membrane.: (□) TCE, (◇) PCE, (○) Benzene, (△) Toluene, (×) EBU, (▽) EBZ.

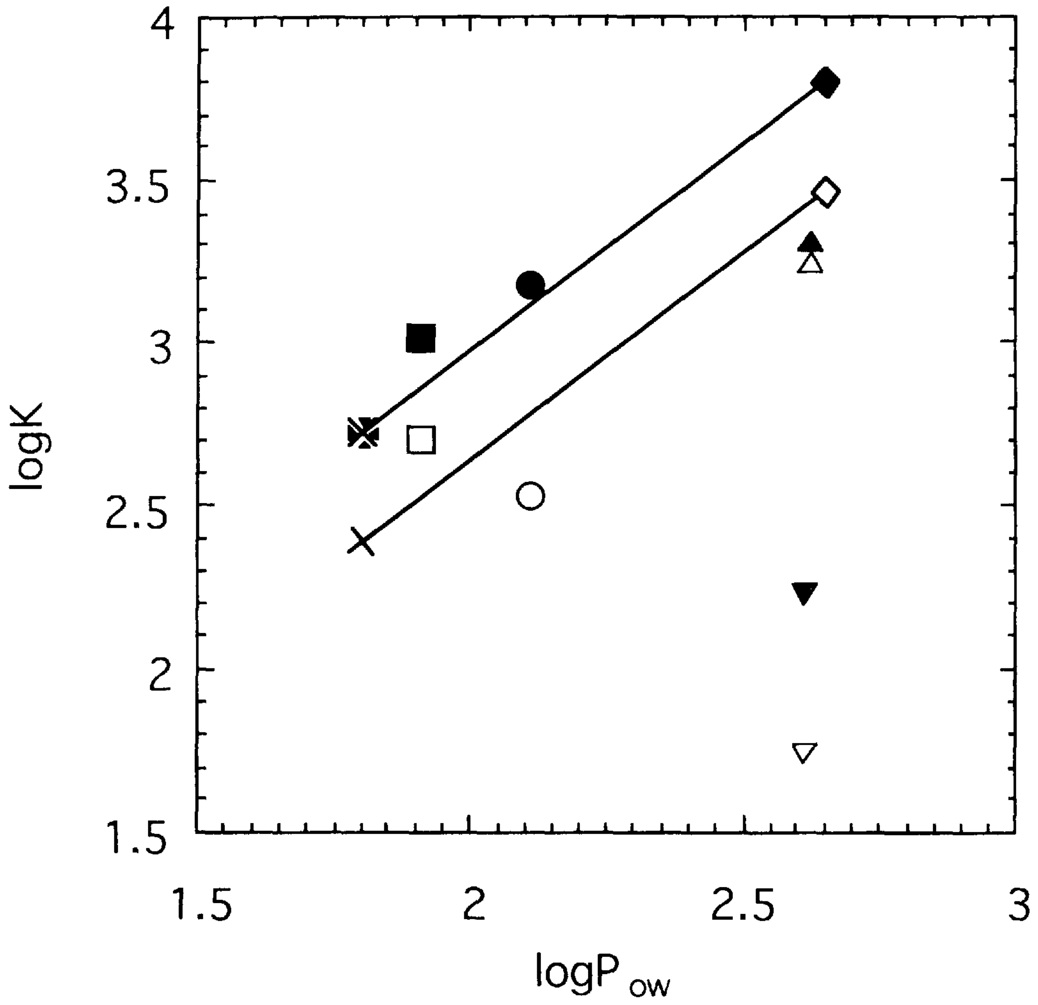

Fig. 7.9 Relationship between the hydrophobicity of VOC and the sorption in grafted PDMS membrane.: (□) TCE, (◇) PCE, (○) Benzene, (△) Toluene, (×) EBU, (▽) EBZ, open: for PDMS membrane, closed: for grafted PDMS membrane.

Table 7.3 Sorption and dffusion data of various VOCs for PDMS and grafted PDMS membrane

Compound	logPow	logK		Degree of sorption in PDMS membrane (mol / PDMS-100g)	Molecular volume (cm^3 / mol)	Separation factor (α_D)	
		PDMS membrane	grafted PDMS membrane			PDMS membrane	grafted PDMS membrane
TCE	1.91	2.71	3.25	2.04	90.0	0.705	0.918
PCE	2.638	3.48	4.20	1.60	102	0.121	0.133
Benzene	2.103	2.55	3.42	1.05	88.9	0.999	0.809
Toluene	2.626	3.28	3.63	1.45	106	0.214	0.611
EBU	1.805	2.40	2.89	1.34	132	0.934	0.962
EBZ	2.602	1.76	2.27	0.154	144	0.511	0.935

The solubility (logK) for EBZ was low in both the PDMS membrane and the grafted PDMS membrane, while EBZ has a high logPow. Then, the ability of penetrate for VOCs in membrane was investigated. The degree of sorption for the pure VOC liquid in the membranes are shown in Table 7.3. The degree of sorption for TCE, PCE, benzene, toluene and EBU are above 80wt% (above 1mol/PDMS-100mg). The solubility for compounds in a membrane is affected by its dispersion and polarization. Polarization can be considered using the Pow value. The ability of dispersion is determined by diffusivity. The degree of sorption for EBZ was low, 23.1wt% (0.154mol/PDMS-100mg). The molecular volume of EBZ is much greater than the other VOCs ,therefore, the diffusivity of EBZ is low. Hence, the degree of sorption for EBZ was low and the solubility for EBZ was low in the membrane.

7.3.4 Effect of the VOC properties on the diffusion

Pervaporation performance of a membrane is determined by both the sorption and the diffusion characteristics of the permeating components in the membrane.

The relationship between the separation factor during permeation (α_{pv}), the separation factor during sorption(α_S), and the apparent separation factor during diffusion (α_D) is given by Eq.(7.9).

$$\alpha_{pv}=\alpha_S \cdot \alpha_D \quad (7.9)$$

α_D is described by Eq.(7.10) using Eq.(7.4), (7.7) and (7.9).

$$\alpha_D=\{Y(1-Y')\}/\{(1-Y)Y'\} \quad (7.10)$$

where Y and Y' denote the concentration of VOCs in the permeate solution and in the swollen membranes for the same feed solution, respectively. α_D was calculated by Eq.(7.10) using the sorption isotherms in Fig.7.8 and the pervaporation in Fig.7.5. α_D as a function of the VOCs concentration in the feed solution is shown Table 7.3 for the PDMS membrane and the grafted PDMS membrane, respectively. The diffusivity for benzene and EBU was high in both the PDMS membrane and the grafted PDMS membrane. The diffusivity for PCE was low in both the PDMS membrane and the grafted PDMS membrane. The molecular volumes and α_D of the VOCs are shown in Table 7.3. The molecular volumes of benzene and EBU are much smaller than the other VOCs that their diffusivities is high. PCE has four Cls with so larger molecular volume, therefore, the diffusivity is very low.

Permselectivity determined by the sorption and the diffusion characteristics of the permeating components in the membrane. The permselectivity of PCE and toluene were high. Because the molecular volume of the VOCs is grater than water and the permeate quickly penetrates in a rubbery membrane like PDMS, permselectivity was not affected by the diffusivity. Solubility significantly affects the permselectibity during pervaporation through hydrophobic rubbery membrane.

7.4 Conclusions

The pervaporation properties of various VOC aqueous solutions through the grafted PDMS membrane were studied in this investigation. The pervaporation performance of a membrane is determined by both the sorption and the diffusion characteristics of the permeating components in the membrane. The sorption and diffusion for VOC-water mixture during pervaporation through the PDMS membrane and HDFNMA grafted PDMS membrane were studied.

In the grafted PDMS membrane, the best separation performance was due to introducing the hydrophobic polymer, poly(HDFNMA). During pervaporation, the components which permeate and membrane interface each others. The phenomenon was significantly observed in pervaporation for the ternary mixture through the grafted PDMS membrane.

The solubilitiy (logK) for PCE and toluene which have a high logPow, were high in both the PDMS membrane and the grafted PDMS membrane. The solubility (logK) for EBU which have low logPow was low in both the PDMS membrane and the grafted PDMS membrane. The solubility (logK) for EBZ was low in both the PDMS membrane and the grafted PDMS membrane, while EBZ has a high logPow. The solubility for compounds in a membrane is affected by its dispersion and polarization. Polarization can be considered using the Pow value. The ability of dispersion is determined by diffusivity. The degree of sorption for EBZ was low compared to the other VOCs. The molecular volume of EBZ is much greater than the other VOCs ,therefore, the diffusivity of EBZ is low. Hence, the degree of sorption for EBZ was low and the solubility for EBZ was low in the membrane. PCE has four Cls with a much larger molecular volume, therefore, the diffusivity is very low.

Permselectivity is determined by the sorption and the diffusion characteristics of the permeating components in the membrane. The permselectivity of PCE and toluene was high in this study. Because the molecular volume of the VOCs is grater than water and the permeate quickly penetrates in the rubbery membrane like PDMS, permselectivity was not affected by diffusivity. Solubility significantly affects the permselectibity during pervaporation through the hydrophobic rubbery membrane.

7.5 Acknowledgments

The authors are grateful to Fuji Systems Corporation for providing the PDMS membranes.

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Chapter 8. Characterization of Graft-Polymerized PDMS Membranes with Fluoroalkyl Methacrylate by Simultaneous Irradiation using Gamma Ray and their Permeation Behavior for Chlorinated Hydrocarbon-Water Mixtures

8.1 Introduction

The purification of ground water and waste water, which are contaminated with chlorinated hydrocarbons, is desired and has been studied[1,2]. Pervaporation can be useful compared with these conventional methods, because of the flexibility in design, the low energy cost and the possibility of solvent recycling[1~19]. Polydimethylsiloxane (PDMS) membrane has been the most widely used and studied material to perform VOCs extraction because of its high permeability[20]. Fluorinated polymers have been studied for their hydrophobicity based on their low surface energy[9,21,22]. The improvement of PDMS membranes using fluoroalkylmethacrylates (FALMA) have been expected and investigated to enhance the affinity of PDMS for chlorinated hydrocarbons in this study. For this improvement, blending of PDMS and poly(FALMA) is difficult due to the low affinity of PDMS for poly(FALMA). There is the possibility of preparing graft or block copolymers of them. Graft and block copolymers, compared to mixtures of the corresponding polymers, often make it possible to join incompatible polymers in that form[23].

A radiation source which has high energy and the possibility of industrial use has been studied[24~47]. Compared with other irradiations[48], gamma ray radiation has high energy and can control the degree of grafting in order to obtain compatible flux and selectivity. Preirradiation and simultaneous irradiation have been known as methods of radiation-induced graft polymerization[24]. Preirradiation is a method in which the monomer is reacted with the polymer which has been irradiated in advance[24]. The preservation of radicals is necessary for this method. Simultaneous irradiation is a method in which the monomer and polymer are irradiated simultaneously[25]. In this chapter, simultaneous irradiation was studied.

Membranes that have a phase-separated structure in a composite with PDMS and the incompatible polymers have been reported [22,49~53]. The papers reported on membranes which were prepared by casting of the block copolymer and graft copolymer solutions or crosslinking them. The membranes were more hydrophobic at the air-side surface than at the glass-side surface. The preparation of the membranes composed of a homogeneous mixture of incompatible polymer domains is difficult, while homogeneous membranes are better for evaluation of the permeation of the membrane and application to a membrane process.

As PDMS is a silicone rubber and the preservation of radicals is difficult, the large amount of degree of grafting can not be obtained by preirradiation method. Radiation-induced graft polymerization by simultaneous irradiation using the Gammacell ^{60}Co source has the possibility of radical reaction of the monomer absorbed in the membrane with excellent penetration and is expected to synthesize novel and useful membranes with a homogeneous composition of PDMS and poly(FALMA).

In chapter 3~7, the solute properties, the interaction and the sorption-diffusion mechanism that effect on the permeation behavior through the rubbery untreated PDMS membrane and the grafted membranes by preirradiation method were investigated.

In this chapter, the novel grafted membranes which have high grafted amount and phase-separated structure in composite with PDMS and the incompatible polymer, poly(FALMA), which had the effect of increasing the selectivity for chlorinated hydrocarbons, were synthesized by simultaneous irradiation method using a ^{60}Co source. The grafted amount by simultaneous irradiation was rich and the permeation behavior will be expected to be differ from the rubbery untreated PDMS membrane and the grafted membranes by preirradiation method. The grafted PDMS membrane by simultaneous irradiation was characterized and used for pervaporation. This chapter reports the characterization of the grafted PDMS membranes by simultaneous irradiation, and their permeation behavior of chlorinated hydrocarbon-water mixtures compared to the PDMS membrane and the grafted PDMS membranes by preirradiation method.

8.2 Experimental

8.2.1 Graft polymerization of fluoroalkyl methacrylate by ^{60}Co source

Commercial PDMS membranes (Fuji Systems Corporation), 50μm thick, were used throughout this work. The chemical structure of PDMS and 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA) is shown in Fig.8.1. HDFNMA (Daikin Fine Chemical Laboratory Corporation) was used as received to avoid homopolymerization. Methanol, acetone and trichloroethylene (TCE) (Special grade,Waco Pure Chemical Industries, Ltd.) were used as received.

The procedure of graft polymerization was simultaneous irradiation as reported by G. Odian et al.[27]. A schematic diagram of the apparatus is shown in Fig.8.2.

First, PDMS membranes (7×7cm) and HDFNMA solution in ampoules were degassed and sealed under vacuum simultaneously. The ampoules were then irradiated from a ^{60}Co source at 25°C. After the irradiation was ended, the membranes were washed and soaked in acetone for 24h to remove the monomer and homopolymer with acetone. The membranes were then dried for 48 hours in an evacuated vessel. The degree of grafting was calculated as follows:

$$\text{Degree of grafting}(\%)=(W_1-W_0)/W_0 \mathrm{X} 100 \quad (8.1)$$

where W_0 and W_1 denote the weight of the PDMS membrane and the grafted PDMS membrane, respectively.

Poly(HDFNMA), a homopolymer polymerized by a ^{60}Co source was dissolved at a concentration of 5g/100ml in acetone. A glass viscometer was used to measure the kinematic viscosity at 25 °C. The relative viscosity was calculated as follows:

Relative viscosity $\eta_{rel}=\eta/\eta_o=\rho t/\rho_o t_o=t/t_o$ (8.2)

η: Kinematic viscosity of 5g/100ml poly(HDFNMA) solution

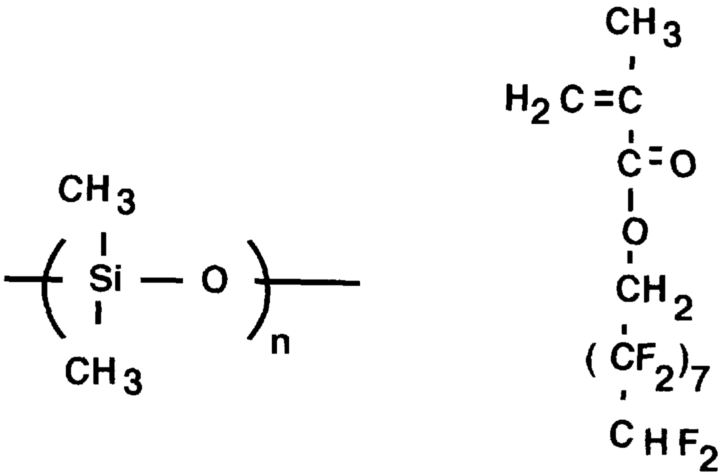
η_o: Kinematic viscosity of acetone

ρ: Density of 5g/100ml poly(HDFNMA) solution

ρ_o: Density of acetone

t: Fluid time of 5g/100ml poly(HDFNMA) solution

t_o: Fluid time of acetone



Polydimethylsiloxane

(PDMS)

1H,1H,9H-hexadecafluorononyl methaclyrate

(HDFNMA)

8.1 Structure of PDMS and HDFNMA

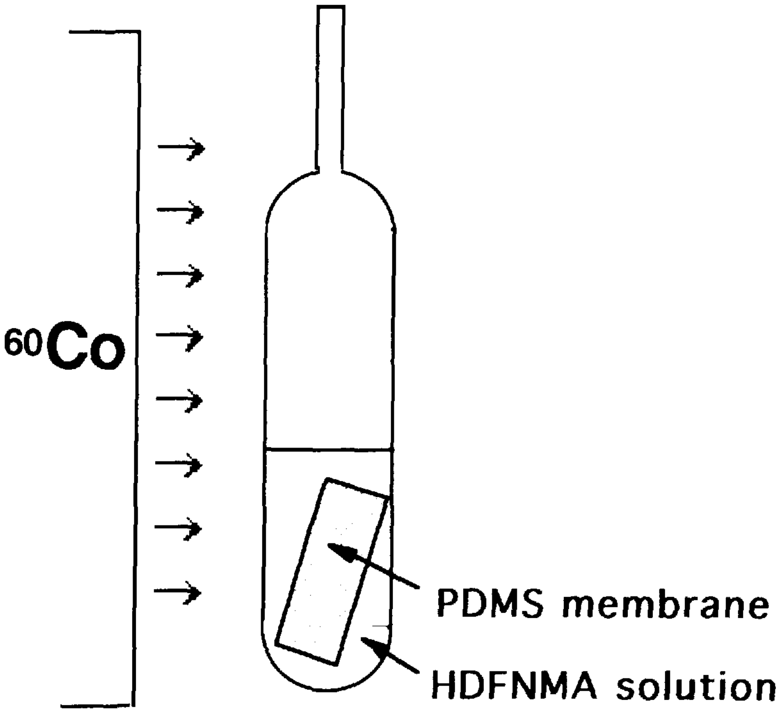


Fig. 8.2 Apparatus for the graft polymerization by ^{60}Co.

8.2.2 Characterization of the grafted PDMS membrane

The FT-IR/ATR spectra were obtained by 1800 FT-IR/ATR spectroscopy (Perkin-Elmer Co., Ltd.). The instrument was operated at cycle=50. The KRS-5 (TlBr-T(II)) internal refraction element (IRE) was used at an incident angle of 45°.

The wide angle X-ray diffraction (WAXD) spectra were obtained with a 1200 X-ray diffractometer using a Cu anode (Rigaku -Denki Co., Ltd.). The instrument was operated at 40kV-20mA, with $\lambda = 1.54$ at 20°C. The scan speed was $2\theta = 2.00°/\text{min}$ for 3~50°.

The differential scanning calorimeter (DSC) curve was obtained using a DSC7(Perkin-Elmer Co., Ltd.). The DSC scan starts from -150°C and is measured up to 300°C. The rate of temperature increase is usually 10°C/min.

X-ray photoelectron spectroscopy(XPS) spectra were obtained with an IPS-9000SX (JEOL, Ltd.) using MgKα exciting radiation (1253.6eV). The X-ray gun was operated at 10eV with a sample chamber vacuum of less than $5\text{X}10^{-9}$Torr. The XPS spectra were recorded at two electron emission angles(θ) of 30° and 90°.

8.2.3 Pervaporation experiment and sorption measurement

The pervaporation experiments were performed as in the previous study[26] using the continuous-feed type at 25°C. The feed solution was circulated through the cell and the feed tank. The effective membrane area in the cell was 19.6cm^2. The pressure at the permeation side was kept below 10Torr by a vacuum pump. Upon reaching steady state flow conditions, the permeate was collected in traps cooled by liquid nitrogen(-196°C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate, flux(J), was obtained by Eq.(8.3)

$$J = Q/At \quad (8.3)$$

where Q is the amount permeated during experimental time interval t and A is the effective surface area. The TCE flux was calculated from the total flux and the permeate composition. The concentration of TCE in the feed and permeate solution was determined by gas chromatography using an FID detector. The separation factor, α_{pv}, was calculated as

$$\alpha_{pv}=\{Y(1-X)\}/\{(1-Y)X\} \qquad (8.4)$$

where X and Y denote the concentration of TCE in the feed and permeate solution, respectively.

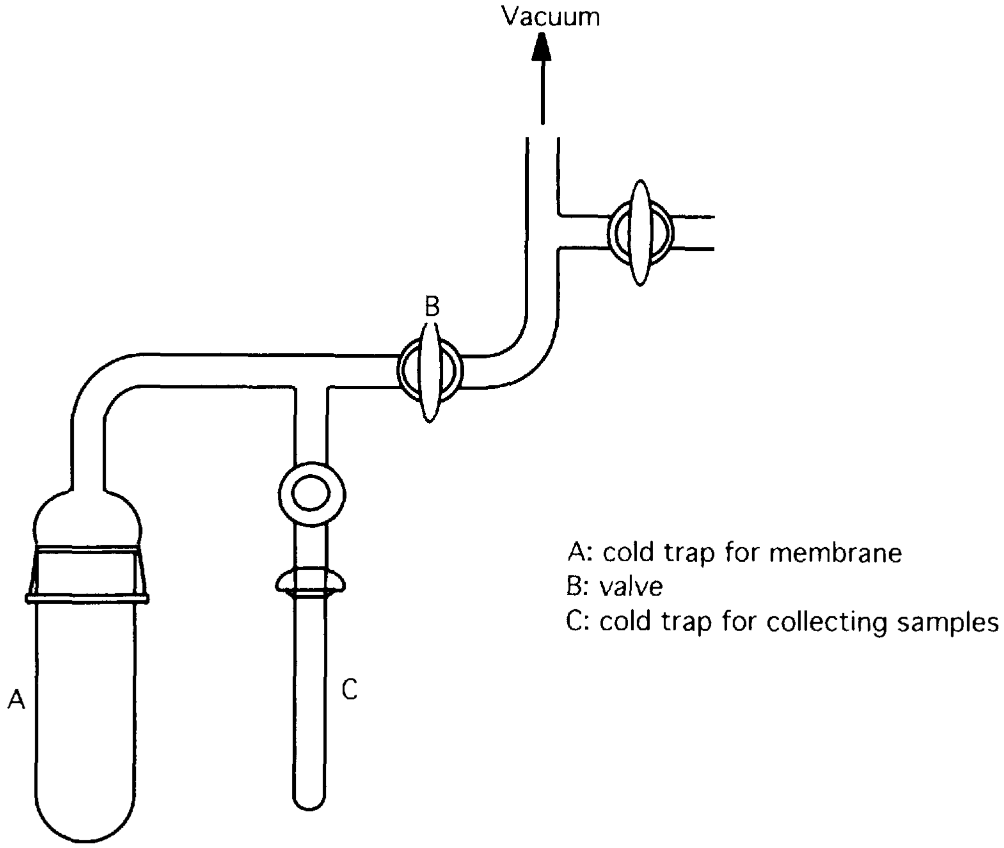


Fig. 8.3 Apparatus for the composition measurement in the membrane.

The dried and weighed membrane was immersed in TCE solution and sealed at 25°C until equilibrium was reached. The membrane was then taken out of the vessel, wiped quickly with filter paper and weighed. The degree of sorption of TCE solution into the membranes was measured as

$$\text{Degree of sorption}(\%)=(W_1-W_0)/W_0 X 100 \quad (8.5)$$

where W_0 and W_1 denote the weight of the dried membrane and the swollen membrane, respectively. The concentration of TCE solution soaked in the membrane was determined using the apparatus in the schematic diagram shown in Fig.8.3. The membrane on reaching equilibrium was taken out of the vessel, wiped quickly with filter paper and placed in trap A. The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, cock B was closed and the TCE solution soaked in the membrane and vaporized by heating with a drier was collected in cooled traps. The concentration of TCE solution in the feed and the soaked membrane was determined by gas chromatography. The separation factor, α_s, was calculated as

$$\alpha_s=\{Y'(1-X)\}/\{(1-Y')X\} \quad (8.6)$$

where X and Y' denote the concentration of TCE in the feed solution and the swollen membranes, respectively.

8.3 Results and discussion

8.3.1 Graft polymerization of fluoroalkyl methacrylate by 60Co source

The effect of irradiation time on the degree of grafting at a fixed HDFNMA content or irradiation source strength was investigated. Various conditions in simultaneous irradiation and the degree of grafting are given in Table 8.1. The membranes grafted at dose rate of 0.5Mrad/h were brittle and unsuitable for use as membranes. The membranes grafted at dose rates of 0.1 Mrad/h were not so brittle. For the PDMS membranes soaked in 30 or 100 wt% HDFNMA and irradiated at 0.1 Mrad/h, HDFNMA was grafted equally in the whole membrane and the grafted PDMS membrane was semipermeable, while in 50 or 75 wt%, the membranes were grafted too much and were unsuitable for use as membranes.

Table 8.1 The degree of grafting under various conditions in simultaneous irradiation

Dose rate of irradiation (Mrad/h)	HDFNMA (wt% in MeOH)	Degree of grafting (wt%) Irradiation time (h) 1	2	3	4	5
0.5	30	17.8		69.9		46.7
0.1	30	21.3	98.1	98.4	131	96.6
0.1	50	85.1		-^{a}		-^{a}
0.1	75	142		220		-^{a}
0.1	100	105	138	133	136	143

a : Grafted too much and unsuitable for use as membranes.

The dependence of the degree of grafting and membrane thickness on irradiation time is shown in Fig.8.4. The degree of grafting and membrane thickness at a fixed HDFNMA content and a dose rate of irradiation was increased with increasing irradiation time. When the irradiation time or irradiation strength increase, the crosslinking between inter- or intrachains of individual polymers can take place significantly compared to the grafting reaction. The crosslinking reaction contributes to membrane performance. When the membranes were grafted at a dose rate of 1Mrad/h, the crosslinking reaction took place significantly and the grafted membranes were not swelled in the solvent. In this study, the effect of irradiation time and HDFNMA content on the crosslinking reaction and grafting reaction were investigated. The extent of the crosslinking reactions is a function of the thickness and HDFNMA composition of a membrane and would be different between membranes with different membrane thickness or between the grafted PDMS and homo-poly(HDFNMA) membranes under a given reaction condition. In this chapter, the thicknesses of the membranes before graft-polymerization were constant, and the effect of the HDFNMA composition was investigated. The homopolymer, poly(HDFNMA), polymerized at 0.1Mrad/h, was dissolved in acetone. Poly(HDFNMA) polymerized of 30wt% HDFNMA was dissolved in acetone completely, while poly(HDFNMA) polymerized of 100wt% HDFNMA did not dissolve completely and became a gel.

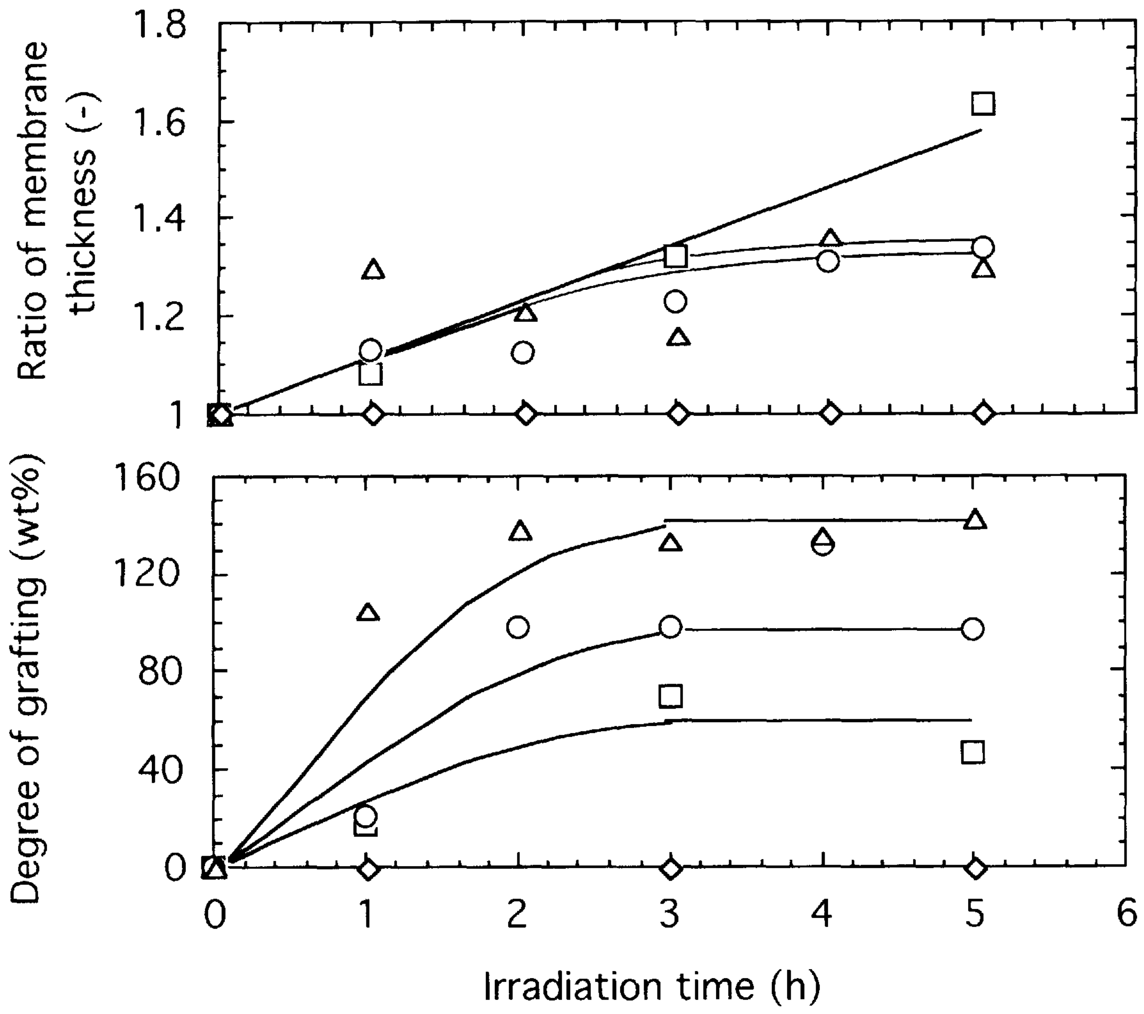


Fig. 8.4 Dependence of the degree of grafting and membrane thickness on irradiation time: (□) membrane irradiated in 30wt% HDFNMA at 0.5Mrad/h, (○) in 30wt% at 0.1Mrad/h, (△) in 100wt% at 0.1Mrad/h, (◇) in MeOH at 0.1Mrad/h.

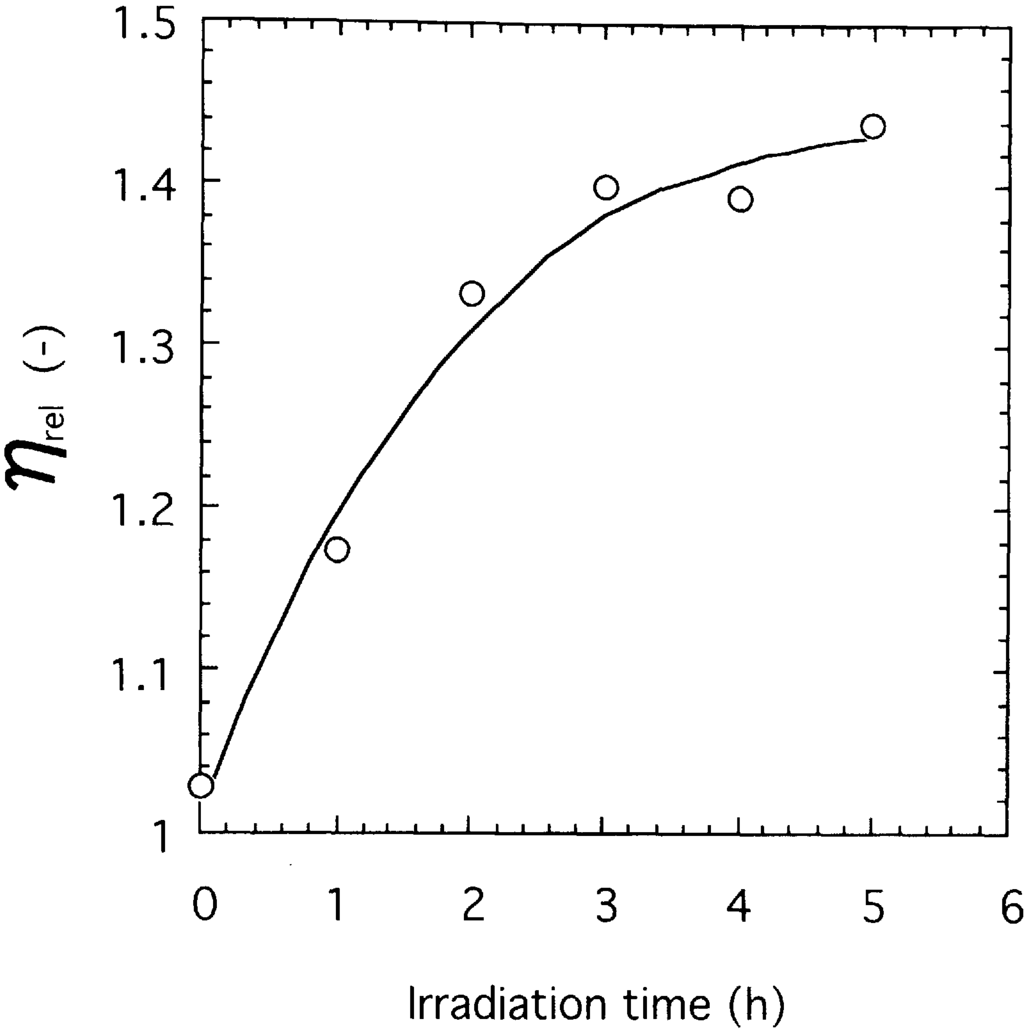


Fig. 8.5 Dependence of viscosity of poly(HDFNMA) on irradiation time.

Poly(HDFNMA) polymerized of 100wt% HDFNMA was crosslinked, because the HDFNMA content was high and the density of the radicals produced by irradiation was high. The results show that the grafted HDFNMA of 100wt% HDFNMA was crosslinked. The poly(HDFNMA) made of 30wt% HDFNMA by irradiation was viscous and dissolved in acetone completely. The grafted HDFNMA of 30wt% HDFNMA was not crosslinked. The relative viscosity of poly(HDFNMA) polymerized of 30wt% HDFNMA at 0.1Mrad/h as a function of the irradiation time is shown in Fig.8.5. The viscosity was increased with irradiation time. The results showed that the degree of polymerization was increased with irradiation time.

8.3.2 Characterization of the grafted PDMS membrane

The FT-IR/ATR of the grafted PDMS membranes is shown in Fig.8.6. After the PDMS was grafted with HDFNMA, a characteristic new peak was observed near 1150 and 740 cm^{-1}. The peaks are characteristic peaks of poly(HDFNMA). The intensity of these peaks was increased with the grafted amount.

Fig.8.7 shows the WAXD patterns of the grafted PDMS membrane. As reported by Nakamae[54], the lower 2θ of the inner halo is assigned to the intersegmental distance of the polymer, and the larger 2θ of the outer halo is assigned to the intrasegmental distance of the polymer. The halo for PDMS was observed at $2\theta=12°$and 21°.The halo for poly(HDFNMA) was observed at $2\theta=17°$and 40°. Intersegmental and intrasegmental distances of poly(HDFNMA) were narrower than those for PDMS. For the grafted membrane, $2\theta=17°$and 40° values of the halo were observed in addition to $2\theta=12°$and 21° for PDMS, and the intensity of the halo for poly(HDFNMA) increased with increasing degree of grafting. Furthermore, no new halo was observed for the grafted PDMS membranes. PDMS and poly(HDFNMA) existed individually in the grafted PDMS membranes. The semipermeable grafted PDMS membrane is considered to have a microphase-separated structure, i.e., a separated structure of PDMS and grafted HDFNMA[54]. PDMS is a rubbery polymer and it clearly has no crystalline structure based on the diffraction patterns.

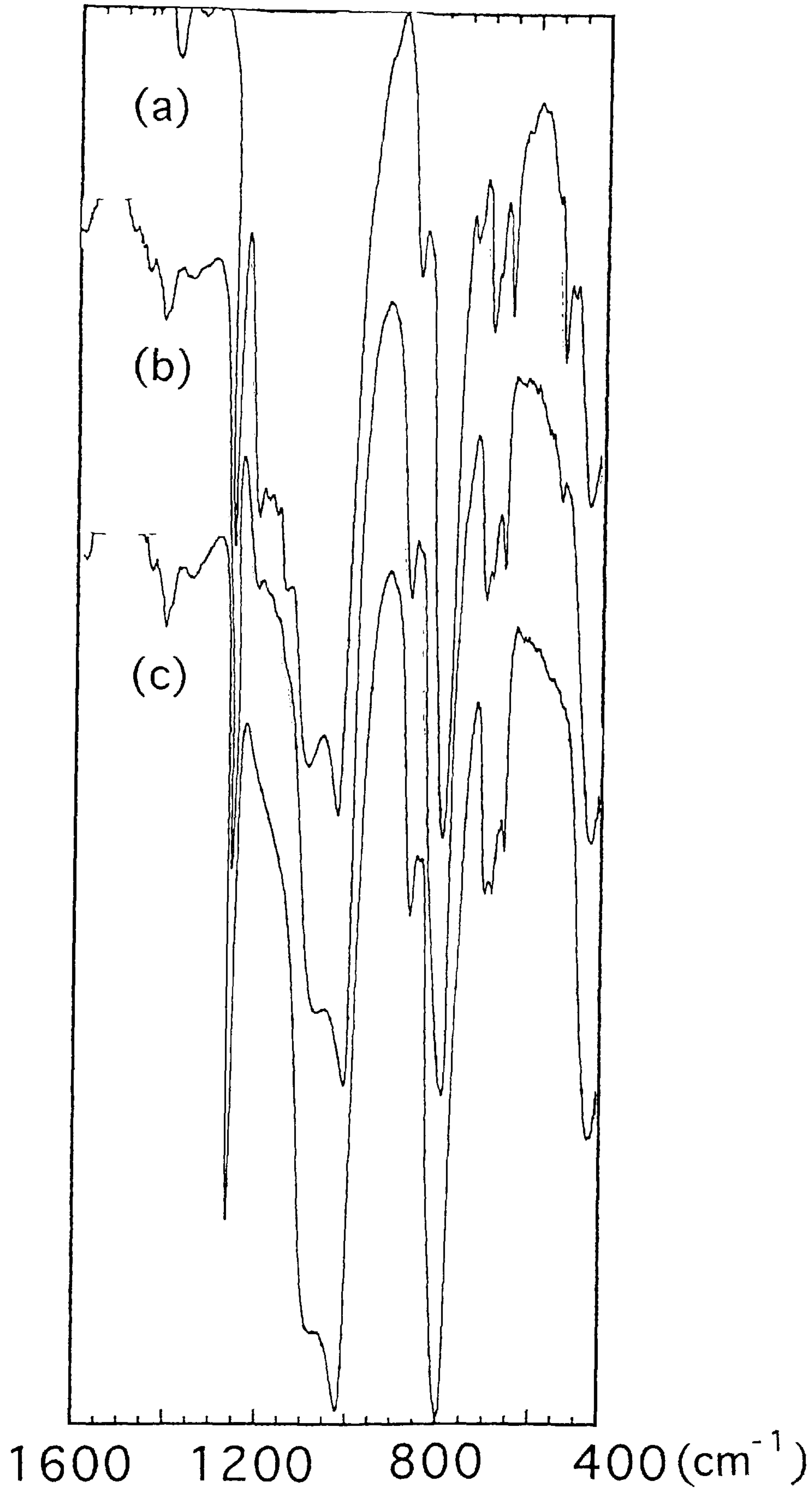


Fig. 8.6 FT-IR/ATR spectra of PDMS membranes before and after graft polymerization of HDFNMA: (a) membrane irradiated at 0.1Mrad/h for 5h in 100wt% HDFNMA, (b) for 1h in 30wt% HDFNMA; (c) PDMS.

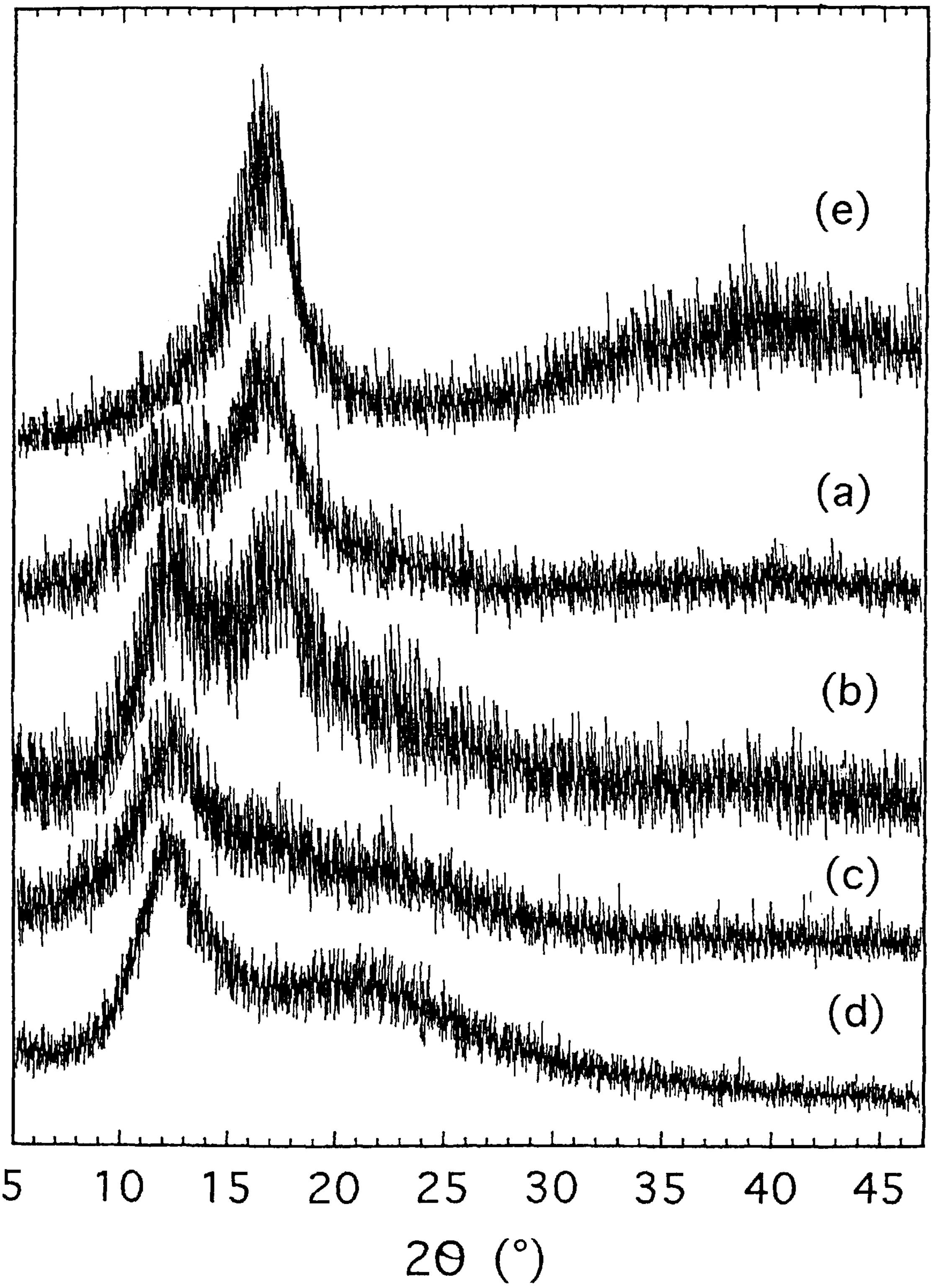


Fig. 8.7 Wide angle X-ray diffraction patterns of PDMS and grafted PDMS membranes: (a) membrane irradiated in 30wt% HDFNMA at 0.1Mrad/h for 5h, (b) for 3h, (c) for 1h; (d) PDMS; (e) poly(HDFNMA).

From the diffraction patterns of the region of poly(HDFNMA), no crystalline structure was observed in the membrane. In the separation processes in nonporous membranes, it has been found that both sorption and diffusion depend on the degree of crystallization. Gas and liquid can permeate the amorphous regions preferentially compared with the crystal regions[55]. Furthermore, the intersegmental and intrasegmental distances of the polymer also affect the permeability[4].

The DSC curves of the grafted PDMS membranes are shown in Fig.8.8. For the membrane after grafting with HDFNMA, the endothermic peak of the internal friction energy between the macromolecular chains for PDMS was observed at -124°C. The peak for the homopolymer of HDFNMA polymerized by irradiation was not observed in the range of -150°C~300°C. Fig.8.9 shows the correlation between the internal friction energy for the macromolecular chains (J/g) at -124°C and the degree of grafting for the grafted PDMS membranes. The internal friction energy between molecular chains (J/g) for the grafted PDMS membranes was decreased with increasing degree of grafting. The peak of the internal friction energy between the macromolecular chains (J/g) for the grafted PDMS membranes was obtained at the same temperature for PDMS; hence, it is considered that the grafted PDMS membranes have the microphase-separated structure of PDMS and grafted HDFNMA[56]. The linear relationship between the internal friction energy between macromolecular chains (J/g) and the degree of grafting is better for membranes soaked in 100 wt% HDFNMA and irradiated at 0.1 Mrad/h. Because the quantity of PDMS in a unit volume of the grafted PDMS membranes which was soaked in 100 wt% HDFNMA and irradiated at 0.1 Mrad/h is constant, the internal friction energy between macromolecular chains for the membranes irradiated in 100 wt% HDFNMA was in inverse proportion to the degree of grafting. The poly(HDFNMA) regions in the membranes soaked in 100 wt% HDFNMA and irradiated at 0.1Mrad/h were dispersed quite homogeneously.

The surface morphologies of the grafted PDMS membranes were analyzed by XPS spectra. The XPS spectra are shown in Fig.8.10. By grafting with HDFNMA, the fluorine

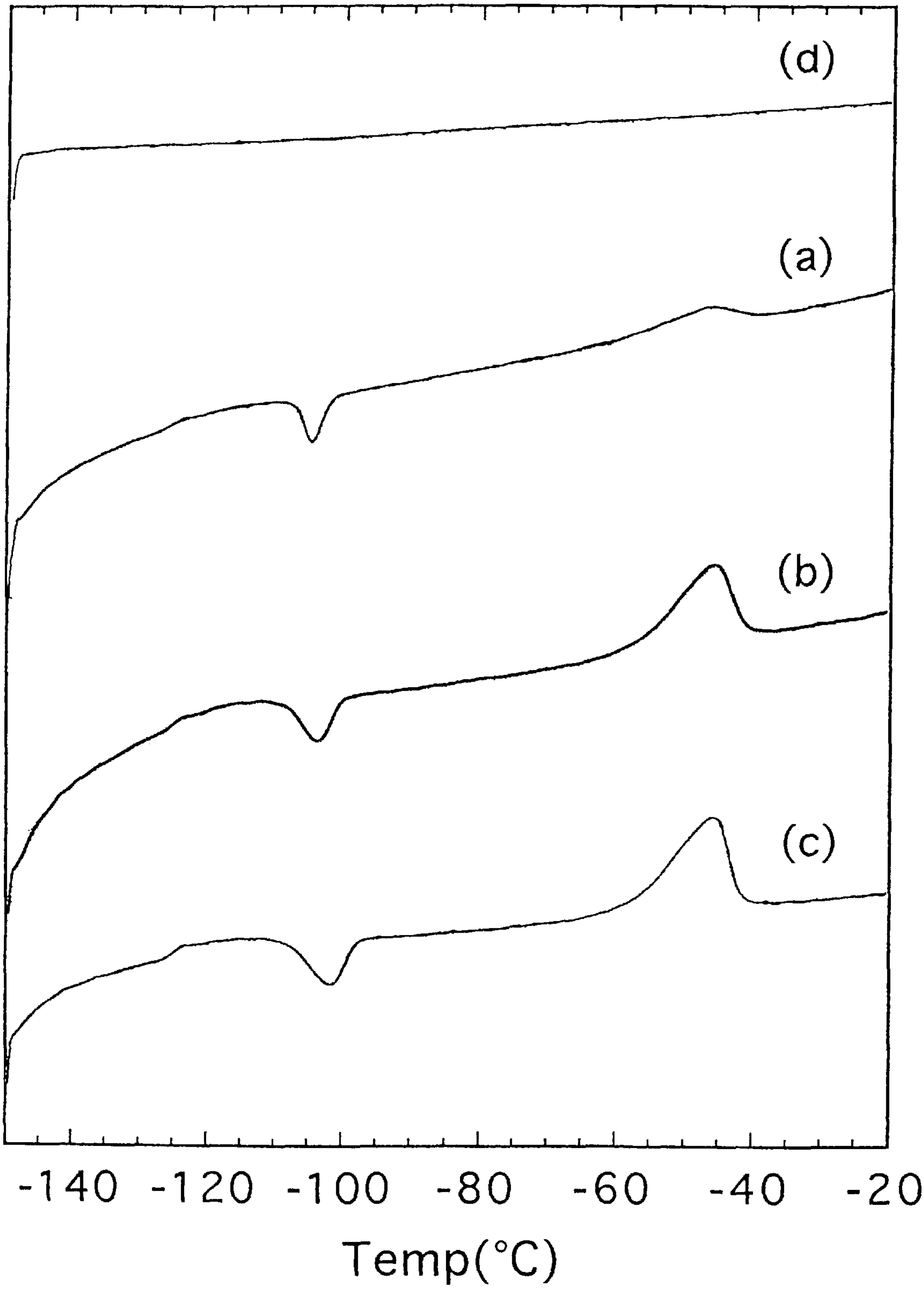


Fig. 8.8 DSC curve of PDMS and grafted PDMS membranes: (a) membrane irradiated at 0.1Mrad/h for 5h in 100wt% HDFNMA, (b) for 1h in 30wt% HDFNMA; (c) PDMS; (d) poly(HDFNMA).

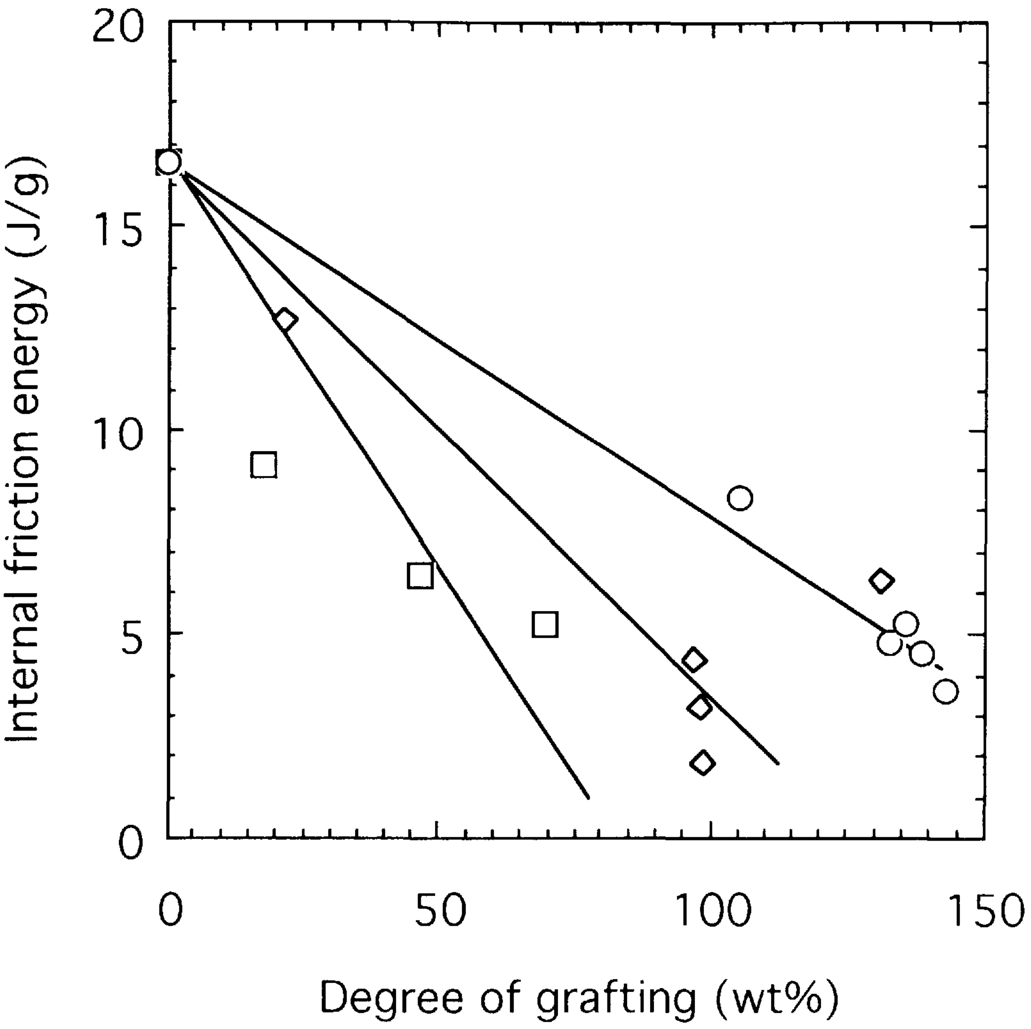


Fig. 8.9 Dependence of the internal friction energy between molecular chains on the degree of grafting of the grafted PDMS membranes: (□) membrane irradiated in 30wt% HDFNMA at 0.5Mrad/h, (◇) in 30wt% at 0.1Mrad/h, (○) in 100wt% at 0.1Mrad/h.

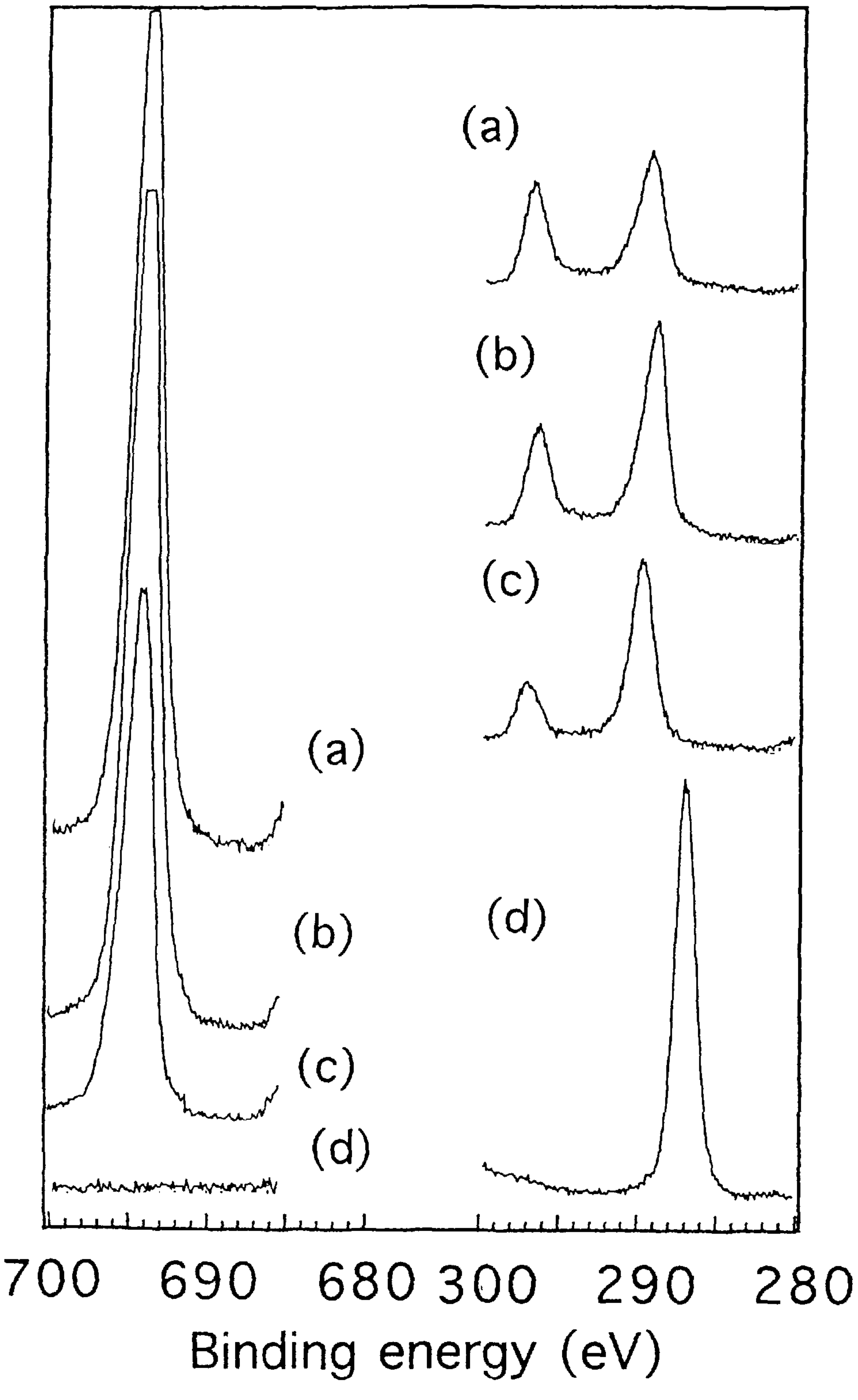


Fig. 8.10 XPS spectra of PDMS and grafted PDMS membranes: (a) membrane irradiated in 100wt% HDFNMA at 0.1Mrad/h for 5h , (b) for 3h, (c) for 1h; (d) PDMS.

Table 8.2 Fluorine to silicon, oxygen to silicon and carbon to Silicon atomic ratios for the surface of PDMS and grafted PDMS membranes by XPS Analysis

HDFNMA in MeOH (wt%)	Irradiation time (h)[a]	Electron emission angle (°)	Atomic ratio[b]			F/Si calculated by degree of grafting
			F/Si	O/Si	C/Si	
100	1	30	2.71	1.41	2.82	2.50
		90	1.61	1.50	2.72	
100	3	30	3.29	1.40	2.96	3.15
		90	3.50	1.59	3.21	
100	5	30	5.54	1.41	3.61	3.39
		90	6.62	1.83	4.07	
0	5	30	-[c]	1.19	1.75	
		90	-[c]	1.37	1.85	
PDMS		90	-[c]	1.44	1.87	

a : Dose rate of irradiation:0.1Mrad/h.

b : F/Si:Fluorine atomic ratio(%) / Silicon atomic ratio(%).
O/Si:Oxygen atomic ratio(%) / Silicon atomic ratio(%).
C/Si:Carbon atomic ratio(%) / Silicon atomic ratio(%).

c : Not detected.

atom was detected and the binding energy shift associated with the structure of fluorinated(CF, CF_2) and carbonyl(C=O)carbon species was shown[57,58]. The ratios of fluorine, oxygen, carbon, and silicon atoms were analyzed and calculated for a few nm beneath the surface on the grafted PDMS membrane at 30° and 90° photoelectron emission angles and are characterized in Table 8.2. In these spectra, the composition of the atoms was determined up to 4.5 and 9nm deep below the surface at photoelectron emission angles of 30° and 90°, respectively[59]. The ratios of fluorine and carbon on the grafted PDMS membranes were increased due to the introduction of HDFNMA by irradiation. The degree of grafting of the membrane, soaked in 100 wt% HDFNMA and irradiated at dose rates of 1 Mrad/hr for 5h, was 143wt%, and the thickness increased about 1.3 times. According to the observation of silicon atoms on the grafted PDMS membrane surface, it is considered that the poly(HDFNMA) domains were dispersed in the entire PDMS membrane homogeneously by irradiation.

The degree of grafting of the grafted PDMS membrane was more than 100wt%, while the degree of sorption of HDFNMA into PDMS membrane was 13wt%. As a result, the following is considered. First, the graft polymerization starts with one region in the PDMS membrane. HDFNMA was then grafted more frequently on the poly(HDFNMA) domain than the PDMS domain due to the affinity of HDFNMA for poly(HDFNMA). The grafting on the poly(HDFNMA) region was promoted to extend the volume of PDMS, and, in turn, the grafted PDMS membrane had a microphase-separated structure.

The ratio of the fluorine atom at 30° was almost the same as that at 90° on the surface of the membrane. The ratio of the fluorine atom by the XPS spectra corresponded to that calculated by the degree of grafting. For the structure of the grafted PDMS membrane, a layer of poly(HDFNMA) was not formed on the surface of the PDMS membrane. The poly(HDFNMA) domains were dispersed into the entire PDMS membrane homogeneously by irradiation.

The domains of poly(HDFNMA) in the grafted PDMS membranes had a particle size which scattered natural light, and the domains were dispersed homogeneously as expected.

8.3.3 Pervaporation for grafted membrane

Fig.8.11 shows the effect of the irradiation time on the flux and the separation factor for TCE solution in pervaporation through a PDMS membrane irradiated in MeOH. The pervaporation of a PDMS membrane irradiated in MeOH was substantially affected by irradiation. The effect of irradiation on the permeability of the PDMS membrane to gases was investigated by M. Minoura et al.[60]. The results suggested that no remarkable difference except for crosslinking in the chemical structure between the unirradiated samples and irradiated samples could be seen, but the effects of irradiation on the transport of gases through the PDMS membranes were negligibly small.

In this chapter of pervaporation through irradiated PDMS, almost the same results were obtained.

Fig.8.12 shows the effect of the irradiation time on the flux and the separation factor for TCE solution in pervaporation through a PDMS membrane irradiated in 30 and 100wt% HDFNMA/MeOH. The flux of the grafted PDMS in 30wt% HDFNMA membranes was increased with increasing irradiation time, and the separation factor was decreased with increasing irradiation time. The degree of grafting and membrane thickness was increased by irradiation. The poly(HDFNMA) region was increased and grown by graft polymerization to extend the volume of PDMS so that the flux of the grafted PDMS membranes was increased. The flux of the PDMS membrane grafted PDMS in 100wt% HDFNMA was constant with increasing irradiation time, and the separation factor was increased with increasing irradiation time. By measurents of the ATR spectra of the grafted PDMS membranes, no characteristic peak of crosslinking between inter- or intrachains of individual polymers was observed. However, the homo-poly(HDFNMA), polymerized of 100wt% HDFNMA at 0.1 Mrad/h, was not dissolved in the solvent and became a gel. The crosslinking reactions affect both the sorption and permeation behavior. The more the crosslinking occurs, the less the permeants are sorbed into the membrane and the slower they permeate through the membrane. The flux of the membranes grafted and crosslinked in 100wt% HDFNMA was lower than that of the membranes grafted in 30wt%. The grafted amount, the degree of crosslinking and the permselectivity of the membrane grafted in 100wt% HDFNMA was increased with increasing irradiation time.

The flux as a function of the TCE concentration in the feed solution is shown in Fig.8.13. For the PDMS and the membranes irradiated in MeOH, the flux was almost constant with increasing feed concentration. For the membranes grafted with HDFNMA, the flux was decreased with feed concentration. The water flux and TCE flux as a function of the TCE concentration in the feed solution are shown in Fig.8.14 for the grafted PDMS membranes. For the PDMS membrane irradiated in 100wt% HDFNMA for 1h, the water flux was almost constant with increasing feed concentration, and for the more grafted PDMS

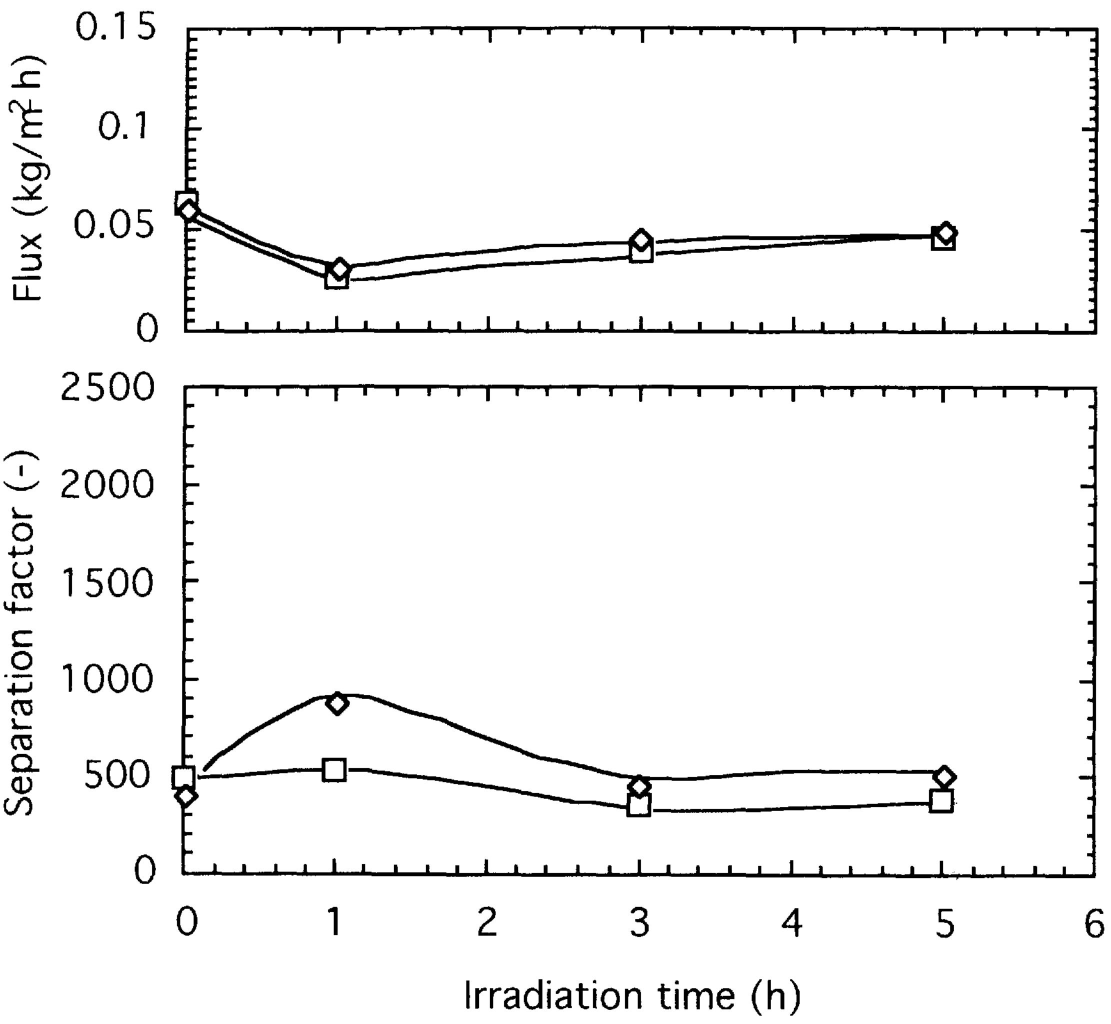


Fig. 8.11 Effect of irradiation time on the flux and separation factor (α_{pv}) of TCE-water mixtures in pervaporation through irradiated PDMS membrane at 25°C: (□) 0.01wt% feed concentration; (◇) 0.025wt%.

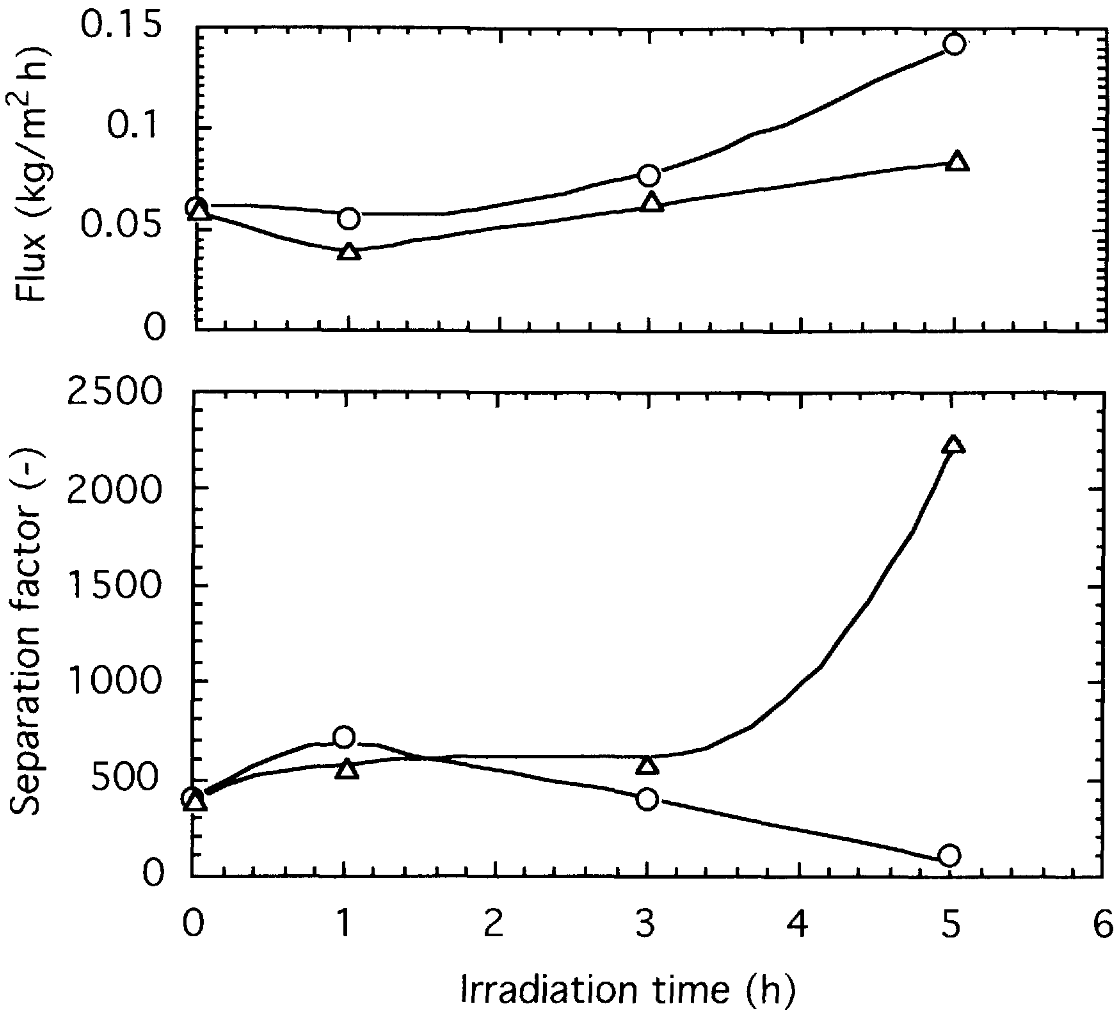


Fig. 8.12 Effect of irradiation time on the flux and separation factor(α_{pv}) of TCE-water mixtures in pervaporation through grafted PDMS membranes at 25°C: (○) 0.025wt% feed concentration through membrane irradiated at 0.1Mrad/h in 30wt% HDFNMA, (△) 0.025wt% feed concentration through membrane irradiated at 0.1Mrad/h in 100wt% HDFNMA.

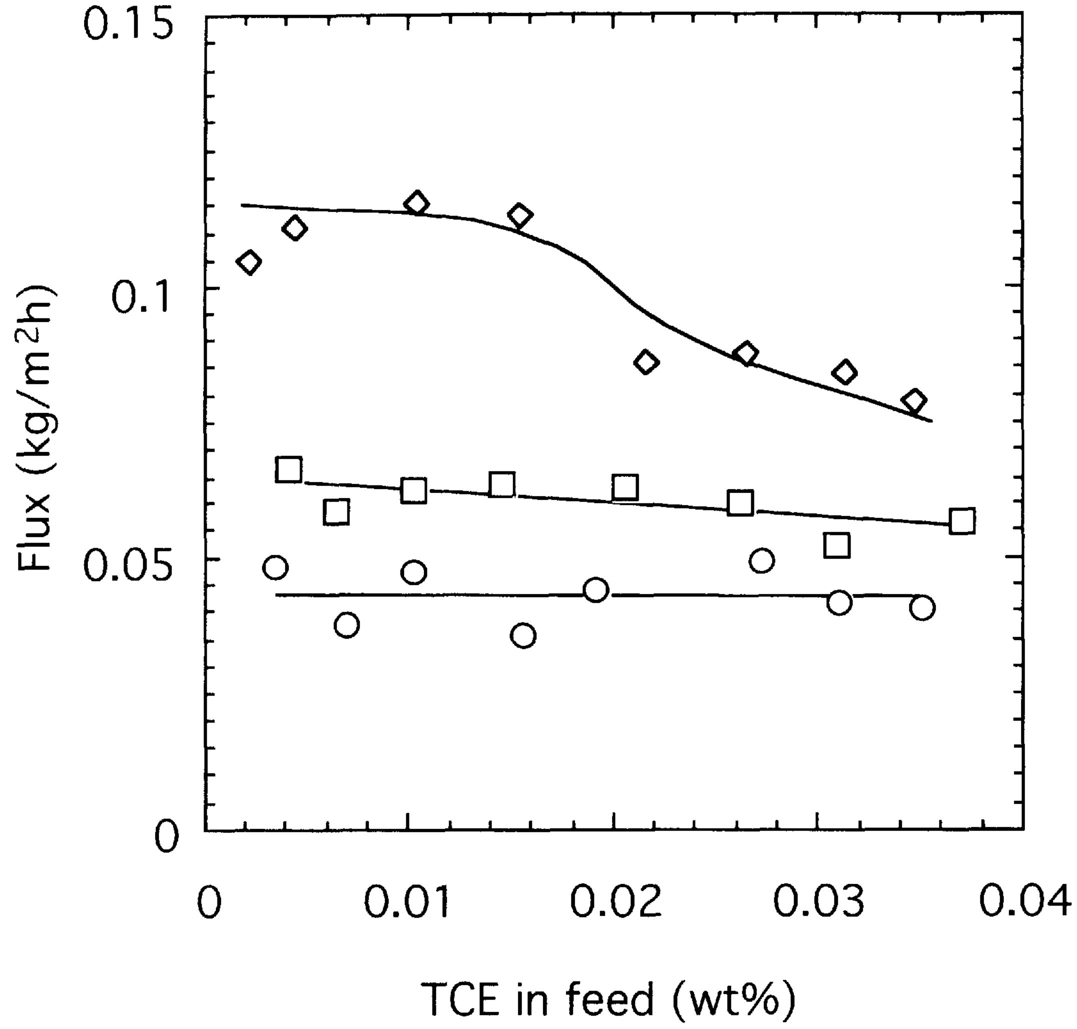


Fig. 8.13 Effect of feed concentration on flux for TCE-water mixtures in pervaporation through grafted PDMS membranes at 25°C: (○) membrane irradiated in 100wt% HDFNMA at 0.1Mrad/h for 5h, (◇) in MeOH at 0.1Mrad/h for 5h; (□) PDMS.

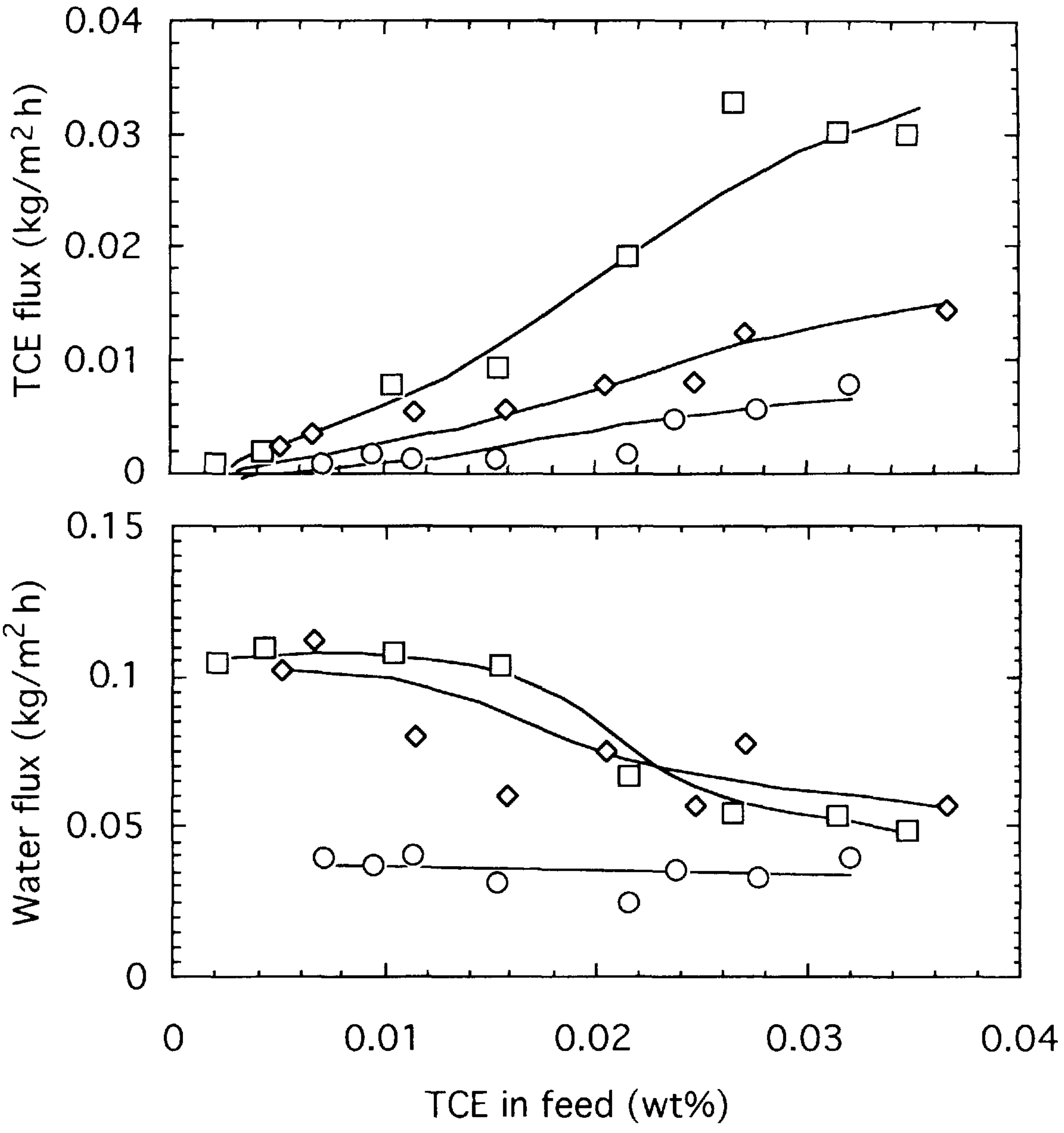


Fig. 8.14 Effect of feed concentration on flux for TCE-water mixtures in pervaporation through grafted PDMS membranes at 25°C: (○) membrane irradiated in 100wt% HDFNMA at 0.1Mrad/h for 1h; (◇) for 3h; (□) for 5h.

membrane, especially that irradiated in 100wt% HDFNMA for 5h, the water flux was still further decreased with increasing feed concentration. For all the membranes, the TCE flux was increased with increasing feed concentration, and especially for the membrane irradiated in 100wt% HDFNMA for 5h, the tendency was significant.

In chapter 3, for the membranes modified using HDFNMA by UV irradiation, the flux was decreased with increasing feed concentration. Due to the introduction of the hydrophobic polymer, HDFNMA, the TCE quantity sorbed into the membrane was so high that the diffusion of water was prevented; in turn, the flux was decreased. In this chapter, similar phenomena were observed.

The relationships between the TCE concentration in the feed and permeate are shown in Fig.8.15. For all the membranes, the TCE concentration in the permeate was increased with increasing feed concentration, and especially when the membranes was irradiated in 100wt% HDFNMA for 5h, the increase was significant.

The separation factor, α_{pv} as a function of the TCE concentration in the feed solution is shown in Fig.8.16. α_{pv} was increased significantly with increasing feed concentration for the membrane irradiated in 100wt% HDFNMA for 5h. In the grafted PDMS membrane, the best separation performance was shown due to the introduction of the hydrophobic polymer, poly(HDFNMA).

8.3.4 Pervaporation for poly(fluoroalkyl methacrylate) membrane

The solution of poly(HDFNMA), a homopolymer polymerized at 30wt% at 0.1Mrad/h for 5h, was cast. The membrane of poly(HDFNMA) polymerized for 5h, a membrane with a thickness of 270μm, was used for pervaporation. The flux as a function of the TCE concentration in the feed solution is shown in Fig.8.17. The total and water flux were almost constant with increasing feed concentration. TCE flux was increased with increasing feed concentration, and the rate was restrained at high feed concentration.

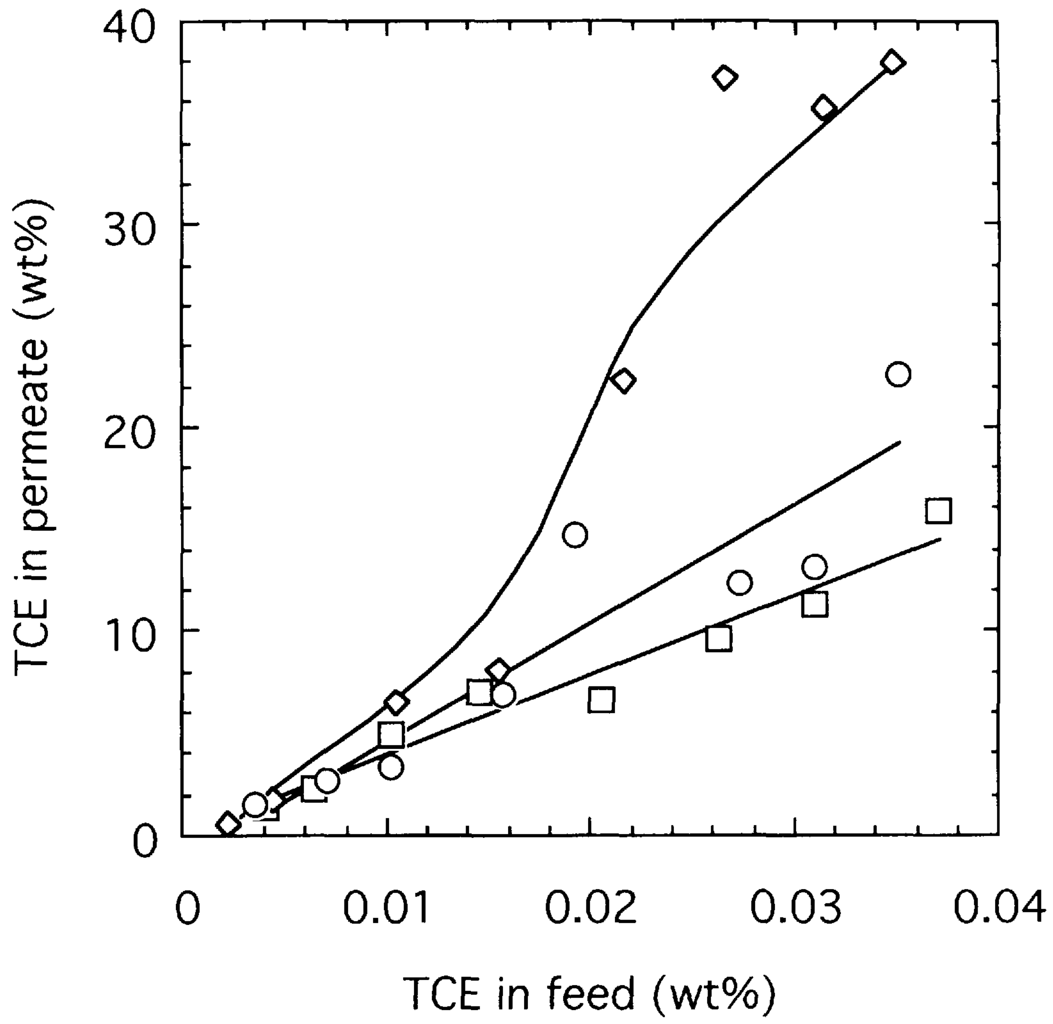


Fig. 8.15 Relationship between TCE concentration in feed and permeation in pervaporation through grafted PDMS membranes at 25°C: (○) membrane irradiated in 100wt% HDFNMA at 0.1Mrad/h for 5h, (◇) in MeOH at 0.1Mrad/h for 5h; (□) PDMS.

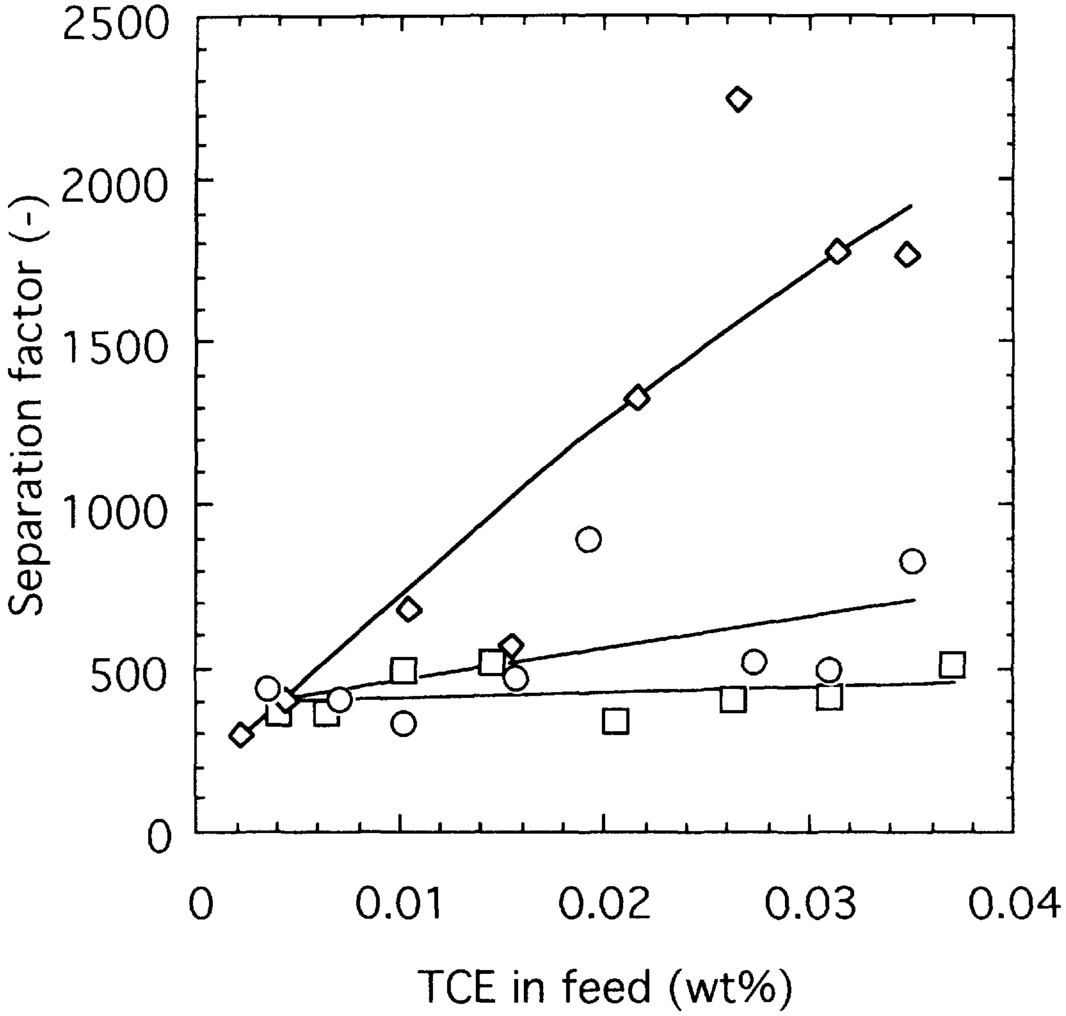


Fig. 8.16 Effect of feed concentration on separation factor (α_{pv}) in pervaporation through grafted PDMS membranes at 25°C: (◇) membrane irradiated in 100wt% HDFNMA at 0.1Mrad/h for 5h, (○) in MeOH at 0.1Mrad/h for 5h; (□) PDMS.

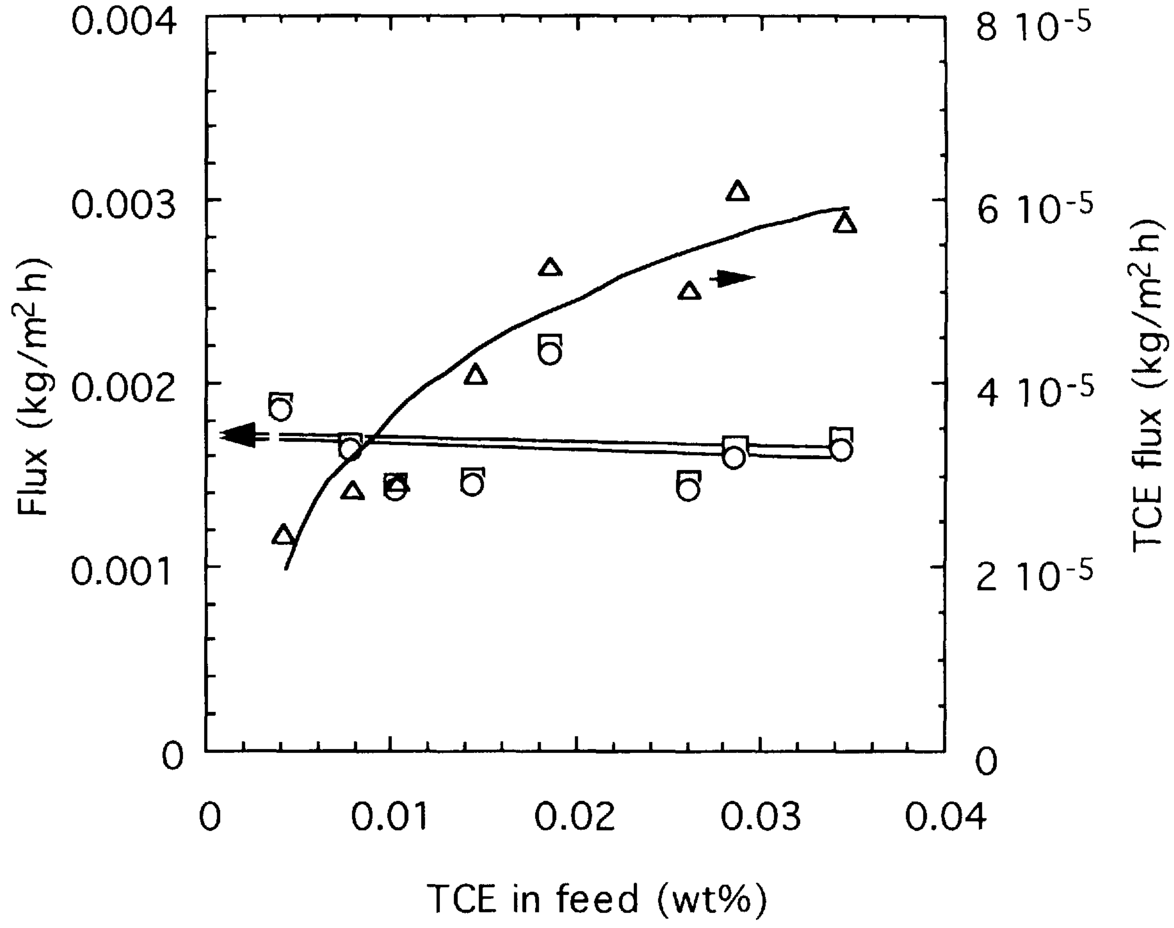


Fig. 8.17 Effect of feed concentration on flux for TCE-water mixtures in pervaporation through poly(HDFNMA) membranes at 25°C: (□) total flux; (○)water flux; (△)TCE flux.

The thickness of the poly(HDFNMA) membrane was 270μm, around five times as thick as grafted PDMS and PDMS membranes. The volume of the flux through the poly(HDFNMA) membrane was one to thirty~ninety times the volume of the flux through the grafted PDMS and PDMS membranes. The flux was inversely proportional to the membrane thickness[61]. It is predicted that the flux of the poly(HDFNMA) membrane is one fifth of the flux through the grafted PDMS and PDMS membranes, if the poly(HDFNMA) membrane had the same permeability as the grafted PDMS membranes. As we mentioned in the previous report, the intersegmental and intrasegmental distances in poly(HDFNMA) were narrower than those in PDMS. Hence, it is considered that the diffusion of the permeates was decreased and a low flux was obtained for the poly(HDFNMA).

The diffusivity of TCE molecules must be much lower than that of water due to the larger molecular size of TCE. In the poly(HDFNMA) with low permeability to permeates, the TCE-permeselectivity was restrained.

Miyata et al.[21,22] reported the characteristics of permeation and separation for aqueous ethanol solutions through methyl methacrylate (MMA) dimethylsiloxane (DMS) copolymer membranes with microphase-separation. They mentioned that, due to the high solubility and good diffusivity of ethanol molecules in the PDMS phase of the rubber state, the PDMS phase transports ethanol better than water.

Furthermore, the mass transport takes place solely in the amorphous polymer phase, not at all in the crystalline phase, and only part of the interface area is available for permeation in the semi-crystalline phases[55]. The grafted PDMS membrane had a microphase-separated structure, i.e., a separated structure of PDMS and graft-polymerized HDFNMA. The permselectivity of TCE was high, due to the introduction of the hydrophobic polymer, poly(HDFNMA). The permeation mechanism for the grafted PDMS membranes is shown in Fig.6.18. For the pervaporation performance of the HDFNMA-grafted PDMS membrane, the following was considered. The permeability of the PDMS phase was significantly great

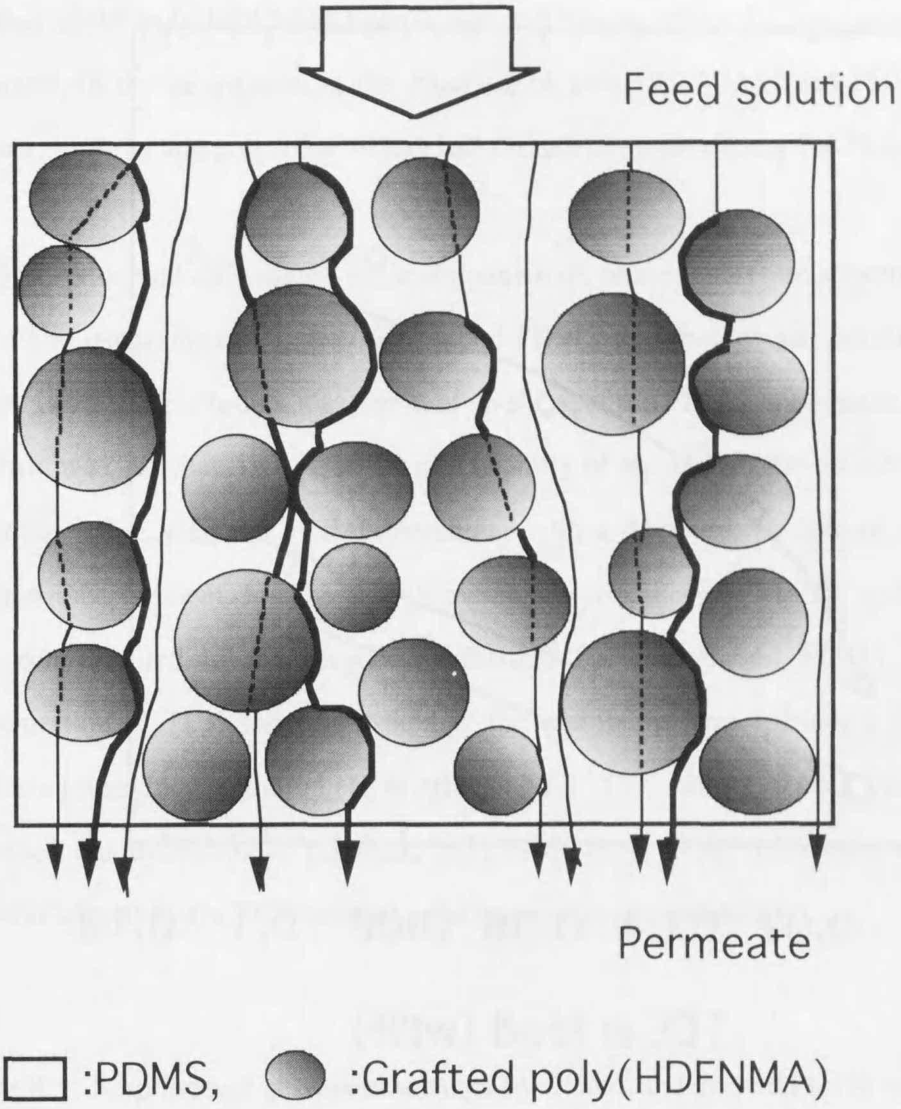


Fig. 8.18 Tentative illustration of the permeation through the grafted PDMS membrane for TCE-water mixture.

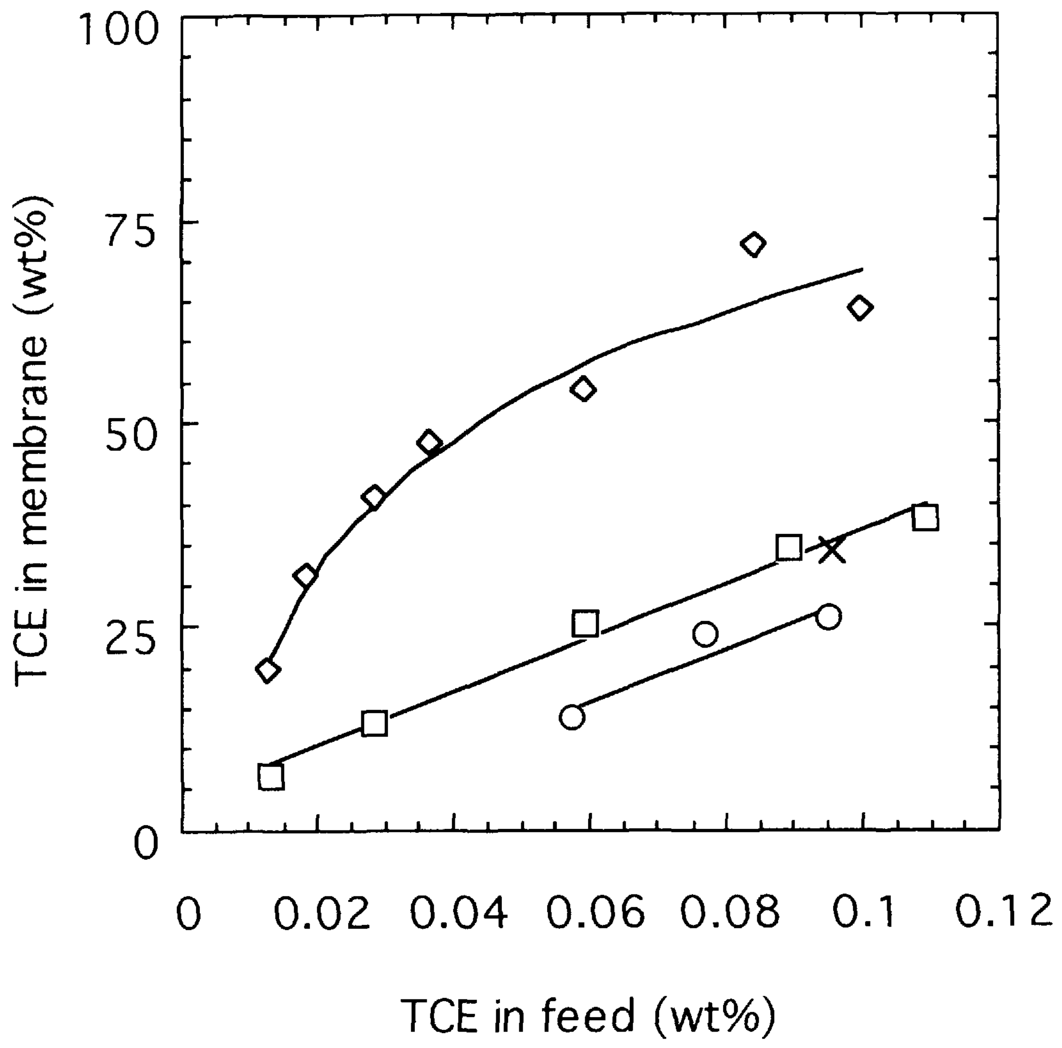


Fig. 8.19 Sorption of TCE on grafted PDMS membranes as a function of the feed concentration at equilibrium: (◇) membrane irradiated in 100wt% HDFNMA at 0.1Mrad/h for 5h; (○) in MeOH at 0.1Mrad/h for 5h; (×)PDMS 50μm; (□)PDMS 200μm.

and that of the poly(HDFNMA) phase was too low to affect the total permeation directly. However, in the permeation at the interface of poly(HDFNMA) and PDMS, it played an important role in that poly(HDFNMA) had a much stronger affinity for TCE than for water.

8.3.5 Sorption and diffusion of the membrane with phase separation structure

The isotherms of sorption for grafted PDMS membranes are presented in Fig.8.19. Below 1wt% TCE solution, the degree of swelling of the PDMS membrane with a thickness of 50μm was less than 1wt%, too small a quantity of solution in the membrane to determine the composition. Hence, a PDMS membrane with a thickness of 200μm was used in this sorption measurement. For the PDMS membrane irradiated in MeOH and PDMS, straight lines can be fited to the sorption isotherms. For the grafted PDMS membranes, the concentration of TCE solution soaked in the membrane was increased significantly with increasing feed concentration. It is effective for TCE sorption into the membrane to introduce the hydrophobic polymer, poly(HDFNMA). The membrane that had a high sorption selectivity for TCE showed great separation performance.

Table 8.3 Sorption and pervaporation data for PDMS and grafted PDMS membrane

	Sorption data			Pervaporation data			
Membrane	TCE in feed (wt%)	TCE in membrane (wt%)	Separation factor (α_S)	TCE in feed (wt%)	TCE in membrane (wt%)	Separation factor (α_{pv})	Separation factor (α_D)
PDMS irradiated in HDFNMA 100wt% at 0.1Mrad for 5h	0.0123	19.9	2010	0.0104	6.63	684	0.340
	0.0280	40.9	2470	0.0265	37.4	2250	0.912
PDMS	0.0131	6.90	564	0.0102	4.83	496	0.879
	0.0282	13.2	538	0.0263	9.55	402	0.747

The relationship between the separation factor in permeation (α_{pv}), the separation factor in sorption(α_S), and the apparent separation factor in diffusion (α_D) is given by Eq.(8.7).

$$\alpha_{pv}=\alpha_S \cdot \alpha_D \quad (8.7)$$

α_D can be described in Eq.(8.8) using Eq.(8.4) and (8.6).

$$\alpha_D=\{Y(1-Y')\}/\{(1-Y)Y'\} \quad (8.8)$$

where Y and Y' denote the concentration of TCE in the permeate solution and the swollen membranes under the same feed solution, respectively.

α_{pv},α_S,α_D are shown in Table 8.3. α_D values calculated by Eq.(8.8) using the sorption isotherms in Fig. 8.19 and the pervaporation in Fig.8.15 as a function of the TCE concentration in the feed solution are shown in Fig.8. 20. The results show that α_D of the grafted PDMS membrane was significantly increased with increasing feed concentration.

The permeation of TCE and water molecules in pervaporation through the grafted PDMS membranes is concluded to be the following; The mass transport takes place significantly in the PDMS phase. At the interface of poly(HDFNMA) and PDMS, a high solubility performance of TCE molecules was shown. At a low feed concentration of TCE solution, the diffusivity of TCE molecules must be much lower than that of water due to the larger molecular size of TCE. At a high concentration of TCE solution, TCE was sufficiently sorbed into the membrane. The diffusion of water was prevented by the TCE molecules, and in turn, the permeselectivity of TCE was significantly increased.

In this chapter, the PDMS membranes were improved with graft polymerization of HDFNMA by simultaneous irradiation method. The permeability of the PDMS phase was significantly great and that of the poly(HDFNMA) phase was too low to affect the whole permeation of the grafted PDMS membrane directly. However, in the permeation, at the interface of poly(HDFNMA) and PDMS, poly(HDFNMA) showed excellent solubility performance for TCE. In order to enhance the selectivity of a rubber polymer membrane

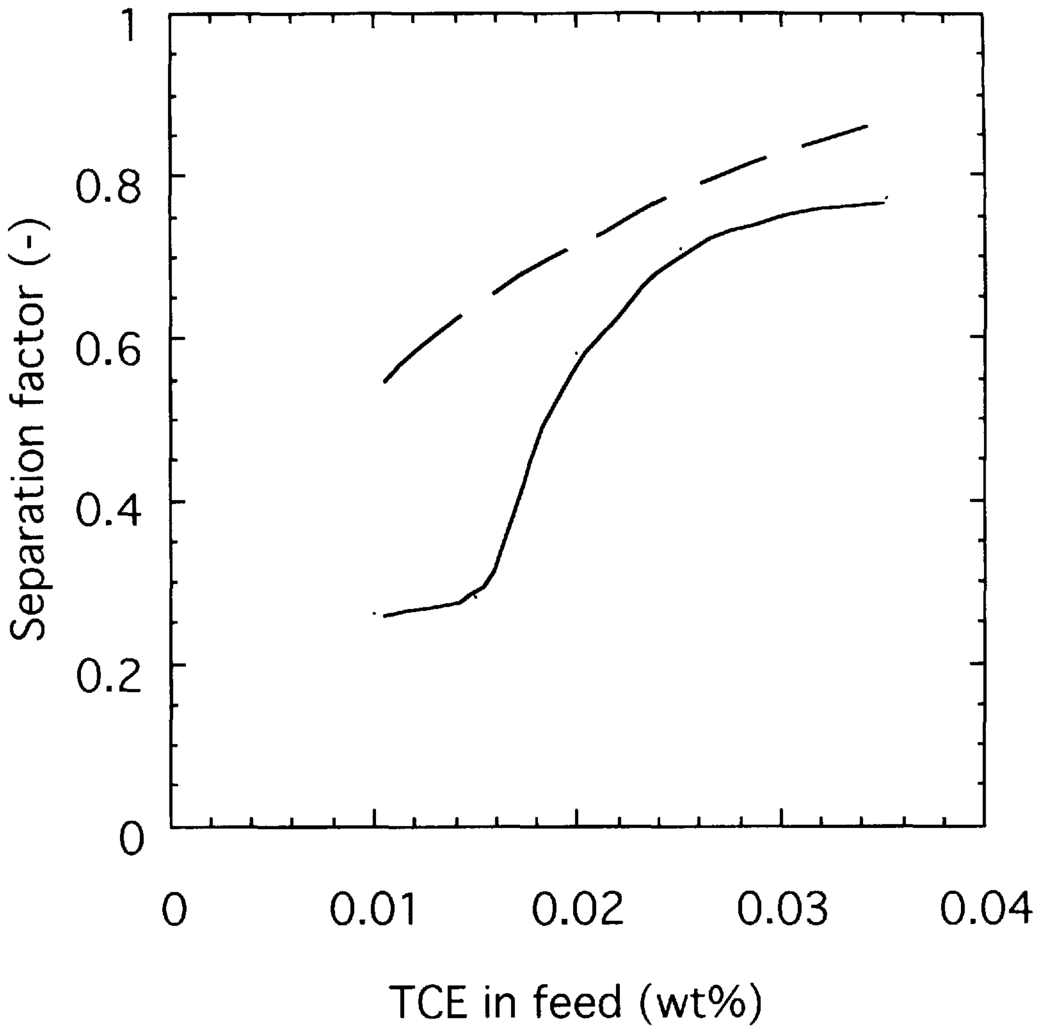


Fig. 8.20 Effect of feed concentration on the separation factor (α_D) in pervaporation through PDMS and grafted PDMS membrane at 25°C: (-) membrane irradiated in 100wt% HDFNMA at 0.1Mrad/h for 5h; (...)PDMS.

which has a high permeability, such as PDMS, it is effective to introduce a material which has a high solubility.

8.4 Conclusions

In this chapter, we improved the PDMS membrane with graft polymerization of HDFNMA, which has the effect of increasing the selectivity for chlorinated hydrocarbons, by a ^{60}Co source and characterized the grafted PDMS membrane. Simultaneous irradiation is a method in which that monomer and polymer are irradiated simultaneously. In this chapter, simultaneous irradiation was studied. The grafted amount by simultaneous irradiation was rich. Therefore, the permeation behavior was differ from rubbery untreated PDMS membrane and the little grafted PDMS membrane by preirradiation in previous chapters.

The grafted PDMS membranes had a microphase-separated structure, i.e., a separated structure of PDMS and grafted HDFNMA. For the graft polymerization, the following is considered. First, the graft polymerization starts with one region in the PDMS membrane. More HDFNMA was then grafted on the poly(HDFNMA) domain than the PDMS domain due to the affinity of HDFNMA for poly(HDFNMA). The grafting on the poly(HDFNMA)region was promoted to extend the volume of PDMS, and, in turn, the grafted PDMS membrane has a microphase-separated structure. The poly(HDFNMA) domains were dispersed into the entire PDMS membrane homogeneously by irradiation. For the membranes soaked in 100 wt% HDFNMA and irradiated at 0.1Mrad/h, the poly(HDFNMA) domains were dispersed quite homogeneously.

In the grafted PDMS membranes, the best separation performance was shown with the introduction of the hydrophobic polymer, poly(HDFNMA). The concentration of TCE sorbed into the membrane was high, due to the introduction of the hydrophobic polymer, poly(HDFNMA). The membrane that had a high solubility selectivity for TCE showed great separation performance. The permeability of the PDMS phase was significantly great and that of the poly(HDFNMA) phase was too low to affect the whole permeation of the grafted

PDMS membrane directly. However, poly(HDFNMA) had a much stronger affinity for TCE than for water. Thefore, the permeability and permeselectivity of TCE on the surface of poly(HDFNMA) and PDMS are high, and the permeation on the surface played important role in the permeation through the grafted PDMS membrane. At a low feed concentration of TCE solution, the diffusivity of TCE molecules must be much lower than that of water due to the larger molecular size of TCE. At a high concentration of TCE solution, TCE was sufficiently sorbed into the membrane, so that the diffusion of water was prevented by the TCE molecules; in turn, the permselectivity of TCE was increased significantly.

The permeation behavior of the grafted membranes which have high grafted amount and phase-separated structure in composite with PDMS and poly(HDFNMA) was differ from rubbery untreated PDMS membrane and the little grafted PDMS membrane by preirradiation. Not only solute properties and interaction but also membrane structure effected on the permeation behavior.

8.5 Acknowledgments

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Chapter 9. Permeation Behavior of Poly(1H,1H,9H-Hexadecafluorononyl Methacrylate)-filled Poly(1-Trimethylsilyl-1-Propyne) Membranes for Volatile Organic Compound-Water Mixtures

9.1 Introduction

The permselectivity for glassy polymers can be also determined by the sorption-diffusion mechanism like as rubbery polymer membrane. The sorption of permeate component can be controlled by the affinity for the membrane material. The diffusion can be described as the permeation rate of component through the membrane.

Poly(1-trimethylsilyl-1-propyne) (PMSP) membrane has the highest permeability of all polymeric membranes and its permeation property has been studied[1-13]. The permselectivity of volatile organic compounds (VOC) through PMSP was enhanced due to modification of fluoroalkyl methacrylate by T. Nakagawa, et. al.[3].

In chapter 8, polydimethylsiloxane (PDMS) membrane which is a rubbery polymer membrane, was grafted by 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA) using ^{60}Co source and simultaneous irradiation method. In the pervaporation application of the grafted PDMS membrane, the selectivity for trichloroethylene (TCE) was enhanced due to introduce hydrophobic polymer, poly(HDFNMA) (PHDFNMA). At a high concentration of TCE solution, the diffusion of water was prevented by TCE molecules sorbed in the membrane, in turn, the permselectivity of TCE was increased significantly.

PMSP is a glassy polymer and has a lot of microvoids[1]. The permselectivity in PMSP membrane is controlled by the microvoids and the permeation behavior is different from rubbery polymer membranes like as PDMS membrane[1]. In this chapter, the PMSP membrane was filled with PHDFNMA and the sorption-diffusion mechanism in pervaporation was investigated compared to the grafted PDMS membrane.

9.2. Experimental

9.2.1 Membrane preparation

PMSP (Shin-etsu Chemical Co., Ltd.) was used throughout this work. HDFNMA (Daikin Fine Chemical Laboratory Corporation), ethyl butanoate (EBU) (Special grade,Wako Pure Chemical Industries, Ltd.), and 2-propanol (Kanto Chemical Co., Inc.) were used as received.

The HDFNMA in ampoules were degassed and sealed under vacuum. The ampoules were irradiated at dose rates of 0.1 Mrad/h for 5h from a ^{60}Co source at 25 °C. After the irradiation was finished, The obtained polymer, the PHDFNMA was soaked, washed in acetone and dried under vacuum. The PHDFNMA was ground into a powder by an auto grinder (Nitto Science Co., Ltd.). and sieved using a JIS 28801 Testing Sieve with a 45 micron aperture (Tokyo Screen Co., Ltd.).

The PMSP was purified by the solution precipitation method using a toluene-methanol system. The purified PMSP was dissolved in toluene to 2.0 wt% and cast onto a glass plate. To the cast solution was added the sieved PHDFNMA powder and then dried under vacuum.

9.2.2 Pervaporation experiment and sorption measurement

The pervaporation experiments were performed as in a previous study[14~17] using the continuous-feed type at 25 °C. The feed solution was circulated through the cell and the feed tank. The grafted surface of the membrane was kept in contact with the feed solution in the cell. The effective membrane area in the cell was 19.6 cm^2. The pressure on the permeation side was kept below 10 Torr by vacuum pumps. Upon reaching steady-state flow conditions, the permeate was collected in traps cooled by liquid nitrogen (-196 °C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate of the solution, the total flux (J), was obtained using eq.9.1.

$$J=Q/At \qquad (9.1)$$

where Q is the amount that permeated during the experimental time interval, t, and A is the effective surface area. The EBU and water flux were calculated from the total flux which is the permeation rate of the solution (J) and the permeate composition.

The concentration of EBU in the feed and permeate solution was determined by gas chromatography using an FID detector. The EBU concentration in the permeate was high, which is far beyond its solubility limit in water. The phase separation took place in the permeate. 2-Propanol was then added to the permeate solution. The permeate solution was homogenized and analyzed to determine the EBU concentration. The separation factor during pervaporation, α_{pv}, was calculated as:

$$\alpha_{pv}=\{Y(1-X)\}/\{(1-Y)X\} \quad (9.2)$$

where X and Y denote the concentrations of EBU in the feed and permeate solutions, respectively, and their concentration unit is weight percent (wt%).

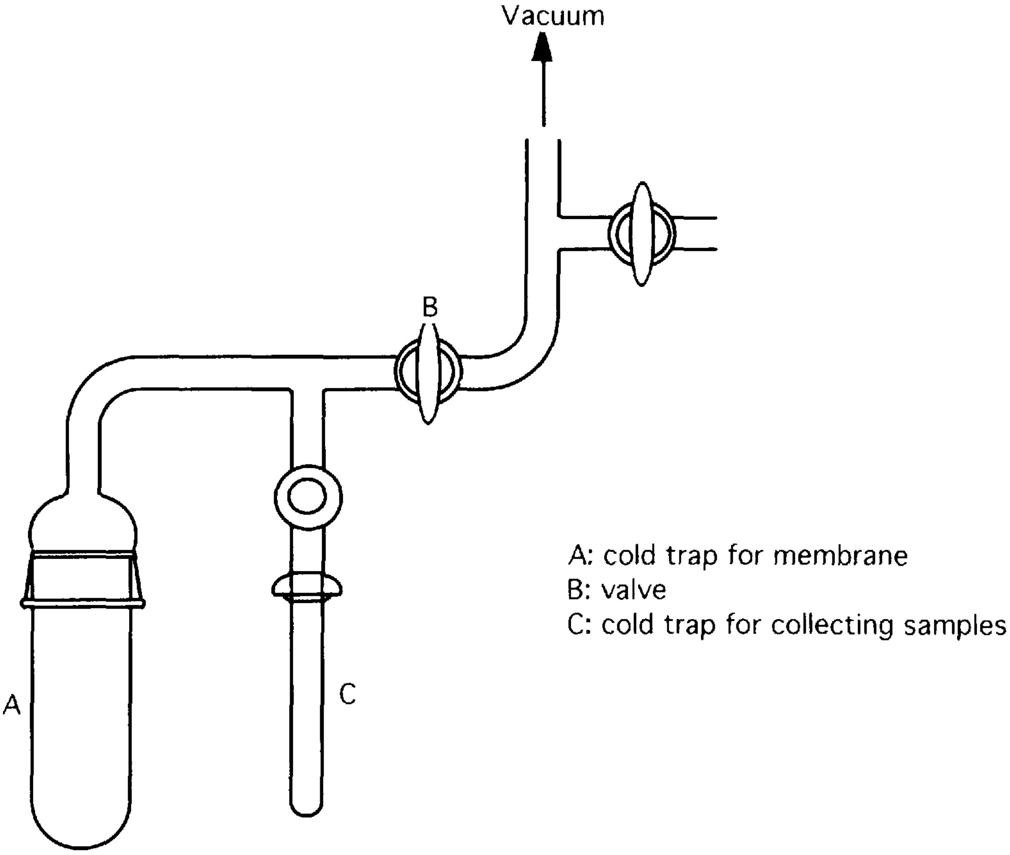

Fig. 9.1 Apparatus for measurement of the composition in the membrane.

The dried and weighed membrane was immersed in the EBU solution or EBU liquid and sealed at 25 °C until equilibrium was reached. The membrane was then removed from the vessel, quickly wiped with filter paper and weighed. The degree of sorption of the EBU liquid from the EBU solution into the membranes was measured as:

$$\text{Degree of sorption}(\%)=(W_3-W_2)/W_2\times 100 \quad (9.3)$$

where W_2 and W_3 denote the weights of the dried membrane and the swollen membrane, respectively.

The concentration of the EBU solution soaked into the membrane was determined using the apparatus shown in Fig.9.1. Upon reaching equilibrium, the membrane was removed from the vessel, quickly wiped with filter paper and placed in cold trap A. The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, valve B was closed, and the EBU solution soaked in the membrane was vaporized by heating with a drier and collected in cold trap C.

The concentrations of EBU solution in the feed and the soaked membrane were determined by gas chromatography the same as in the pervaporation experiment. The separation factor during sorption, α_s, was calculated as:

$$\alpha_s=\{Y'(1-X)\}/\{(1-Y')X\} \quad (9.4)$$

where X and Y' denote the concentrations of EBU in the feed solution and the swollen membranes, respectively, and their concentration unit is weight percent (wt%).

9.3 Results and discussion

9.3.1 Pervaporation of PHDFNMA-filled PMSP membrane

The effect of the PHDFNMA powder contents on the Flux and separation factor for the EBU/water mixture during pervaporation through the PHDFNMA-filled PMSP membrane is shown in Fig.9.2.

In chapter 8, the PDMS membrane was grafted by HDFNMA using a ^{60}Co source and simultaneous irradiation method. The permeation behavior of the grafted PDMS membrane during pervaporation was investigated. At a low feed concentration

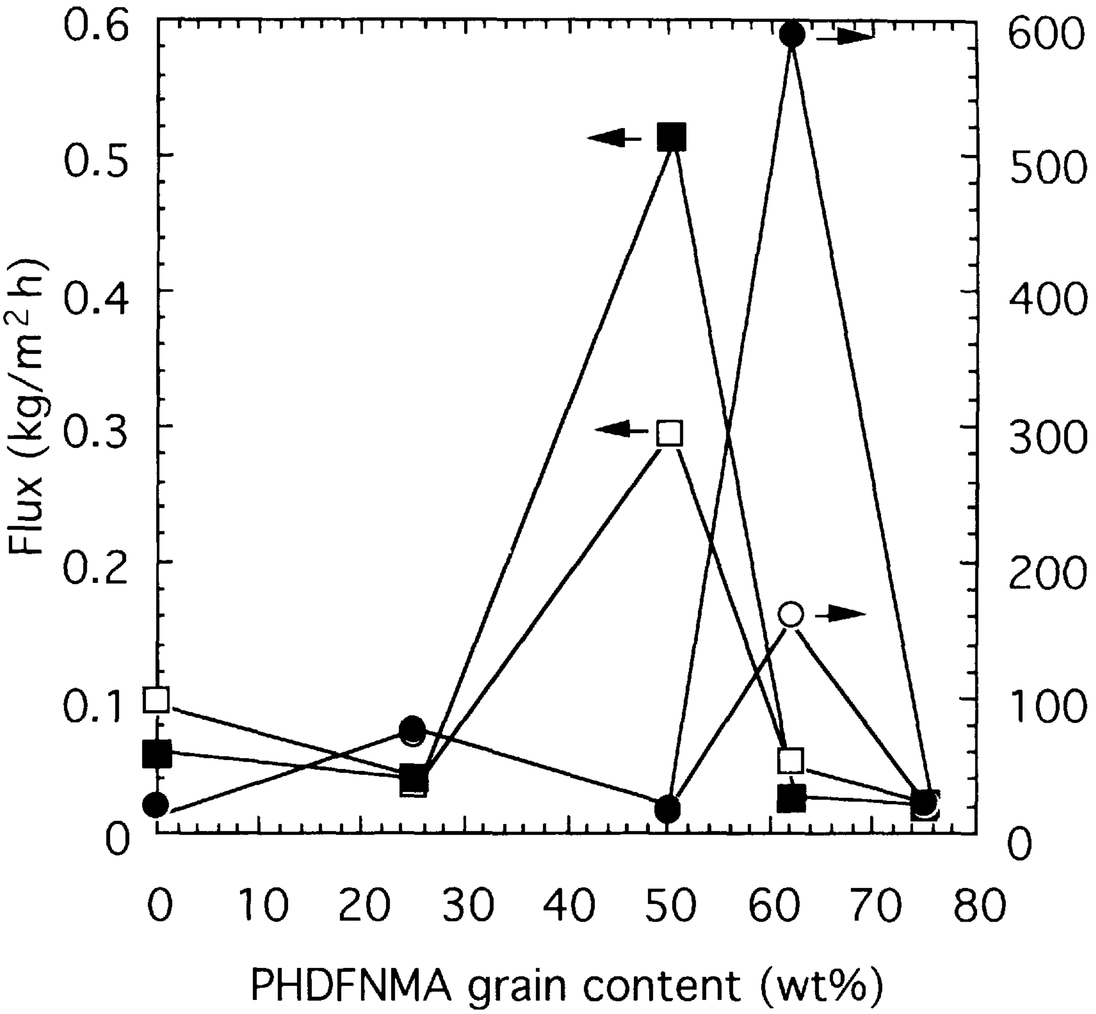

Fig. 9.2 Effect of the PHDFNMA powder contents on the flux and separation factor for the EBU/water mixture during pervaporation through the PHDFNMA-filled PMSP membrane.: (□) flux, (○) separation factor, open: for 0.01wt% feed solution, closed: for 0.02wt% feed solution

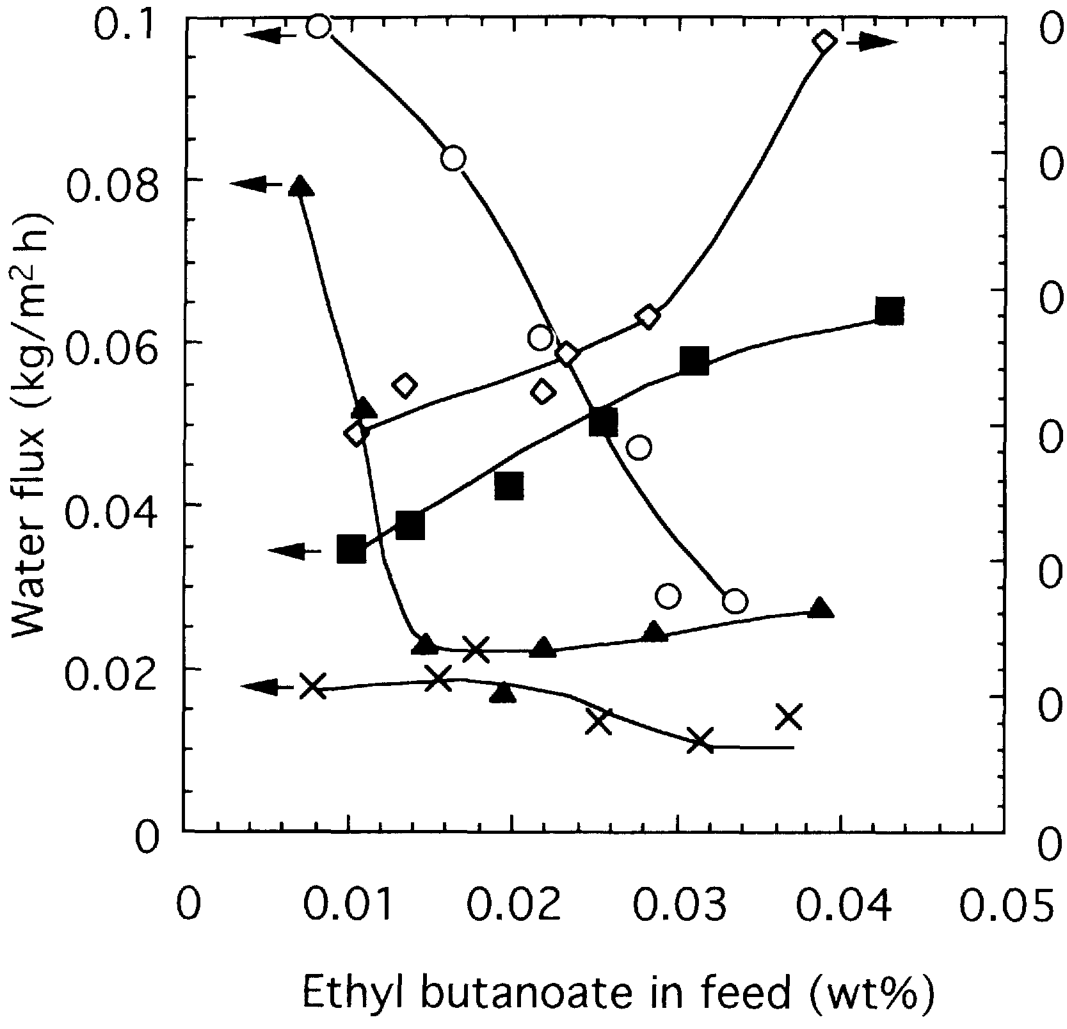

Fig. 9.3 Water flux as a function of the feed EBU concentration during pervaporation through the PHDFNMA-filled PMSP membranes.: (■) 25wt%, (◇) 50wt%, (▲) 62wt%, (×) 75wt% PHDFNMA-filled PMSP membrane, (○) PMSP membrane

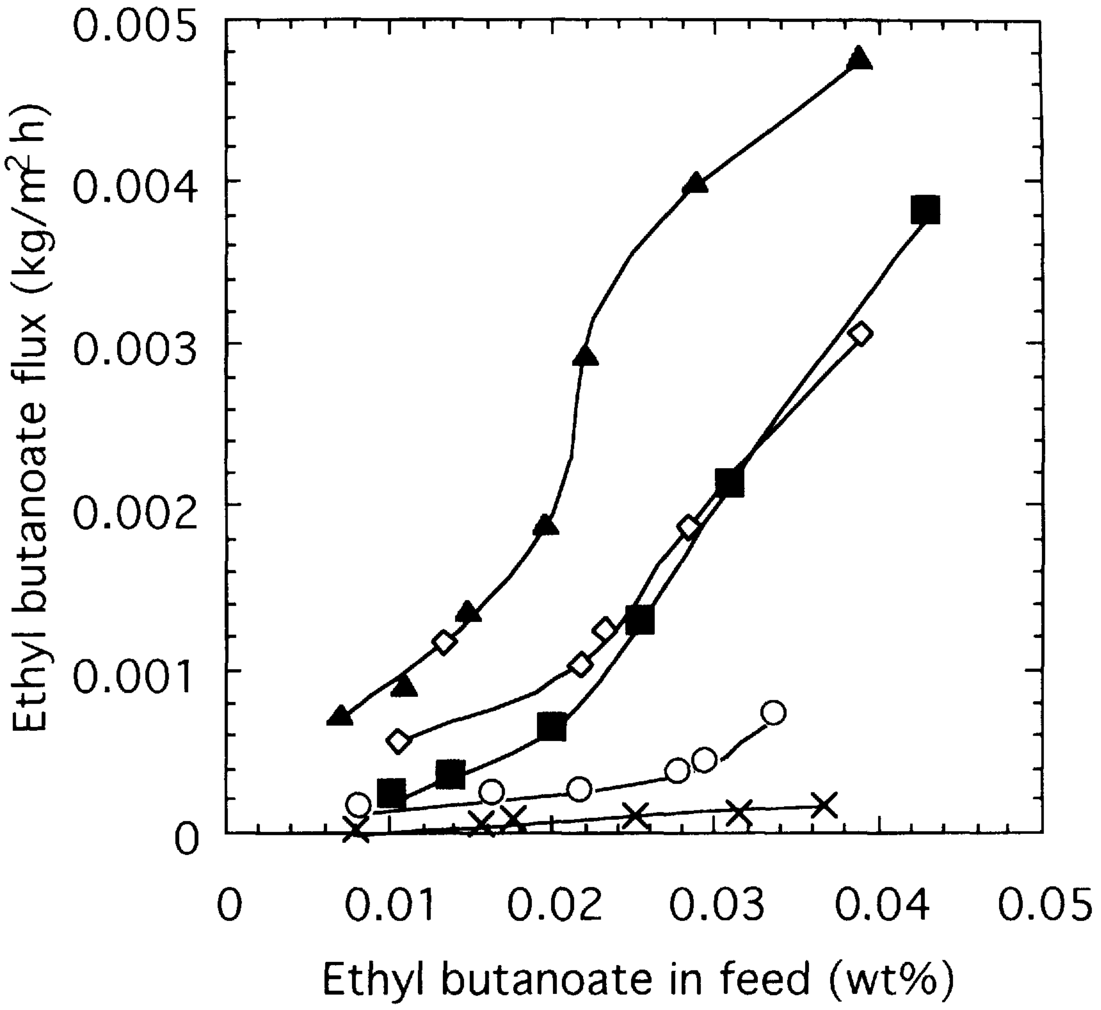

Fig. 9.4 EBU flux as a function of the feed EBU concentration during pervaporation through the PHDFNMA-filled PMSP membranes.: (■) 25wt%, (◇) 50wt%, (▲) 62wt%, (×) 75wt% PHDFNMA-filled PMSP membrane, (○) PMSP membrane

of trichloroethylene (TCE) solution, the diffusivity of the TCE molecule was much lower than that of water due to the larger molecular size of TCE. As TCE was sufficiently sorbed into the membrane at a high concentration of TCE solution, the diffusion of water was prevented by the TCE molecules, in turn, the permselectivity of TCE was significantly increased.

The flux increased until maximum was reached for the 50wt% HDFNMA-filled PMSP membrane and then decreased with increasing PHDFNMA powder contents. The separation factor was increased due to introducing the hydrophobic polymer, PHDFNMA. As the PMSP layer was thin in the 50wt% PHDFNMA-filled PMSP membrane, the flux increased. However, as the PHDFNMA powder content increased the filled PHDFNMA prevented the permeation and the flux decreased.

The water flux as a function of the EBU concentration in the feed solution is shown in Fig.9.3 for the PHDFNMA-filled PMSP membranes. The water flux increased with the feed concentration for the 25, and 50wt% PHDFNMA-filled PMSP membranes. For the 62, and 75wt% PHDFNMA-filled PMSP membranes and PMSP membrane, the water flux decreased with the feed concentration. The water flux for the 62wt% PHDFNMA-filled PMSP membrane significantly decreased. The EBU flux as a function of the EBU concentration in the feed solution is shown in Fig.9.4 for the PHDFNMA-filled PMSP membranes. For all the membranes, the EBU flux increased with the feed concentration, and especially for the 62wt% PHDFNMA-filled PMSP membrane, this tendency was significant. The microvoids in the PMSP membrane play a important role in the permselectivity. As the EBU quantity sorbed into the PMSP membrane increased with the feed EBU concentration, the diffusion of water was prevented, in turn, the water flux decreased. For the 25, and 50wt% PHDFNMA-filled PMSP membranes, as the PMSP layer was thin and the sorbed EBU was high, the PHDFNMA-filled PMSP membranes were plasticized and the flux increased. For the 62wt% PHDFNMA-filled PMSP membrane, as the EBU quantity sorbed into the PHDFNMA-filled PMSP membrane significantly increased with the feed EBU concentration due to the hydrophobic PHDFNMA, the diffusion of water was prevented, in

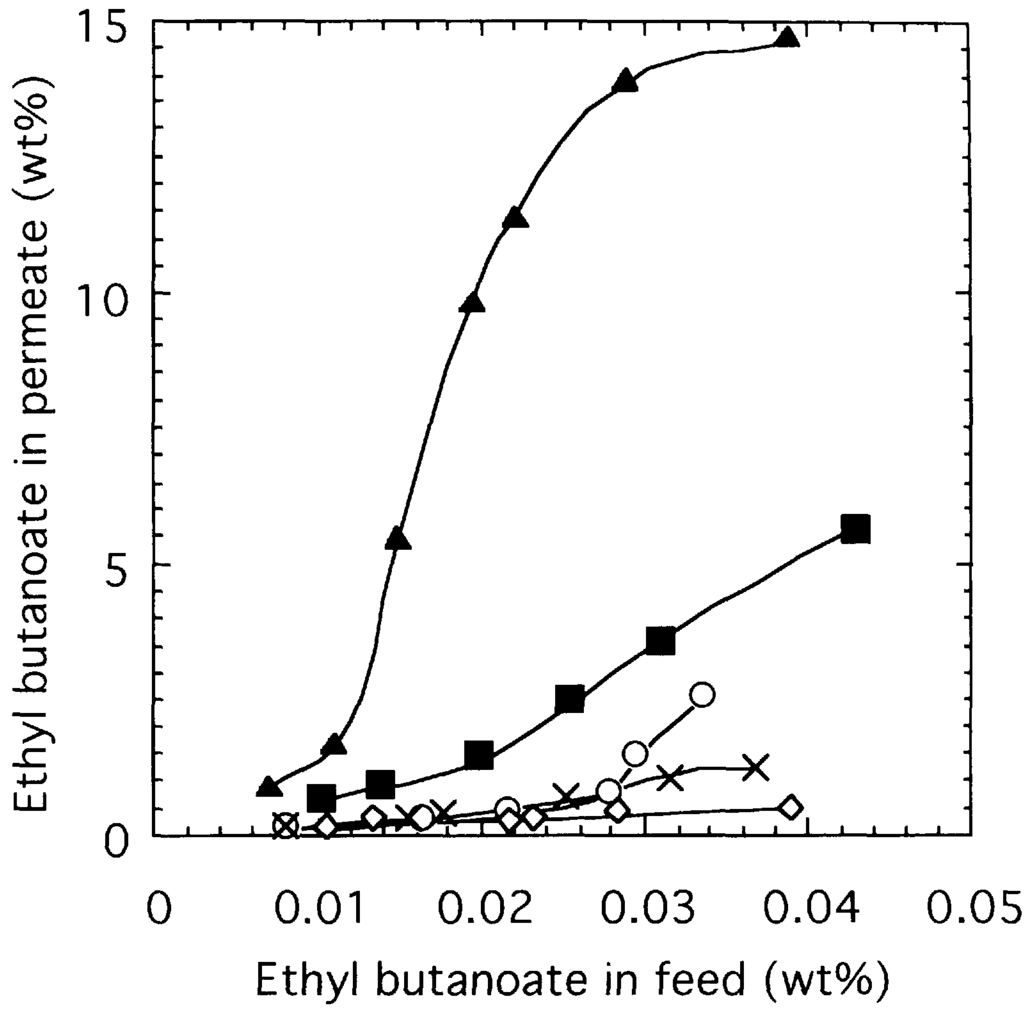

Fig. 9.5 Relationships between the EBU concentration in the feed and permeate during pervaporation through the PHDFNMA-filled PMSP membranes.: (■) 25wt%, (◇) 50wt%, (▲) 62wt%, (X) 75wt% PHDFNMA-filled PMSP membrane, (○) PMSP membrane

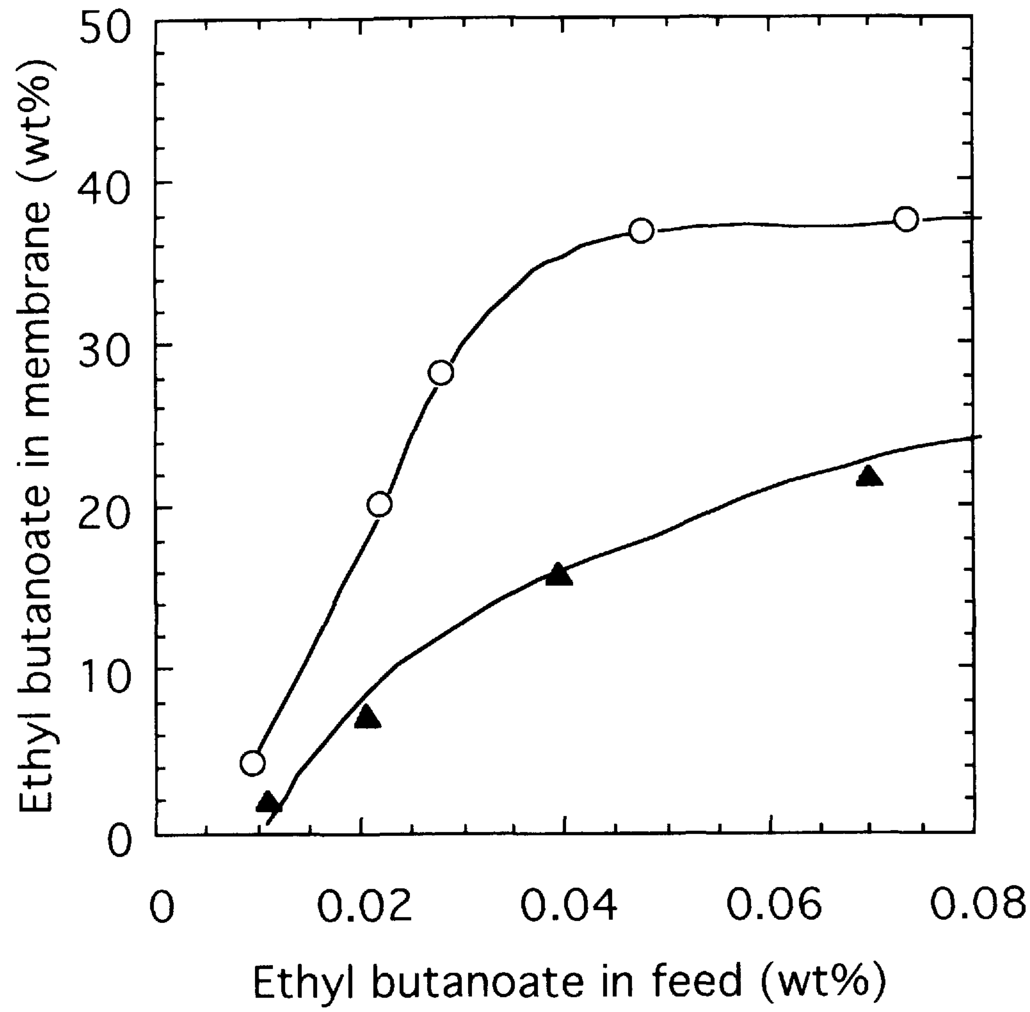

Fig. 9.6 Sorption of EBU on the PHDFNMA-filled PMSP membranes and the PMSP membrane as a function of the feed concentration at equilibrium.: (▲) 62wt% PHDFNMA-filled PMSP membrane, (○) PMSP membrane

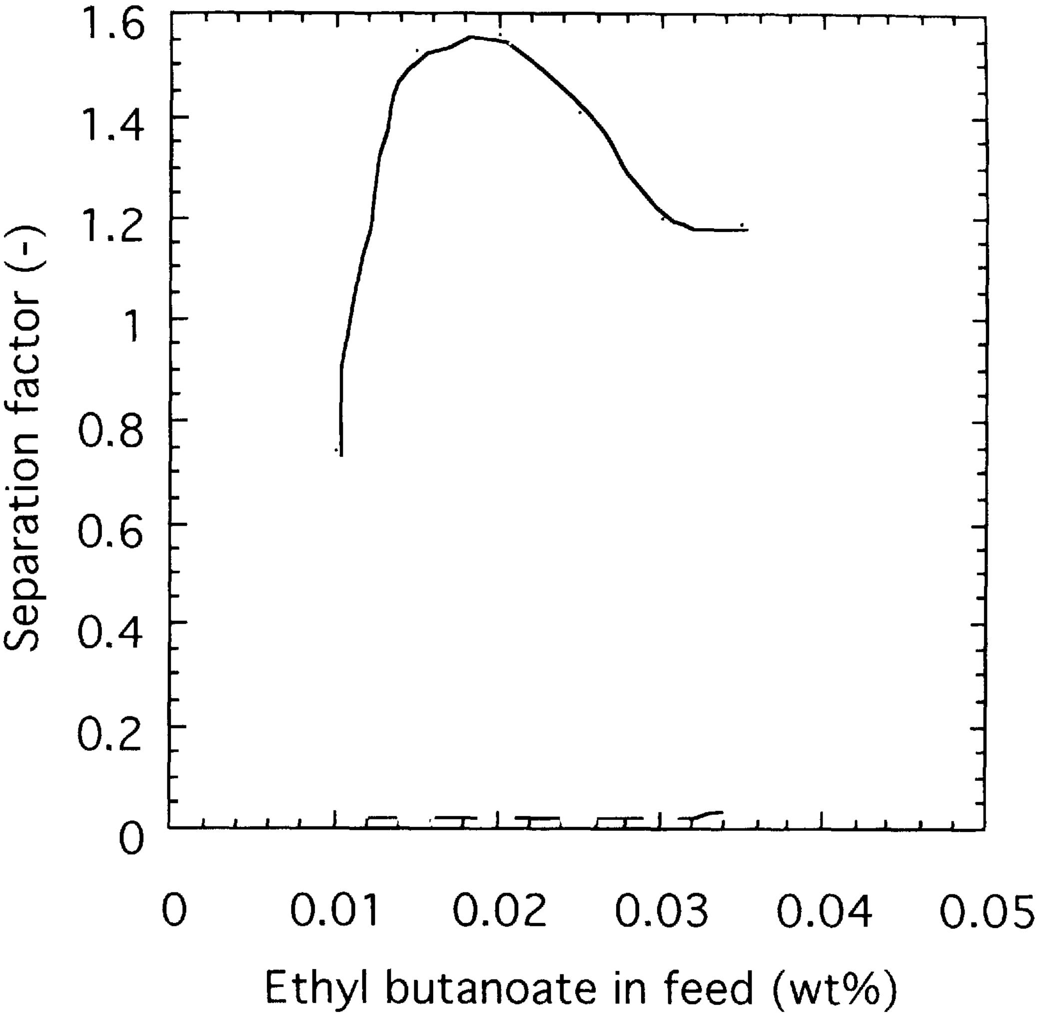

Fig. 9.7 Effect of feed concentration on the separation factor (α_D) during pervaporation through the PHDFNMA-filled PMSP membrane and the PMSP membrane.: (-) 62wt% PHDFNMA-filled PMSP membrane, (...)PMSP membrane

turn, the flux decreased. For the 75wt% PHDFNMA-filled PMSP membrane, as the filled PHDFNMA prevented the permeation, the fluxes of water and EBU were low.

The relationships between the EBU concentration in the feed and permeate are shown in Fig. 9.5 for the PHDFNMA-filled PMSP membranes. For all the membranes, the EBU concentration in the permeate increased with the feed concentration, and especially for the 62wt% PHDFNMA-filled PMSP membrane, the increase was significant.

9.3.2 Sorption and diffusion of PHDFNMA-filled PMSP membrane

The sorption isotherms for the 62 wt% PHDFNMA-filled PMSP membranes and PMSP membrane are shown in Fig.9.6. For both membranes, the concentration of the EBU solution soaked in the membrane linearly increased with the feed concentration at low feed concentrations, but the increase was minor at high feed concentration. The concentration of the EBU solution soaked in the PHDFNMA-filled PMSP membrane was low compared to the PMSP membrane.

PMSP is a glassy polymer and has many microvoids. The sorption into the PMSP membrane was controlled by the microvoids. As the PHDFNMA-filled PMSP membrane has few microvoids, the sorption of EBU was low compared to the PMSP membrane.

The relationship between the separation factor during permeation (α_{pv}), the separation factor during sorption(α_S), and the apparent separation factor during diffusion (α_D) is given by Eq.(9.5).

$$\alpha_{pv}=\alpha_S \cdot \alpha_D \quad (9.5)$$

α_D can be described by Eq.(9.6) using Eq.s (9.2) and (9.4).

$$\alpha_D =\{Y(1-Y')\}/\{(1-Y)Y'\} \quad (9.6)$$

where Y and Y' denote the concentration of EBU in the permeate solution and swollen membranes for the same feed solution, respectively. α_D was calculated by Eq.(9.6) using the sorption isotherm in Fig. 9.6 and the pervaporation in Fig. 9.5. α_D as a function of the EBU concentration in the feed solution is shown in Fig. 9.7. The α_D of the PMSP membrane was constant with increasing feed concentration. For the PHDFNMA-filled PMSP, it significantly increased with the feed concentration until a maximum, then decreased and became constant.

The sorption and diffusion of EBU and water molecules during pervaporation through the PHDFNMA-filled PMSP membrane were considered as follows.

At a low feed concentration, the diffusivity of the EBU molecule was much lower than that of water due to the larger molecular size of EBU. As EBU was sufficiently sorbed into the membrane, the diffusion of water was prevented by the EBU molecules, in turn, the permselectivity of EBU was significantly increased. At a high feed EBU concentration, the diffusion of water increased and the diffusion of EBU decreased to a constant as the PHDFNMA-filled PMSP membrane was plasticized.

9.4 Conclusions

In this study, the glassy PMSP membrane was filled with PHDFNMA and the sorption-diffusion mechanism during pervaporation was investigated and compared to the grafted rubbery PDMS membranes.

The separation performance was increased due to introducing the hydrophobic polymer, PHDFNMA, compared to the PMSP membrane. Especially, for the 62wt% PHDFNMA-filled PMSP membrane, the permselectivity was significantly enhanced.

The water flux for the 62wt% PHDFNMA-filled PMSP membrane significantly decreased. For all the membranes, the EBU flux increased with the feed concentration, and especially for the 62wt% PHDFNMA-filled PMSP membrane, this tendency was significant. The microvoids in the PMSP membrane play an important role in the permselectivity. As the EBU quantity sorbed into the PHDFNMA-filled PMSP membrane increased with the feed EBU concentration, the diffusion of water was prevented, in turn, the water flux decreased.

The concentration of the EBU solution soaked in the PHDFNMA-filled PMSP membrane was slight compared to the PMSP membrane. The PMSP has many microvoids. The permeate molecule was mainly sorbed in the microvoids. As the PHDFNMA-filled PMSP membrane has few microvoids, the sorption of EBU was low compared to the PMSP membrane.

The sorption and diffusion of EBU and water molecules during pervaporation through the PHDFNMA-filled PMSP membrane were considered as follows by calculation of the apparent separation factor during diffusion (α_D);

At a low feed concentration, the diffusivity of the EBU molecule was much lower than that of water due to the larger molecular size of EBU. As EBU was sufficiently sorbed into the membrane, the diffusion of water was prevented by the EBU molecules, in turn, the permselectivity of EBU was significantly increased. At a high feed EBU concentration, the diffusion of water increased and the diffusion of EBU decreased to a constant as the PHDFNMA-filled PMSP membrane was plasticized. The permeation behavior of the PHDFNMA-filled PMSP membranes were differ from the grafted rubbery PDMS membranes.

9.5 Acknowledgments

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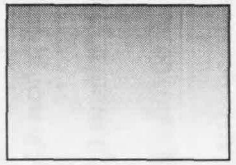
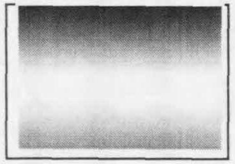
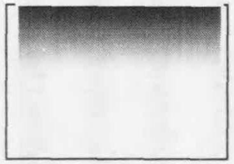
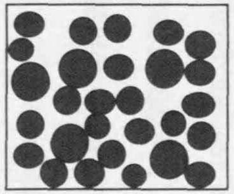
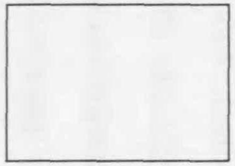
Chapter 10. Conclusions

The PDMS membranes were grafted by fluoroalkyl methacrylates (FALMA) using various irradiation source. FALMA had the effect of increasing the selectivity for VOCs. The grafted PDMS membrane had the difference of polymer structure by various irradiation methods. The permeation properties of the various grafted PDMS membranes were characterized.

The basic permeation behavior for PDMS membrane was investigated. The hydration effect on the sorption-diffusion mechanism for various organic compounds is important phenomena for permeation behavior and was investigated in pervaporation through the PDMS membrane. The water molecules hydrate the solute molecules. The motion of the water molecules are prevented in the solute vicinity. The water flux increased until a maximum at a low feed solute concentration because the hydration promoted water diffusion. However, at the high feed concentration, solute was concentrated in the PDMS membrane and permeate. Almost all water molecules are concerned with hydration when the concentration of (water molecules)/(solute molecules) is the same as the hydration number. When the actual concentration was over this concentration, the water molecules hydrate to several solute molecules and the motion of the water molecules is prevented. During pervaporation, the solute was concentrated in the PDMS membrane and the diffusion of water molecules was prevented. When the dissociate solute mole fraction was a low, the concentration of permeate solution was a low mole fraction and the degree of dissociation is high. Hence, the permeation of organic ions affected the total dissociate solute permeation. The sorption selectivity of organic ion is low. The organic ion molecules is larger than water molecule and the diffusivity is not so high. The enrichment factor of dissociated compounds was low in the solution with a high degree of dissociation. At the high feed concentration, the solution was concentrated in the membrane and the degree of dissociation is low. The solute has high sorption selectivity. The solute flux significantly increased with increasing feed concentration until hydration prevents diffusion. The diffusivity of solute and water molecules are prevented by hydration when the concentration of (water molecules)/(solute

Table 10.1 Various grafted PDMS membranes in this study

Irradiation source	Irradiation method	Degree of grafting	Membrane structure	Membrane strength	Separation factor (α_{TCE})	Flux	Relationship feed concentration and permeate concentration
UV	Simultaneous irradiation	Around 1wt%		Like PDMS	930 (0.025wt% feed)	28gm^{-2}h^{-2} (0.025wt% feed)	Linear
Electron beam	Preirradiation	~ 10wt%		Brittle	1100 (0.025wt% feed)	120gm^{-2}h^{-2} (0.025wt% feed)	Linear
Plasma	Preirradiation	~ 10wt%		Like PDMS	1800 (0.025wt% feed)	32gm^{-2}h^{-2} (0.025wt% feed)	Linear
γ -ray	Simultaneous irradiation	18wt% ~ 220wt%		Some brittle	300 (Low feed concentration) ~ 2300 (High feed concentration)	79 (High feed concentration) ~ 120gm^{-2}h^{-2} (Low feed concentration)	Not linear
PDMS					400 (0.025wt% feed)	60gm^{-2}h^{-2} (0.025wt% feed)	Linear

molecules) is the same as the hydration number. It is concluded that not only the volume of penetrate but also the hydration considerably affect on the diffusivity. It was suggested that the enhancement of solubility of PDMS membrane was important to minimize the effect of the selectivity decrease for dissociate penetrates.

Various grafted PDMS membranes in this study are shown in Table 10.1. As the first step of improvement, the PDMS membrane in which FALMA and alkylmethacrylates (ALMA) were sorbed, was irradiated by UV and utilized in pervaporation. The polymerized FALMA and ALMA were contained in a modified membrane. The contained amounts of FALMA and ALMA were low, around 1wt%. The almost same values were obtained for each FALMA and ALMA. The sorbed TCE in the modified membrane increased with increasing length of the fluorinated side chain of FALMA, i.e., the number of fluorine atoms. The membrane that showed the best separation performance was the membrane having the highest TCE concentration in the sorbed solution. It was concluded that the partition coefficients for chlorinated hydrocarbons increased with the increase in n-fluoroalkyl chain length of the n-fluoroalkyl methacrylates, and, in turn, the permselectivity increased. With increasing feed concentration, water diffusivity decreased. Due to the introduction of a hydrophobic polymer, FALMA, the TCE quantity sorbed into the membrane was so high that the diffusion of water was prevented, in turn, the flux decreased.

The PDMS membrane was grafted by electron beam which would be expected to give more grafted amount than UV. The effect of solubility and diffusibility of a monomer on graft polymerization by electron beam according to solubility parameter, octanol-water partition coefficient (Pow) and the molecular volume of the monomer was investigated. When the difference of $\delta_{solvent}$ and $\delta_{polymer}$ is smaller, solvent and polymer are mixed more homogeneously. The difference of δ_{FALMA} and δ_{PDMS} is small but the sorpted FALMA amount in PDMS membrane was low. The grafted amount was not affected by the solubility parameter. The difference in the sorpted amount or grafted amount was little when considering the difference of the logPow. The sorpted amount for ALMA that have low molecular volume was high. The sorpted amount for FALMA that have high molecular volume was low. Compared to each other in the same group of FALMA or ALMA, the sorpted and grafted amount for the monomer which has low molecular volume was high, and the sorpted and grafted amount for monomer which has high molecular volume was low. The various grafted amounts were obtained for FALMA and ALMA in different from the modification by UV irradiation.

The pervaporation for the PDMS membrane, PDMS membrane irradiated by electron beam, grafted PDMS membranes was investigated. The total flux for the irradiated PDMS membranes by electron beam was high compared to the un-irradiated PDMS membrane. It is thought that the PDMS membranes were made brittle by electron beam irradiation. FALMA grafted PDMS membranes showed excellent sorption and pervaporation separation performance. Among them, PFPMA grafted PDMS membrane which had a high grafted amount and F/Si ratio had high permselectivity for TCE. In pervaporation through the PDMS and grafted PDMS membrane, the TCE concentration and TCE flux in the permeate were increased with increasing feed concentration. In the grafted PDMS, the best separation performance was shown, due to the introduction of the hydrophobic polymer, poly(FALMA).

The PDMS membrane was improved by the graft polymerization with 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA) by plasma, which had a long n-fluoroalkyl chain and the effect on increasing the selectivity for VOCs with low reacted amount. The plasma technique can perform radical formation on the surface of the polymer materials and give little damage to them. When the pervaporation is used as analytical method, it is expected that the relationship between the feed concentration and the permeate concentration is observed to be linear as well as for PDMS. The use for easy quantitative analysis of the pervaporation through plasma-grafted PDMS membranes was investigated. After the irradiation, the degassed HDFNMA was introduced into the reactor, the PDMS membranes were soaked in HDFNMA and then grafted. The graft polymerization was promoted in the PDMS membrane. The degree of grafting on the inside and reverse side of the PDMS membranes was lower than on the surface.

The radical produced on the surface significantly increased with increasing plasma power. The degree of grafting and oxidation simultaneously increased. The flux of the grafted PDMS membrane increased with increasing plasma power. The degree of grafting increased with increasing plasma irradiation time. The flux of the grafted PDMS membrane was constant regardless of the plasma irradiation time. When the PDMS membranes were irradiated at 10W for 180s and grafted, the grafted membranes were not brittle and the permselectivity increased. The hydrophobicity of the grafted PDMS membranes was effectively increased due to introducing the hydrophobic polymer, poly(HDFNMA). Because the grafted amount of the plasma grafted PDMS membrane was little and the advantage of rubbery PDMS membrane remained, the relationship between the feed concentration and the permeate concentration was observed to be linear. The feed concentration is able to be introduced from the permeate concentration. The pervaporation through the grafted PDMS membrane could to be used for easy quantitative analysis.

The sorption and diffusion of the permeate solute is important for the permeation behavior same as the solute properties and interaction. The sorption and diffusion for various VOC-water mixture during pervaporation through the PDMS membrane and HDFNMA grafted PDMS membrane by plasma preirradiation were investigated. The grafted PDMS membrane showed the best sorption and separation performance. During pervaporation, the components which permeate and membrane interface each others. The phenomenon was significantly observed in pervaporation for the ternary mixture through the grafted PDMS membrane. The TCE flux was prevented by benzene during pervaporation of the TCE-benzene-water mixture through the grafted PDMS membrane.

PCE and toluene have high logPow and had high solubility in both the PDMS membrane and the grafted PDMS membrane. EBU have low logPow and had low solubility in both the PDMS membrane and the grafted PDMS membrane. The solubility for EBZ was low in both the PDMS membrane and the grafted PDMS membrane, while EBZ has a high logPow. The solubility for compounds in a membrane is affected by its dispersion and polarization. Polarization can be considered using the Pow value. The ability of dispersion is determined by diffusivity. The degree of sorption for EBZ was low compared to the other VOCs. The molecular volume of EBZ is much greater than the other VOCs ,therefore, the diffusivity of EBZ is low. Hence, the degree of sorption for EBZ was low and the solubility for EBZ was low in the membrane. PCE has four Cls with a much larger molecular volume, therefore, the diffusivity is very low.

Permselectivity is determined by the sorption and the diffusion characteristics of the permeating components in the membrane. The permselectivity of PCE and toluene was high. Because the solute quickly permeates in the rubbery membrane like PDMS, permselectivity was not affected by diffusivity. Solubility significantly affects the permselectibity during pervaporation through the hydrophobic rubbery membrane. The solution-diffusion mechanism for various VOCs based on their properties were important.

The PDMS membrane was improved with graft polymerization of HDFNMA, which has the effect of increasing the selectivity for chlorinated hydrocarbons, by a ^{60}Co source and characterized the grafted PDMS membrane. Simultaneous irradiation is a method in which that monomer and polymer are irradiated simultaneously. The grafted amount by simultaneous irradiation was more than by preirradiation methods, and the permeation behavior will be expected to be differ from the rubbery untreated PDMS membrane and the grafted membranes by preirradiation method. The grafted and polymerized HDFNMA by a ^{60}Co simultaneously irradiation was swollen but not dissolved in solvent, different from poly(HDFNMA) grafted by electron beam and plasma preirradiation. The grafted PDMS membranes had a microphase-separated structure, i.e., a separated structure of PDMS and grafted HDFNMA. The graft polymerization started with one region in the PDMS membrane. More HDFNMA was grafted on the poly(HDFNMA) domain than the PDMS domain due to the affinity of HDFNMA for poly(HDFNMA). The poly(HDFNMA) domain was grown by grafting. The poly(HDFNMA) domains were dispersed into the entire PDMS membrane homogeneously by irradiation.

The grafted PDMS membrane by simultaneous irradiation was applied to pervaporation, and their permeation behavior was compared to the PDMS membrane and the grafted PDMS membranes by preirradiation method. In the grafted PDMS membrane, the concentration of TCE sorbed into the membrane was high, due to the introduction of the hydrophobic polymer, poly(HDFNMA). The membrane that had a high solubility selectivity for TCE showed great separation performance. The permeability of the PDMS phase was significantly great and that of the poly(HDFNMA) phase was too low to affect the whole permeation of the grafted PDMS membrane directly. However, poly(HDFNMA) had a much stronger affinity for TCE than for water. Thefore, the permeability and permselectivity of TCE on the surface of poly(HDFNMA) and PDMS were high, and the permeation on the surface played important role in the permeation through the grafted PDMS membrane. At a low feed concentration of TCE solution, the diffusivity of TCE molecules must be much lower than that of water due to the larger molecular size of TCE. At a high concentration of TCE solution, TCE was sufficiently sorbed into the membrane, so that the diffusion of water was prevented by the TCE molecules; in turn, the permselectivity of TCE was increased significantly. The interesting permeation phenomena was obtained for this grafted membrane.

In this study, the permeation properties of the grafted PDMS membranes by various irradiation methods were characterized. The permeation behavior was differ from rubbery untreated PDMS membrane and the little grafted PDMS membrane by preirradiation. It was cleared that the membrane structure effected on the permeation behavior significantly.

Further, PMSP membrane was filled with poly(HDFNMA) (PHDFNMA) and the sorption-diffusion mechanism in pervaporation was investigated compared to the grafted PDMS membrane. The separation performance was increased due to introduce hydrophobic polymer, PHDFNMA compared to PMSP membrane. At low feed concentration, the diffusivity of EBU molecule was much lower than that of water due to the larger molecular size of EBU. As EBU was sorbed enough into the membrane, the diffusion of water was prevented by the EBU molecules, in turn, the permselectivity of EBU was increased signifientIy. At high feed EBU concentration, the diffusion of water increased and the diffusion of EBU decreased to be constant as the PHDFNMA-filled PMSP membrane was plasticized. In case of the HDFNMA grafted PDMS membrane by simultaneous irradiation, the membrane was not plasticized because the PDMS membrane is rubbery polymer but crosslinked. Because the PMSP membrane is glassy polymer but has high solubility for organics, the PHDFNMA-filled PMSP membrane was plasticized and the permeation behavior was differ from the grafted PDMS membrane.

Appendix. Analysis of Hydrophilic Volatile Organic Compounds by Pervaporation (for chapter 6)

A.1 Introduction

In recent years, the various environmental organic pollutants that influence human health have become a social problem. The analysis technique to measure most of these compounds is complex and requires a long time[1,2]. For example, organic compounds to be analyzed are extracted with solvents, absorbed on an adsorption column and distilled[1,2]. However, the water samples are required to concentrate before being subjected to the analyzer. It is also important to concentrate and analyze the water samples quickly at the field. Hence, pervaporation as easy extraction technique for such an analysis has been studied and used[3~11]. If a straight line relationship is apparent for the concentrations on the feed side and on the penetration side, it can be utilized as the calibration curve and applied as a simple analytical method. (described in chapter 6) Up to now, various environmental organic pollutants sensitively and simultaneously analyzed by a gas chromatograph mass spectrometer (GC-MS) which can detect them of μg/l levels. As the introduction of liquid water to the GC-MS should be avoided, the introducing of a permeated vapor to the GC-MS without cooling provides a cost savings. The extraction of volatile hydrophilic organic compounds from water has difficulties[1,2] and a conventional extraction method has been required. A Polydimethylsiloxane (PDMS) membrane, which has a high permeability to gases and liquids,[12] can contribute to an easy and sensitive analysis. In this study, the permeated vapor of the volatile hydrophilic organic compounds in the pervaporation trough PDMS was subjected to GC-MS and analyzed. The degree of linearity and sensitivity was investigated and its applicability as an analytical method was evaluated.

A.2 Pervaporation experiment and analytical measurement

Commercial PDMS membranes (Fuji Systems Corporation), 50 μm thick, were used throughout this study. Butyl acrylate, 2-butanone, 1,4-dioxane (Special grade, Wako Pure

Chemical Industries, Ltd.), acrylonitrile , methyl-t-butyl ether, bis(2-chloroethyl) ether (Special grade, Kanto Chemical Co., Inc.), methanol, fluorobenzene in methanol (1mg/ml) and bromofluorobenzene in methanol (1mg/ml) (for volatile organic compounds measurement, Kanto Chemical Co., Inc.) were used as received. The physical and chemical properties of the compounds used in this study are listed in Table A1.

Table A1 Various hydrophilic organic compounds used in this study

Compounds	Molecular weight	Boiling point ℃	Water solubility wt%	Former extraction methods
Methyl-t-butyl ether	88.15	55.2	Slightly soluble	Purge & Trap
Acrylonitrile	53.03	77.3	7.5	Steam distillation & Solvent (or solid phase) extraction, Purge & Trap
2-Butanone	72.1	79.6	22.6	Solvent extraction
1,4-Dioxane	88.1	101.6	Soluble	Solid phase extraction
Butyl acrylate	128.17	146	0.2	
Bis(2-chloroethyl) ether	143.01	178.5	1.1	Steam distillation & Solid phase extraction, Purge & Trap
Fluorobenzene (Internal standered 1)	96.1			
4-Bromofluorobenzene (Internal standered 2)	175			

The pervaporation experiments were performed as in a previous study[13]. The permeated vapor was cooled to a liquid and subjected to gas chromatography with flame ionization detection (GC-FID). The enrichment factor, βpv, was calculated as

$$\beta pv = Y/X \qquad (A.1)$$

where X and Y denote the concentration of the solute in the feed and permeate solution, respectively.

This analytical pervaporation method was performed as reported by Luque de Castro et al.[4-6]. In this analytical pervaporation, the permeated vapor was subjected to GC-MS without cooling. Fluorobenzene and bromofluorobenzene were used as the internal standards to minimize the analysis error.

A.3 Results and discussion

A.3.1 Pervaporation for hydrophilic volatile organic compounds

Table A2 Enrichment factors for pervaporation in this analytical method at various temperatures[a]

	Enrichment factor in pervaporation at 0.005wt% feed concentration (±S.D.)	
Compounds	25℃	60℃
Methyl-t-butyl ether	41±5.7	104±19
Acrylonitrile	34±6.3	87±9.3
2-Butanone	36±6.7	102±27
1,4-Dioxane	20±3.9	74±17
Butyl acrylate	45±4.3	68±8.9
Bis(2-chloroethyl) ether	26±5.6	77±10

a : n=4

S.D.: Standard division

The feed and permeate concentrations at equilibrium during the pervaporation measurement were determined by GC-FID. The enrichment factor (βpv) of the

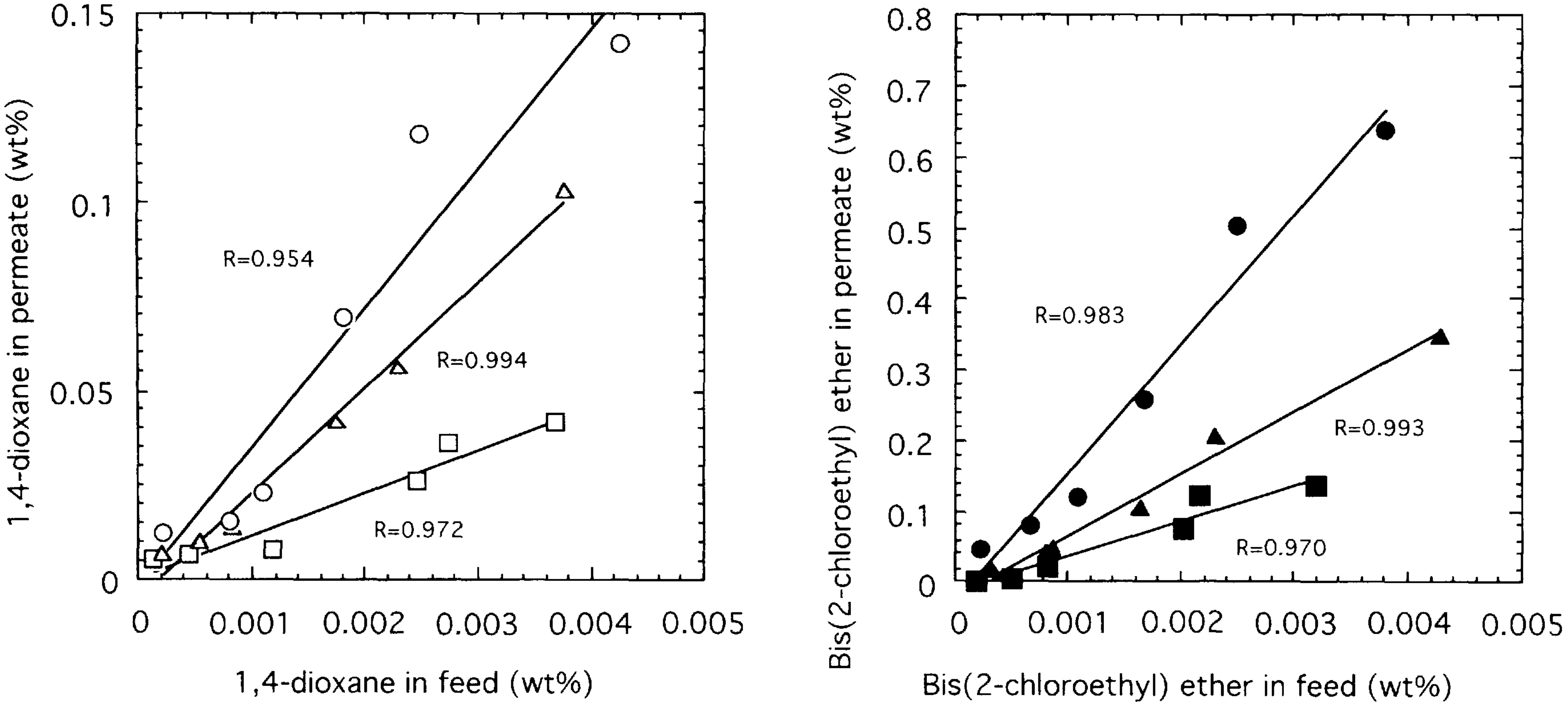


Fig. A1 Effect of feed concentration on permeate concentration for hydrophilic volatile organic compound-water mixtures during pervaporation through PDMS membrane at various temperatures: (□) at 25°C, (△) 40°C, (○) 60°C, open: for 1,4-dioxane, closed: for bis(2-chloroethyl) ether.

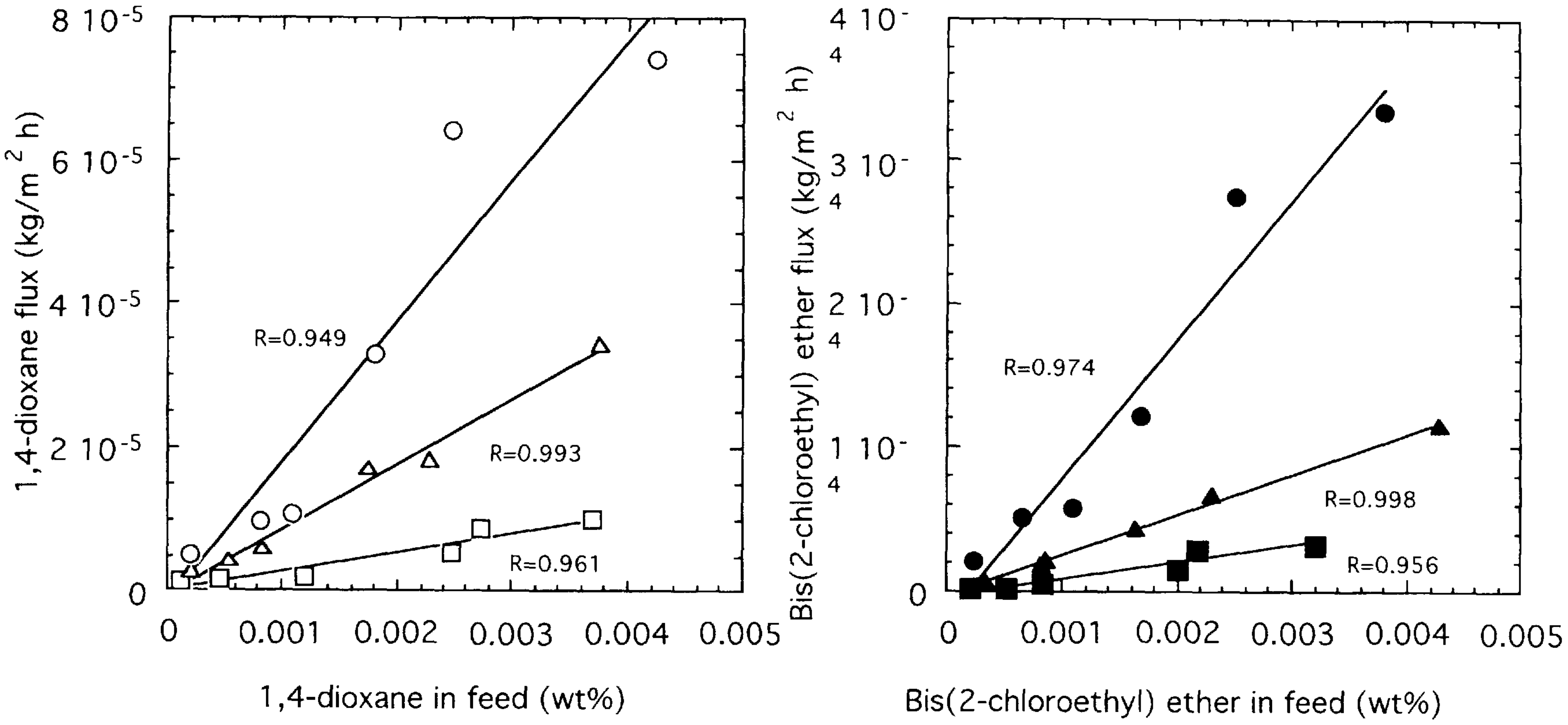


Fig. A2 Effect of feed concentration on solute flux for hydrophilic volatile organic compound-water mixtures during pervaporation through PDMS membrane at various temperatures: (□) at 25°C, (△) 40°C, (○) 60°C, open: for 1,4-dioxane, closed: for bis(2-chloroethyl) ether.

hydrophilic volatile organic compounds at each temperature is given in Table A2. The relationship between the feed and permeate concentrations of the hydrophilic volatile organic compound is shown at various temperatures in Fig. A1. The relationship between the feed and permeate concentrations was found to be linear. If a straight line relationship between the feed and permeate concentrations is obtained, the relationship can be utilized as calibration curve. The hydrophilic volatile organic compound flux as a function of the concentration of the hydrophilic volatile organic compounds in the feed solution is shown at various temperatures in Fig. A2. The relationship was observed to be linear. In this analytical pervaporation, the permeated vapor was subjected to GC-MS without cooling. When the relationship between the permeate amount of solute vapor for a unit time, i.e., solute flux and feed solute concentration was found to be linear, it could be used as a calibration curve for a simple analysis method. The flux of the hydrophilic volatile organic compounds was high at high temperature.

A.3.2 Analytical pervaporation of hydrophilic volatile organic compounds

The hydrophilic volatile organic compound solution with a known concentration was introduced into the analytical pervaporation cell. The permeated vapor was subjected to GC-MS. The calibration curve was based on the relationship between the solution concentration and the GC-MS peak area. The influence of temperature on the calibration curve for each compound using this analytical method is shown in Table A3. At 25 °C, the vapor of the compounds was only slightly detected in the cell. When the vapor permeated at 25°C and the inside of the cell was heated with a dryer, each compound was detected. Also, for some compounds, the calibration curve became a straight line with good sensitivity when the vapor of the compounds was permeated at 40 °C and then analyzed. When the vapor of the compounds permeated at 60 °C was analyzed, for most of the compounds had calibration curves that were straight lines with good sensitivity. The operating temperature at 60 °C was the best for this analytical method. During the pervaporation, the vapor of the compounds was cooled to a liquid and then analyzed. In this analytical method, the vapor of the compounds was analyzed without cooling, and at a low operating temperature, the vapor of the compounds can not remain as such and is adsorbed onto the inside of the cell.

Table A3 Correlation coefficients of the calibration curve in this analytical method at various temperatures

		Correlation coefficient of the calibration curve in this analytical method		
Compounds	m/z	25℃	40℃	60℃
Methyl-t-butyl ether	73	−*	0.996	0.987
Acrylonitrile	52	−*	0.900	0.998
2-Butanone	72	−*	−*	0.986
1,4-Dioxane	58	−*	−*	0.992
Butyl acrylate	73	−*	0.995	1.000
Bis(2-chloroethyl) ether	93	−*	−*	0.999

* : Not detected
m/z: Target ion in GC-MS analysis

The recovery was examined for various compounds in river water at 60°C. Each compound was added to the river water at 5 or 200 μg/l. The concentration of the added river water was obtained from the vapor peak area using the calibration curve based on the vapor peak area for the concentration of a known solution. The recovery (R%) and the coefficient of variation (CV%) are shown in Table A4. For a 200 μg/l solution, the recovery was 89~118% with a 16~29% CV value. For a 5 μg/l solution, the recovery was 81~118% with a 6~33% CV value. In this study, the standard solution was made from distilled water.

Table A4 Recovery from the river sample using this analytical method at 60℃^{a}

	5 ppb		200 ppb	
Compounds	R(%)	CV(%)	R(%)	CV(%)
Methyl-t-butyl ether	104	14	95	22
Acrylonitrile	90	6	110	29
2-Butanone	118	31	118	23
1,4-Dioxane	86	33	100	20
Butyl acrylate	100	13	89	16
Bis(2-chloroethyl) ether	81	19	91	24

a : n=5

R(%): Average of recovery(%)

$$\text{CV(\%): Coefficient of variation(\%)} = \frac{\text{Standard division of recovery(\%)}}{\text{Average of recovery(\%)}} \times 100(\%)$$

Since various compounds are contained in environmental water samples, the concentration of the added river water is detected to be higher than the real concentration due to salting-out effect. The control of such effect is being studied. This method can be a convenient way to analyze hydrophilic volatile organic compounds in water samples.

A.4 Conclusion

An analytical pervaporation technique was applied to the extraction of hydrophilic volatile organic compounds in this study. During the pervaporation, the relationship between the feed concentration, permeate concentration and solute flux was found to be linear, and the slope was high at a high operating temperature. In this analytical pervaporation technique, the calibration curves for most of the compounds became straight lines with good sensitivity at a high operating temperature, i.e., 60 °C.

A.5 Acknowledgment

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