

# Separation properties of modified poly[1-(trimethylsilyl)-1-propyne] membrane for volatile chlorinated organic compound

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## Abstract

Recently, it has been reported that the poly[1-(trimethylsilyl)-1-propyne] (PMSP) membrane has a high permselectivity for organic compounds in pervaporation. In this study, the permeation properties of a PMSP membrane modified with various hydrophobic plasticizers for a trichloroethylene(TCE)-water mixtures were investigated by pervaporation. Both total flux and separation factor ( $\alpha_p^{TCE}$ ) of the TCE-water mixtures increased with increasing hydrophobic plasticizer content. In each flux of TCE and water, the former increased while the latter decreased with hydrophobic plasticizer. Moreover, the solubility selectivities ( $\alpha_s^{TCE}$ ) were nearly  $\alpha_p^{TCE}$  over the whole range of the feed composition. Therefore, it was considered that the TCE selectivity was largely attributed to the solubility of TCE in the membranes. These results indicate that hydrophobic plasticizer has a high affinity for TCE and inhibited the permeation of water.

*Keywords:* poly[1-(trimethylsilyl)-1-propyne], pervaporation, plasticizer, solubility selectivities, organic separation

## 1. INTRODUCTION

Membrane technology has been studied since the 1970s and has grown rapidly in recent years [1-2]. The membrane processes are low cost and provide collection with concentration; therefore they became favorably competitive in such areas as water desalination, water purification, and gas separation.

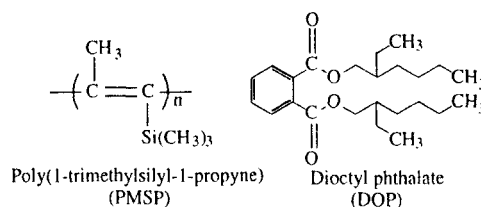
The dependence of underground water is widely utilized as one source of drinking water. However, underground water has been polluted by volatile organic compounds (VOCs) such as trichloroethylene (TCE) and tetrachloroethylene. Therefore, the purification of water by various methods such as use of activated carbon and air stripping, etc, has been focused on. PV using polymeric membranes is one of the potential applications for removing VOCs from water [3-5].

It has been reported that, similar to the polydimethylsiloxane membrane (PDMS), the poly[1-(trimethylsilyl)-1-propyne] (PMSP) membrane exhibits high permselectivity [6] for VOCs in pervaporation because of its high affinity for VOCs. PMSP has a higher flux compared with PDMS; the selectivity is about similar. Because the solubility of the plasticizer for water is generally low, the PMSP membrane is expected to become more hydrophobic due to the plasticizer contained in the PMSP, and high selectivity results from reduction of the water obtained. In this study, the permeation properties in TCE-water mixtures were investigated by PV for the PMSP membrane and PMSP membrane modified with various plasticizers.

## 2. EXPERIMENTAL

### 2.1 Materials and modification

PMSP (Figure 1) used in the experiments was supplied by Shin-etsu Chemical Co, Ltd. The homogeneous PMSP with 145 to 155  $\mu\text{m}$  thickness was prepared using a 2.0wt% casting solution of toluene onto a glass plate. All membranes were preserved under vacuum in a desiccator to keep them fresh. The plasticizers were supplied by Junsei Chemical Co, Ltd.



**Figure 1. Chemical structure of polymer and plasticizer in this study.**

The PMSP membrane was modified by adding various plasticizers containing octyl (2-ethylhexyl) group diocetyl (di2-ethylhexyl)phthalate (DOP), trioctyl (tri2-ethylhexyl) phosphate (TOP), dioctyl (di2-ethylhexyl)sebasate (DOS), tris (2-ethylhexyl) trimellitate (TOT), and using a dehydrochloride reagent tricresylphosphate (TCP) to the casting solution. The combined plasticizer content of the membrane was determined using  $^1\text{H-NMR}$ . The content of each plasticizer was about 14.4-54.5wt%, and the content in percent was calculated by the following formula:

$$\text{Content} = [(W_a - W_b) / W_b] \times 100$$

where  $W_a$  and  $W_b$  are the weight of polymer with and without.

### 2.2 Characterization

PMSP and modified PMSP membranes were confirmed by  $^1\text{H-NMR}$  and Infrared spectram (ATR-IR). The density of the polymer was measured by the volume method from the thickness, weight, and area. The contact angle was measured between the polymer and ultrapure water, which expresses the hydrophobicity or hydrophilicity of the polymer.

The  $d$ -spacing was determined from the diffraction maximum in WDXD, using Bragg's equation  $2d \sin\theta = n\lambda$  ( $\lambda = 1.54 \text{ \AA}$ ), which represents the approximate average intersegmental distance in a polymer.

### 2.3 Pervaporation measurements

PV measurement was performed with a stainless steel cell at 25°C. The permeation area ( $A$ ) of the membrane

was  $6.605\text{cm}^2$ . The feed solution of TCE-water mixtures was circulated using a microtube pump on the upper side of the membrane in order to maintain the feed concentration constant, and the downstream pressure was kept below  $10\text{mmHg}$ . The permeate vapor was trapped using liquid nitrogen. The total flux and selectivity for TCE-water mixtures through the membrane were determined by the weight of permeant and by gas chromatography (GC; FID), respectively. The flux  $J$  was determined by measuring the amount of permeant  $Q$  passed through the membrane during the time interval  $t$  at steady state.

$$J = Q/At$$

The separation factor  $\alpha$  of TCE over water is defined as follows:

$$\alpha = (P_{org}/P_w)(F_{org}/F_w)$$

where  $P_i$  and  $F_i$  are the weight fraction of permeate and feed, and the subscripts *org* and *w* stand for TCE and water, respectively.

#### 2.4 Swelling and sorption measurements

The sorption properties of the membrane were determined as follows. The PMSP and modified PMSP membranes were immersed in both  $0.05\text{wt}\%$  and  $0.08\text{wt}\%$  TCE solutions at  $25^\circ\text{C}$  for 24hr. The swollen membrane was taken off at regular intervals and excess solution was removed by light tamping between filter papers. The membrane was then weighed. The degree of swelling was calculated by the weight of the dry and swollen membranes, according to the following formula.

$$S = [(W_s - W_d)/W_d] \times 100$$

where  $W_s$  and  $W_d$  are the weights of the swollen and dry membrane, respectively. The sorption experiment was carried out by freezing the swollen membrane using liquid nitrogen in a glass vessel. A membrane piece was then heated afterward. The adsorbate was vaporized and collected in another cold trap with liquid nitrogen. As above, the TCE-water composition in the swollen membrane was determined by GC as well as by PV measurement.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of polymer

**Table 1.** Characterization of PMSP and modified PMSP membranes

Membrane	a) Content (wt%)	b) d-spacing (Å)	c) Contact Angle (deg.)	d) Density (g/cm <sup>3</sup> )
PMSP	0.0	9.0	107	0.77
DOP/PMSP(14.4wt%)	14.4	8.8	99	0.86
DOP/PMSP(25.3wt%)	25.3	8.5	98	0.91
DOP/PMSP(36.7wt%)	36.7	8.4 4.4	91	0.93
DOP/PMSP(49.3wt%)	49.3	8.4 4.4	95	0.98
TOT/PMSP(52.5wt%)	52.5	8.3 4.4	98	0.88
DOS/PMSP(48.7wt%)	48.7	8.1 4.4	100	0.84
TCP/PMSP(54.5wt%)	54.5	8.4 4.4	91	0.85
TOP/PMSP(53.2wt%)	53.2	8.5 4.4	96	1.01

a) Thickness:  $145\text{--}155\mu\text{m}$

b) Content of various plasticizer was determined by <sup>1</sup>H-NMR.

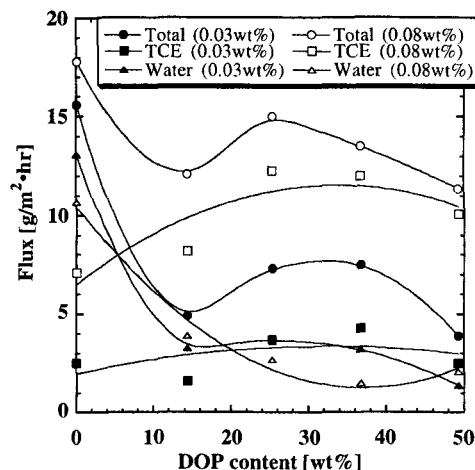
c) Determined by wide-angle X-ray diffraction using Bragg's equation,  $\lambda = 2d\sin\theta$  (Cu-K $\alpha$ ,  $\lambda = 1.54\text{Å}$ )

d) Between polymer and water.

e) Determined by volume method.

Table 1 shows the various characterizations of the PMSP membrane without and with various plasticizers. The *d*-spacing which exhibits the average molecular distance of the polymer chain decreased, whereas the density was increased with the increasing of each plasticizer content. It can be assumed that the membrane was plasticized and the large excess free volume of PMSP was decreased because of the content. Moreover, it is known that the  $T_g$  (glass transition temperature) of the glassy polymer decreases with the plasticizer content because some domains of the PMSP membrane became rubber domains. Therefore, it is considered that the intersegmental distance in the polymer was reduced and that the membrane structure became packed.

#### 3.2 Pervaporation with a modified membrane containing DOP



**Figure 2.** Effect of DOP content on partial and total flux in TCE-water mixtures through PMSP and modified PMSP membranes at  $25^\circ\text{C}$ .

Figure 2 shows the effect of DOP content on TCE, water and total flux by PV. At  $0.03$  and  $0.08\text{wt}\%$  TCE feed composition, the total flux decreased up to a DOP content of  $14.4\text{wt}\%$  and afterward increased with increasing DOP content. The total flux then reduced up to a DOP content of  $49.3\text{wt}\%$  again. The TCE flux increased up to a DOP content of  $36.7\text{wt}\%$ ; on the contrary, the water flux was always reduced with increasing DOP content, indicating that the matrices composed of PMSP and DOP are much more hydrophobic than those composed of only PMSP. These results showed that the water flux always decreased with increasing DOP content because of greater resistance to water.

Figure 3 shows the effect of DOP content on the permeate and separation factor ( $\alpha_p^{\text{TCE}}$ ) in TCE-water mixtures. In both feed compositions, the permeate composition increased with increasing DOP content. It is considered that selective permeation of TCE was caused by the contain DOP content, and the feed solution was condensed. The  $\alpha_p^{\text{TCE}}$  increased with increasing DOP content; in a  $0.08\text{wt}\%$  feed composition about a  $12,000$  value was obtained for PMSP containing DOP ( $49.3\text{wt}\%$ ). The TCE flux increased, the water flux decreased and the difference in both fluxes became larger with increasing

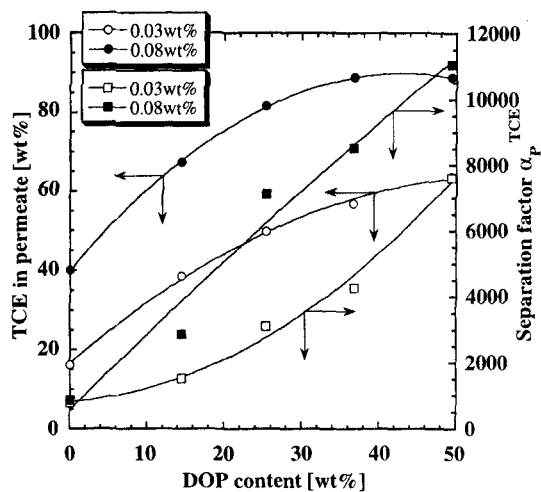


Figure 3. Effect of DOP content on the permeate and separation factor in TCE-water mixtures through PMSP and modified PMSP membranes at 25°C.

DOP content, and then as shown in Figure 2,  $\alpha_p^{\text{TCE}}$  increased. Therefore, it is considered that  $\alpha_p^{\text{TCE}}$  increased with increasing DOP content.

### 3.3 Pervaporation for modified membrane containing various plasticizers

Figure 4 shows the effect of the feed composition on the total flux in TCE-water mixtures for modified membrane containing various plasticizers. The total flux increased with increased feed composition, in particular, with PMSP containing DOP. The total flux has a lower value with lower feed composition because the permeation sites were occupied by plasticizer; however, those increased at higher feed composition together with swelling of the membrane and the total flux for membrane containing plasticizer has approximately same value as the PMSP membrane at 0.10wt% feed composition. In other words, the TCE vapor pressure increased with increasing the feed composition, inciding the TCE concentration gradient increased, on the contrary the water one was not greatly changed. It is considered that the increase of TCE flux is attributed to the acceleration of TCE sorption, dependent on the increase in total flux. The PMSP containing TOP and DOP has a higher total flux, this value being approximately equal to PMSP only at 0.10wt% feed composition.

Figure 5 shows the effect of the feed composition on the separation factor ( $\alpha_p^{\text{TCE}}$ ) in TCE-water mixtures for modified membrane containing various plasticizers. At a higher feed composition, the  $\alpha_p^{\text{TCE}}$  has more a better value because TCE molecules occupy polymer sites, constituting a blocking system for water molecules. It is considered that the solubility was dominant in the separation. The  $\alpha_p^{\text{TCE}}$  has a maximum at about 0.08wt% feed composition, but is reduced afterward. It anticipated that the condensation and solubility selectivities for TCE occurred at higher feed composition, so that the  $\alpha_p^{\text{TCE}}$  increased with increasing feed composition. The difference between TCE and water flux increased with increased feed composition, resulting in an increase in

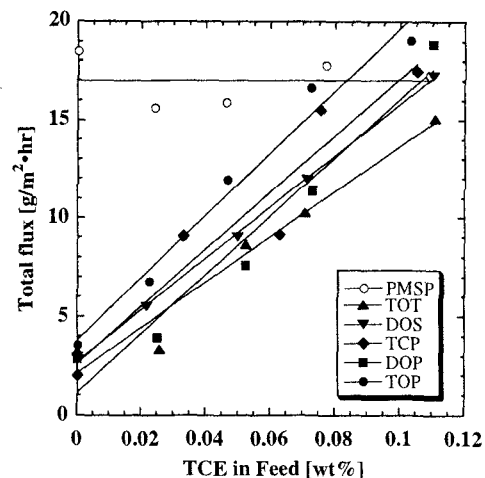


Figure 4. Effect of the feed composition on the total flux in TCE-water mixtures through PMSP and PMSP membranes containing various plasticizers (52±2wt%) at 25°C.

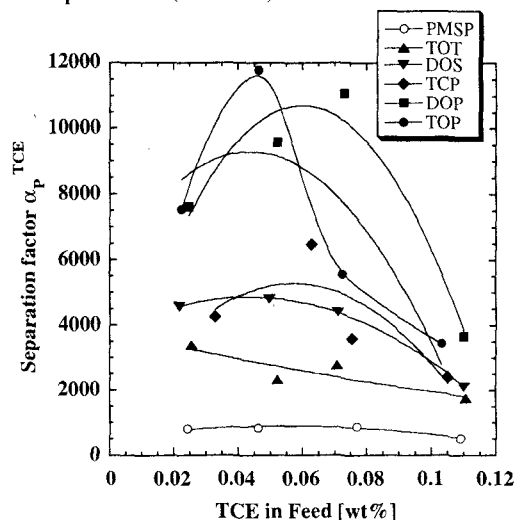


Figure 5. Effect of the feed composition on the separation factor in TCE-water mixtures through PMSP and PMSP membranes containing various plasticizers (52±2wt%) at 25°C.

the  $\alpha_p^{\text{TCE}}$ . Nevertheless, when the feed composition increased to about 0.08wt%, the  $\alpha_p^{\text{TCE}}$  decreased because of swelling as mention above. Namely, both TCE and water molecules (particularly water) permeated with swelling and led to the decrease in  $\alpha_p^{\text{TCE}}$ .

The  $\alpha_p^{\text{TCE}}$  was, at 0.05wt% feed composition, PMSP containing TOP and at 0.08wt% feed composition PMSP containing DOP have the highest separation factor ( $\alpha_p^{\text{TCE}}$ ); about 12,000 in all modified membranes. DOP and TOP have an affinity for TCE in particular and on the other side inhibited the permeation of water. It is considered that the difference in pervaporation results among the plasticizers being caused by the chemical properties of each plasticizer, for example, its solubility in water.

### 3.4 Results of sorption properties measurements and investigation of permeation mechanism

Swelling sorption properties of PMSP and modified PMSP membranes for 0.08wt% and 0.05wt% TCE

**Table 2.** Swelling sorption behavior of PMSP and modified PMSP membranes for TCE-water mixtures at 25°C (feed composition: 0.08, 0.05wt%)

Membrane	Degree of swelling (wt%) <sup>a)</sup>						TCE in membrane (wt%)		Separation factor <sup>b)</sup>			
	0.08wt%			0.05wt%			0.08wt%	0.05wt%	0.08wt%		0.05wt%	
	Total	TCE	Water	Total	TCE	Water			$\alpha_s^{TCE}$	$\alpha_p^{TCE}$	$\alpha_s^{TCE}$	$\alpha_p^{TCE}$
PMSP	33.6	13.3	20.3	27.0	9.0	18.0	39.5	33.4	870	880	1000	830
DOP/PMSP(14.4wt%)	24.4	16.5	7.9	19.1	10.2	8.9	67.6	53.3	2780	2890	2280	3800
DOP/PMSP(25.3wt%)	19.5	13.6	5.9	16.4	8.6	7.8	69.7	53.5	3070	7140	2300	4250
DOP/PMSP(36.7wt%)	18.4	13.2	5.2	14.0	7.9	6.1	71.8	56.3	3390	8530	2580	5300
DOP/PMSP(49.3wt%)	14.3	11.3	3.0	10.1	6.2	3.9	79.0	61.0	5010	11180	3130	9590
TOT/PMSP(52.5wt%)	15.6	10.2	5.4	11.4	6.2	5.2	65.7	54.5	2550	2770	2390	2330
DOS/PMSP(48.7wt%)	13.6	10.5	2.9	10.0	5.5	4.5	76.9	55.2	4440	4420	2460	4820
TCP/PMSP(54.5wt%)	14.6	10.2	4.4	8.6	4.9	3.7	69.9	56.7	3090	3600	2620	6490
TOP/PMSP(53.2wt%)	13.7	10.7	3.0	9.0	6.0	3.0	78.1	66.2	4750	5560	3910	11780

a)  $\{(W_s - W_d)/W_d\} \times 100$ ;  $W_s, W_d$ : weight of membrane, swollen and dry

b) Separation factor  $(\alpha_s^{TCE}) = \frac{Y^{TCE}/Y^{water}}{X^{TCE}/X^{water}}$  Separation factor  $(\alpha_p^{TCE}) = \frac{Y^{TCE}/Y^{water}}{X^{TCE}/X^{water}}$

$Y^{TCE}/Y^{water}$ : weight ratio of TCE to water in the membrane

$X^{TCE}/X^{water}$ : weight ratio of TCE to water in the feed

$Y^{TCE}/Y^{water}$ : weight ratio of TCE to water in the permeate

$X^{TCE}/X^{water}$ : weight ratio of TCE to water in the feed

solutions in water at 25°C are shown in Table 2. At both TCE compositions, the weight fraction of water sorbed into the membrane significantly decreased with increasing DOP content while that of TCE slightly increased up to a DOP content (25.3wt%) but reduced thereafter, indicating that the matrices composed of PMSP and DOP are much more hydrophobic than those composed of only PMSP. The TCE degree of swelling increased up to a DOP content of 25.3wt% in spite of DOP packing, suggesting that DOP has a greater affinity for TCE than the PMSP membrane alone. Moreover, at high concentration this tendency was remarkable. Thus, it can be anticipated that sorption of water into the membrane is inhibited by an increase in feed composition.

The separation factor ( $\alpha_s^{TCE}$ ) of the TCE-water mixtures increased with increasing DOP content. These results lead to the increase in solubility selectivities ( $\alpha_s^{TCE}$ ) for TCE. On the contrary, the solubility of water was indicated to be significantly decreased. At higher concentration, this tendency was remarkable as was the swelling behavior. Therefore, it is considered that the  $\alpha_p^{TCE}$  increased with increasing DOP content as Figure 3 shows. Moreover, the change in the  $\alpha_p^{TCE}$  corresponded to that in  $\alpha_s^{TCE}$ , indicating that solubility selectivity dominantly affects the PV properties of the modified membrane as well as the PMSP membrane for TCE-water mixtures. It is thought that the difference in  $\alpha_s^{TCE}$  for each plasticizer was due to its properties, water solubility, etc. The  $\alpha_s^{TCE}$  for a membrane containing DOP (49.3wt%) had the highest value. In addition, the  $\alpha_s^{TCE}$  has a lower value than the  $\alpha_p^{TCE}$  for membranes containing a plasticizer. It is considered that the apparent  $\alpha_D^{TCE} > 1$  has a value. In general, the diffusivity of water is higher than that of TCE in a swollen layer, due to molecular size. Despite these fact, the apparent  $\alpha_D^{TCE} > 1$  has a value suggesting that water clusters in the membrane. Moreover, the  $\alpha_s^{TCE} >$  the apparent  $\alpha_D^{TCE}$  shows that solubility selectivity dominantly affects the PV properties of the modified membrane as well as the PMSP membrane for TCE-water mixtures.

#### 4. CONCLUSIONS

Over the whole range of TCE feed concentration, the weight fraction of water sorbed compared to the TCE sorbed into the membrane significantly decreased with increasing DOP content, indicating that the matrices composed of PMSP and DOP are much more hydrophobic than those composed of only PMSP. These results lead to a decrease in the solubility of water and an increase in solubility selectivities ( $\alpha_s^{TCE}$ ) for TCE. Therefore, the water flux decreased and the separation factor ( $\alpha_p^{TCE}$ ) in TCE-water mixtures increased with increasing DOP content. Moreover, the change in  $\alpha_p^{TCE}$  corresponded to that in  $\alpha_s^{TCE}$ , indicating that solubility selectivity dominantly affects the pervaporation properties of the modified membrane as well as the PMSP membrane for TCE-water mixtures. The membrane containing other various plasticizers has approximately the same tendency, the difference in pervaporation results among the plasticizers caused by the chemical properties of each plasticizer, for example, its solubility in water. As a result, the PMSP membrane containing DOP (49.3wt%) and TOP (53.2wt%) exhibited a high permselectivity,  $\alpha_p^{TCE} = 12,000$ , which was a 15-fold value, while maintaining a high flux of TCE-water mixtures, compared to PMSP alone. Effective separation in this study was carried out in TCE-water mixtures by pervaporation, and a useful membrane was obtained.

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