

초청강연 III

Application of Membranes for Organic Liquid or Vapor Separation and Design of Plasma-Graft Filling-Polymerized Membranes

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INTRODUCTION

There is much recent interests in applying membrane separation technologies, especially for organic liquid and vapor separation or removing dissolved organics from water. Pervaporation separation can separate azeotropic mixtures and mixtures close to boiling point, and it has a potential for energy saving process instead of distillation. Removal of chlorinated organics from water is other measure application for pervaporation separation. Contaminated pollutant must be removed from water, and a pervaporation can effectively remove the pollutant. Air pollution by organic vapor recently became serious environmental problem, and removing organic vapor from air is important application of the membrane technology.

We have proposed a new type of membrane for organic-liquid and -vapor separation, called the filling-polymerized membrane [1-3]. In the separation of an organic liquid and vapor mixture by an organic membrane, reduction of selectivity occurs due to membrane swelling; hence suppression of this swelling is important for successful separation. The membrane proposed is composed of two materials: the porous substrate and the filling polymer which fills the pores of the substrate. The porous substrate is completely inert to organic liquids, and the filling polymer is soluble with one component in the feed. The filling polymer exhibits permselectivity due to the solubility difference, and the porous substrate matrix restrains the swelling of the filling polymer due to its mechanical strength.

These membranes showed high selectivity and permeability for organic mixtures [1-3] and could remove chlorinated contaminants from water [4,5].

There are many kinds of organic mixtures to separate. A suitable membrane should be prepared for each organic mixture. However, there is no design concept for the suitable membrane. Recently, several researchers reported pervaporation flux prediction of single component [6] or multi component mixtures [7] without any adjustable parameters from transport experiments. Although the method was used for a flux or selectivity prediction, that can be utilized for a design concept.

We tried to predict pervaporation or vapor permeation fluxes through different type of polymer membranes using filling method. The prediction and filling membrane methodology will allow us to design a suitable membrane for each organic-mixture separation.

PLASMA-GRAFT FILLING POLYMERIZATION

Porous high density polyethylene (HDPE) films were used as the substrate. The substrates have thickness of 5-6 μm and 0.02 μm pore size.

Methyl acrylate (MA), butyl acrylate (BA), ethylhexyl acrylate (EHA) lauryl acrylate (LA) and acrylamide (AAm) were used as the graft monomer. The details of grafting was described in elsewhere [1-5].

PERVAPORATION SEPARATION

Pervaporation results of organic/organic mixture through filling type membranes were shown in Table 1. Soluble components in the grafted polymer (A) were preferentially permeated through the membranes in comparison with insoluble components (B). MA grafted polymer showed high selectivity for benzene, methylacetate or chloroform over aliphatic solvents. The polymer has good solubility for chlorinated organics or acetates. Crosslinking treatment increase selectivity, but decrease flux. This is because crosslinking leads to swelling reduction of polymers. Polymer solubility can be changed by copolymerization composition. MA/AAm copolymer showed high solubility for methanol, and the grafted membrane showed high selectivity for methanol over iso-propylalcohol. The solubility change can be predicted by Hansen Solubility Parameters [2,3].

Table 1. Pervaporation results through Filling-Polymerized Membranes (feed temp. = 25 °C)

Grafting monomer	Feed mixture		A conc. in feed [wt%]	A. conc. in perm. [wt%]	Flux [kg/m ² hr]	Separation factor [-]
	A	B				
MA	Benzene	Cyclohexane	50.2	93.7	0.02	14.8
MA	Methylacetate	Cyclohexane	49	94.3	4.9	17.2
MA	Chloroform	n-Hexane	72.3	96.5	5.3	10.6
crosslinked MA	Chloroform	n-Hexane	72	97.3	2.1	13.8
MA/AAm	Methanol	IPA	50	97.9	0.21	46.1

MA: methylacrylate, AAm: acrylamide, IPA: iso propylalcohol

Dependence of TCE concentration in the feed aqueous solution on TCE concentration in the permeate is shown in Figure 1 accompanied with poly (dimethyl siloxane) or polyolefin membranes [8]. The order of selectivity is LA grafted membrane > EHA grafted membrane > BA grafted membrane. The selectivity increased with an increase in the carbon numbers of ester groups in the grafting monomer unit. The results can be explained by an order of membrane hydrophobicity. The dependence of TCE concentration in the feed on the TCE partial flux is shown in Figure 2. Although LA or EHA grafted membranes showed higher selectivity than the BA grafted membrane, all of membranes showed almost the same fluxes within the experimented range. These LA grafted membranes having 20 μm thickness showed much higher selectivity and similar flux in comparison with poly(dimethylsiloxane) or polyolefin membranes having 1 μm thickness [8]. The linear graft chains have large free volume for solute diffusion compared with a usual crosslinked chains, and the substrate matrix could effectively suppress swelling of the grafted polymers. Thus, the filling type membranes showed both higher permeability and selectivity than the usual membranes. The LA grafted membrane concentrated a 0.1 wt% TCE aqueous solution to more than 90 wt% TCE vapor, and the separation factor was around 10,000.

FLUX PREDICTION MODEL

The interaction parameters, χ , between filling polymer and solvents were calculated by UNIFAC-FV Theory [9], and solvent mutual diffusion coefficients in the

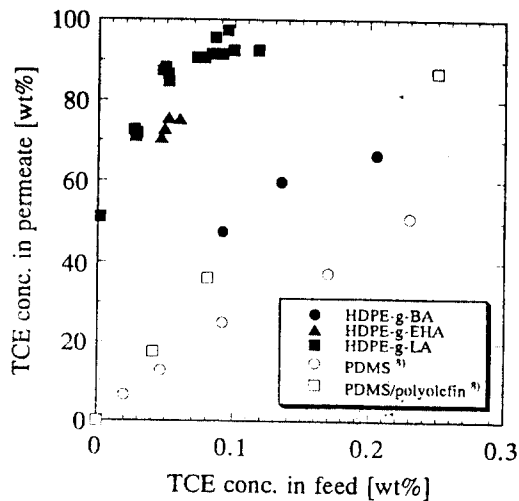


Fig. 1 Relationship between TCE concentration in feed and permeate by pervaporation at 25°C

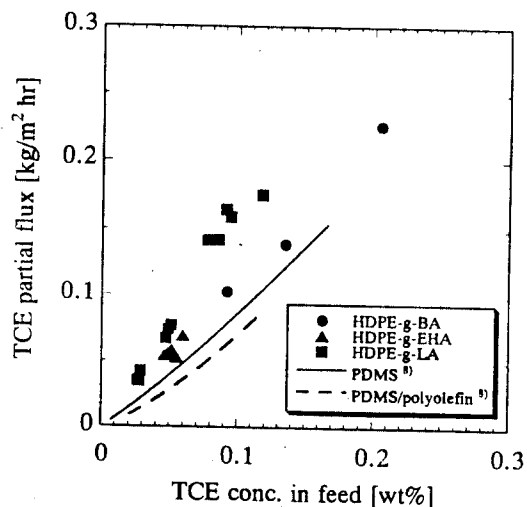


Fig. 2 Relationship between TCE concentration in feed and TCE partial flux at 25°C

filling polymer were estimated by Free-Volume Theory [10]. Usually, crosslinked polymer was used for pervaporation membranes, and the diffusivity can be hardly predicted due to a free volume change by crosslinking. Linear polymers can be used for the filling polymer because of the substrate effect, and parameters for a pure polymer can be used for the filling polymer membrane.

Suppression effect of membrane swelling can be estimated using a model described by tie-segment of the substrate material [11]. Generally, single component permeation through a membrane was satisfactorily described by Fick's law [12]. Those models enable us to calculate the pervaporation or vapor permeation flux through the filling-polymerized membrane without any adjustable parameters

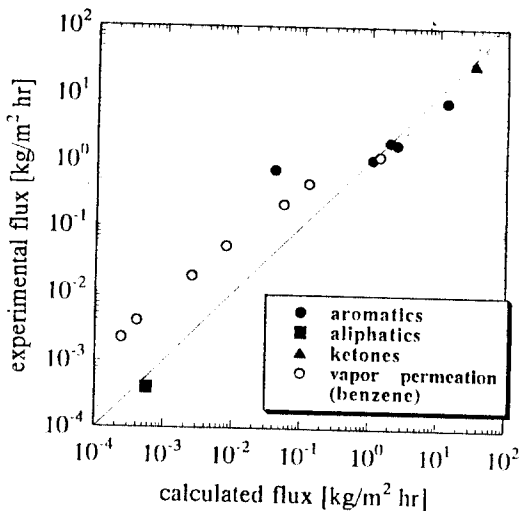


Fig. 3 Comparison between predicted and experimental fluxes through MA-grafted membrane

for a transport system.

Predicted results of organic component fluxes through a MA-grafted membrane were compared with experimental fluxes as shown in Figure 3. Benzene, toluene, ethylbenzene, o-xylene, n-hexane and acetone were used as the feed solvents, and temperature was fixed at 25 °C. Predicted fluxes are in good agreement with experimented values in the wide range between 10^{-4} and 100 kg/m² hr. Dependence of temperature[7] or mechanical strength of porous substrate[6] can be predicted by this method.

DESIGN OF A VOC (BENZENE) REMOVABLE MEMBRANE

Benzene is one of toxic VOC, and benzene must be removed from gasoline vapor or contaminated water. We tried to design a benzene removable membrane using the prediction technique. Table 2 shows predicted benzene flux through filling type membranes with 14 kinds of filling polymer. The table shows acrylates or styrene derivatives have high permeability for benzene.

Benzene solubility to polyacrylates is shown in Figure 4. All polyacrylates we tested showed almost the same solubility in benzene. The predicted lines by UNIFAC-FV model agreed with experiments for other polymers, such as poly(BA) and poly(LA).

Benzene fluxes through grafted membranes are shown in Figure 5. BA or LA grafted membranes showed much higher flux than the MA grafted membrane. Especially, at low vapor pressure region, the BA or LA grafted membranes showed high benzene fluxes. Solubility of benzene to each polyacrylate is not different, thus the diffusivity of benzene in poly(BA) or poly(LA) must be much higher than that in poly(MA). Bigger branch size of monomer structure might make the free volume for diffusion.

Table 2 Predicted benzene flux by pervaporation and benzene fraction in filling polymer at feed side, $v_{sf}(25^{\circ}\text{C})$

filling polymer	methyl acrylate	methyl methacrylate	ethyl methacrylate	vinyl acetate	styrene	α -methyl styrene	p-methyl styrene
v_{sf} [-]	0.58	0.50	0.51	0.52	0.53	0.52	0.54
flux [kg/m ² hr]	1.1	0.7	0.5	0.9	1.0	2.0	1.3
filling polymer	ethylstyrene	styrene butadiene	propylene	iso butyrene	cis-1,4-isoprene	butyl rubber	neoprene
v_{sf} [-]	0.51	0.64	0.39	0.48	0.36	0.25	0.06
flux [kg/m ² hr]	0.7	0.7	0.08	0.01	0.001	5×10^{-6}	4×10^{-5}

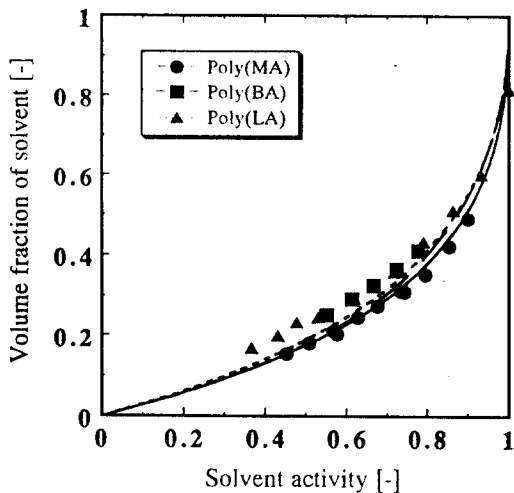


Fig.4 Relationship between benzene activity and volume fraction of benzene in polymer at 25°C
(lines were calculated by UNIFAC-FV model)

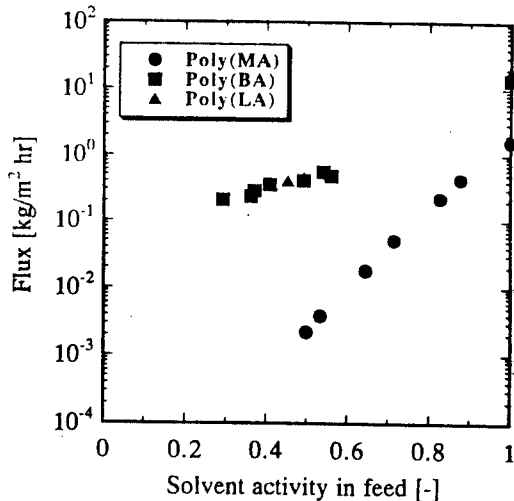


Fig.5 Relationship between benzene activity in feed and benzene flux through grafted membranes at 25°C

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