

# Pervaporation Separation of Phenol-Water Mixtures by Using Silicone Membranes

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## 실리콘 막을 이용한 페놀-물 혼합물의 투과 증발 분리

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**Abstract:** The pervaporation separation experiments of phenol-water mixtures were carried out by using Type 1 (PDMS : crosslinking agent=1 : 0.25) and Type 2 (PDMS : crosslinking agent=1 : 0.35) silicone rubber membranes at 30, 40 and 50°C. The phenol concentrations in the feed to be separated were 500 ppm to 5 wt%. Type 2 membranes were more efficient than Type 1 membranes for the separation of phenol-water mixtures. The phenol concentration of 70wt% was obtained for 5wt% of phenol concentration in the feed at 30°C and 11wt% phenol concentration observed for 500ppm of phenol concentration in the feed at 30°C by using Type 2 membranes.

**요 약:** 페놀-물 혼합 용액에 대하여 Type 1과 Type 2의 실리콘 막을 이용하여 30, 40, 50°C에서 투과 증발 분리 실험을 수행하였다. 이때 공급 원액의 페놀 농도는 500ppm부터 5wt%이었다. 실험 결과, Type 2막이 Type 1막보다 분리 능력이 더 효율적이었다. 공급원액의 농도가 5wt%와 500ppm일 때, Type 2막을 이용하여 투과액의 페놀 농도가 각각 70wt%, 11wt%의 양호한 결과를 얻었다.

## 1. Introduction

In contrast to distillation process which is one of the conventional separation processes in the chemical technologies, the pervaporation processes may be capable of separating the more volatile or the less volatile organic components from the feed liquid mixtures including azeotropic mixtures.

The separations of phenol-water mixtures have not been extensively studied by using the polymeric membranes. The present researches are more con-

centrated on separating the phenol solutions by using the liquid membranes[1-4]. However, there are some difficulties in liquid membrane separation processes, ( i ) choice of the liquid membrane material, ( ii ) stability of the liquid membrane material, ( iii ) this process is not commercialized yet, etc.

Depending on the membrane materials used, the pervaporation of aqueous-organic binary mixtures may be directed at the selective removal of water or at the selective removal of organic compound in the feed. In the latter case, the most widely used mem-

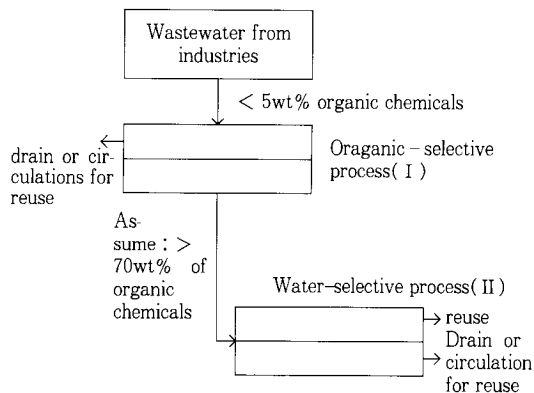


Fig. 1. Schematic diagram of basic concepts in this study.

brane materials are poly (dimethylsiloxane) (PDMS), its copolymer, copolymers of styrene and styrene derivatives, polyether-*block*-polyamides (PEBA), etc[5-7]. Pervaporation of 5wt% phenol solution using PEBA membranes at 40°C showed 75 of enrichment factor ( $\beta$ , defined as phenol mass concentration at permeate/phenol mass concentration at feed), yielding a permeate of 80wt% phenol[5-7]. To produce the pure water from the wastewater containing the organic components, the following concepts could be introduced. This is well illustrated in Fig. 1. As can be seen, the wastewater from the industries containing the phenol compound could be concentrated at the 1st stage of organic-selective process, and then this concentrated phenol solutions flow into the 2nd stage of the water-selective process[8]. The pure water at the down compartment of this stage could be separated and circulated for reuse, and also the purified organics at the above would be reused as solvent.

In this paper, the 1st stage, the organic-selective process, was investigated in more detail.

## 2. Experimental

### 2.1. Materials

Poly(dimethylsiloxane) (PDMS) was supplied by Haeryong Silicone Co. in Korea with crosslinking agent and catalyst. Analytical grade of *n*-hexane as a solvent for PDMS polymers was used and pur-

Table 1. The Compositions of the Casting Solutions for the PDMS Membrane Preparation in Weight

	PDMS	X-linking agents	Catalyst	Solvent
Type 1	1	0.25	0.02	1.5
Type 2	1	0.35	0.02	1.5

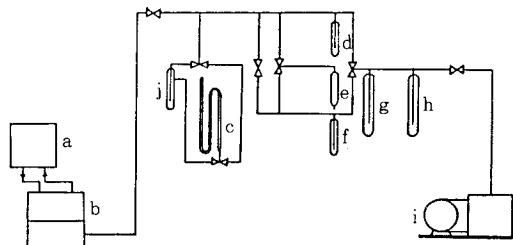
chased from Aldrich Chemical Co. The phenol was analytical grade from Junsei Chemical Co. Used water was the ultra-pure water produced from MPI system.

### 2.2. Membrane Preparation

PDMS membrane were prepared by dissolving preweighed quantities of PDMS, crosslinking agent, catalyst, and solvent together, and the solution stirred at room temperature for 5 hrs. The weighed compositions of the PDMS solution are illustrated in Table 1. The homogeneous solutions were cast onto a teflon plate using a Gardner knife with predetermined drawdown thickness. Then the wet membranes were allowed for solvent to be evaporated in the air and the crosslinking reaction was assumed to be progressed completely during the drying time. The dry membranes were then peeled off, and stored in solutions to be separated for further use. The thickness of the resulting membranes, Type 1 and Type 2, were 200 to 230  $\mu\text{m}$ .

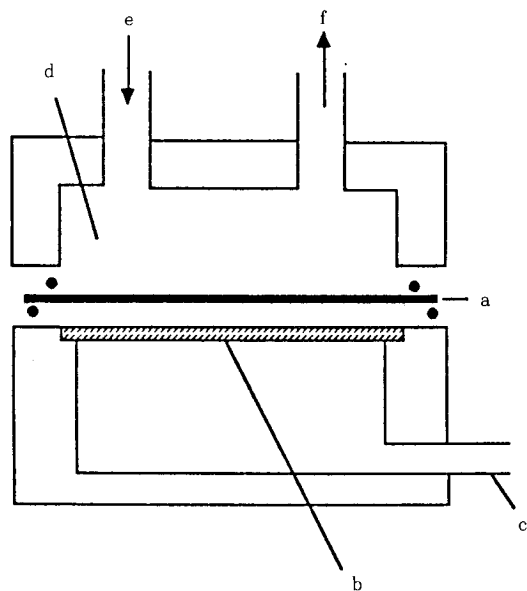
### 2.3. Transport Studies

The apparatus used in this study is illustrated in Fig. 2. The permeation cell (Fig. 3) purchased from the Millipore Corp. was constructed of two stainless steel disks with the filter diameter 4.7cm (effective membrane area : 9.7 $\text{cm}^2$ ). The bottom disk was fitted with a porous steel plate. The membrane was already put in the solution to be separated, was placed on a filter paper on the lower disk and then both disks were bolted tightly together. To maintain the operating temperature, the feed was put on the heater and this heater was connected to the temperature controller. And the feed mixture was continu-



- a. Temperature controlled feed tank  
 b. Permeation cell (Millipore Corp.)  
 c. Vacuum manometer  
 d, f. Cold traps for collecting samples  
 e. Drying tube      g, h. Cold traps  
 i. Vacuum pump      j. Trap

Fig. 2. Schematic diagram of pervaporation apparatus used in this study.



- a. Membrane      e. Inlet tube of feed liquid mixture  
 b. Sintered steel plate      f. Outlet tube of feed liquid mixture  
 c. Stainless steel vapor removal tube  
 d. Liquid reservoir

Fig. 3. Configuration of the membrane cell used in this study.

ously circulated to the membrane cell using the chemical-resistant circulation pump. The two vacuum lines including the small cold traps (the center part of the apparatus) were used for continuous operations. The cold traps were immersed in liquid nitrogen on the vacuum side of the equipment to collect and condense the vapors. The steady-state flux was obtained by weighing the trapped permeate, i. e., the flux data could be determined after 4hrs. operation. The necessary vacuum in the down-stream side during the operations was maintained by a vacuum pump. The vacuum was always kept below 4 mmHg.

The composition analysis of the permeate was done by using the High Pressure Liquid Chromatography (HPLC Waters 501) and U. V. spectrophotometer (Shimadzu Co., Model UV-240). A calibration curve of water-phenol mixtures was prepared using known quantities of the two compounds.

The separation experiments of phenol-water mixtures were carried out by using silicone rubber membranes with different crosslinking degrees, i. e., the ratio of crosslinking agent and PDMS, 0.25 (Type 1) and 0.35 (Type 2) at 30, 40 and 50°C. The phenol concentrations in the feed to be separated were 500, 1000, 5000ppm, 1, 3 and to 5wt%.

### 3. Results and Discussion

The separation factor,  $\alpha$ , calculated in the present work is defined as

$$\alpha_{p/w} = (Y_{\text{phenol}}/Y_{\text{water}})/(X_{\text{phenol}}/X_{\text{water}})$$

where Y's are the weight fractions of permeate and X's are the weight fractions of the feed, respectively.

Fig. 4 shows the permeabilities of the feed mixture with the phenol concentration of 1 to 5wt% in the feed by using Type 1 membranes at various operating temperatures. As expected, the permeabilities increase with increasing the operating temperatures. And the permeabilities decrease with increasing the phenol concentrations in the feed mixtures. According to the the sorption and the diffu-

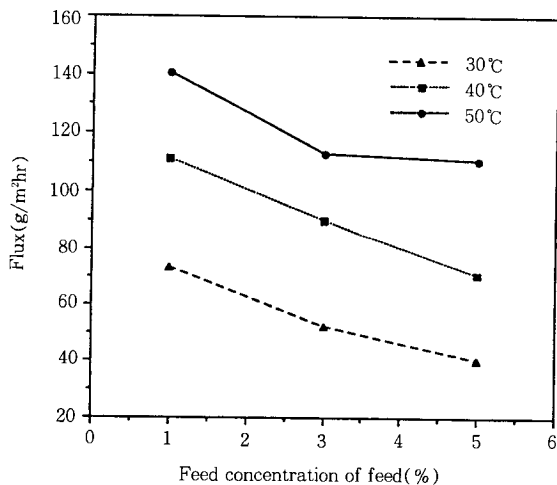


Fig. 4. Permeabilities by Type 1 membranes at 30, 40, 50°C for 1, 3, 5wt% phenol concentration in feed mixtures.

sion studies by Watson and Payne[5], the sorptions of organic chemicals (*n*-alcohols) and water in the silicone rubber membranes showed 0.016(methanol)~0.130(butanol) g/g and 0.0026 g/g for water, respectively, and the diffusion coefficients denoted  $99.0 \times 10^{-10} \text{m}^2/\text{sec}$  for water and  $10.0 \times 10^{-10}$  (methanol)~ $2.5 \times 10^{-10}$  (decanol) $\text{m}^2/\text{sec}$  by a factor of 4. And also they reported that the permeation flux would be determined by the dominance of solubility rather than the diffusivity. Therefore, the organic flux is high with increasing organic concentration in the feed, while the water flux is typically restricted. This may be the apparent explanation for the flux decrease with increasing the phenol concentration in the feed. However, this phenomena would be more evidently described after the studies of the interactions between the permeants and the polymer, and sorption and diffusion studies as a function of organic concentration.

The organic solubility in the silicone membranes may increase with increasing the organic concentration in the feed because of the affinity between the organic component and the polymer. Fig. 7 illustrates the ratio of individual permeation flux of phenol ( $J_p$ ) and individual permeation flux of water ( $J_w$ )

defined as (total permeation rate of mixture)  $\times$  (weight fractions of phenol and water in the permeate), respectively. And Fig 7(b) shows the individual permeabilities of phenol and water at 50°C, respectively.  $J_w$ 's decrease with increasing the phenol concentration at 50°C, while  $J_p$ 's increase as illustrated in Fig. 7(b).

However, this tendency occurred reversely at 30°C through the medium stage at 40°C. The reason for showing this erratic results could be due to the difference of the hydrogen bonding forces between the mixture to be separated and the organophilic polymer. The phenol permeability is hindered by the strong hydrogen bonding force at the low operating temperature, while the phenol permeability can increase since the hydrogen bonding force is weaker at higher operating temperature. This figures show that the decrease degree of  $J_w$ 's with increasing the phenol concentration in the feed is more severe than the decrease or increase degree of  $J_p$ 's at each operating temperature. This still shows the increasing tendency of the ratio of  $J_p$  and  $J_w$  at each operating temperature. The difference between the  $J_p$  and the  $J_w$  at low temperature is not larger than the difference at high temperature, in other words, the ratio,  $J_p/J_w$ , decrease with the operating temperatures. This might be due to the solubility effect on the operating temperatures as described previously. However, the descriptions in the above would be cleared more after the transport phenomena studies.

Fig. 5 shows the separation factors for 1 to 5wt% phenol concentrations in the feed at the same operating temperatures. The separation factors decrease with increasing the phenol concentration and also the operating temperatures. This tendency shows a good agreement with the results of the water-*n*-alcohols-silicone rubber membrane systems proposed by Watson and Payne[5]. The separation factor of ca. 50 can be observed at 30°C and 1wt% phenol concentration in the feed.

Fig. 6 illustrates the phenol concentration in permeate. The phenol concentrations of 33, 40 and 44wt% were obtained at 1, 3 and 5wt% phenol in

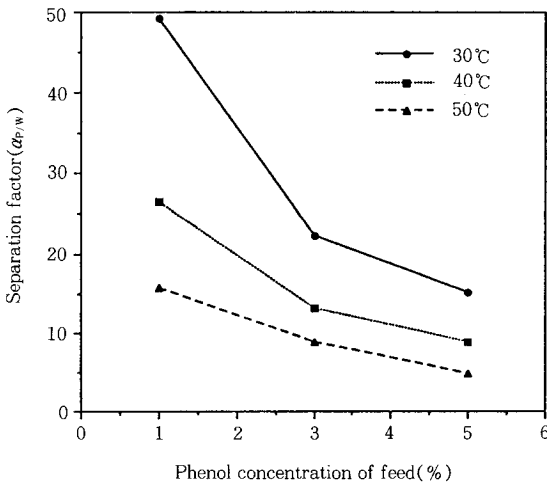
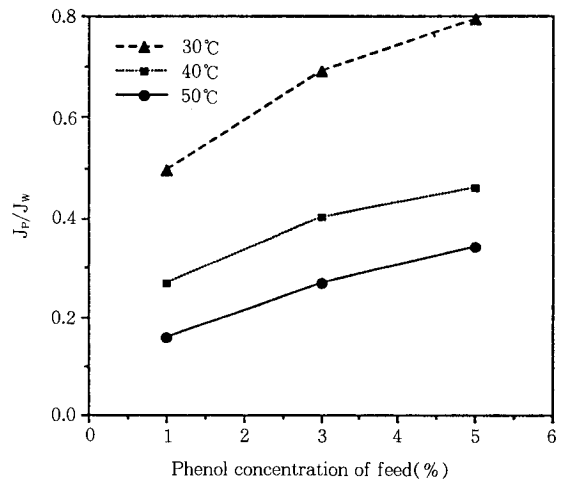


Fig. 5. Separation factors by Type 1 membranes at 30, 40, 50°C for phenol concentrations of 1, 3, 5wt% in feed mixtures.



(a)

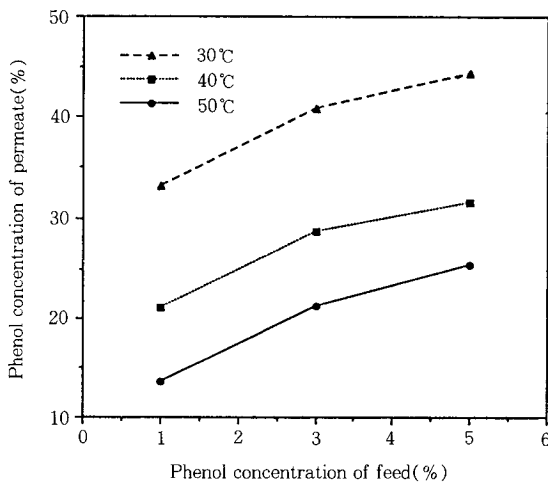
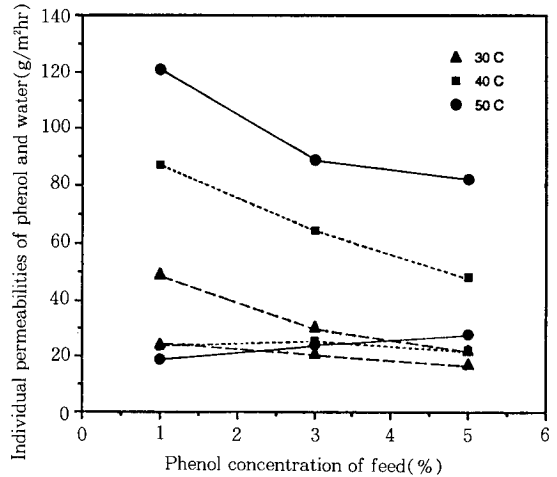


Fig. 6. Phenol concentrations of the permeate by Type 1 membranes at 30, 40, 50°C for phenol concentration of 1, 3, 5wt% in feed mixtures.



(b)

Fig. 7. (a) Ratio of individual permeabilities of phenol ( $J_p$ ) and water ( $J_w$ ) at 30, 40, 50°C for phenol concentration of 1, 3, 5wt% in feed mixtures, (b) The individual permeabilities of phenol and water at each operating temperature ( $J_w$  : above three figures,  $J_p$  : below three figures).

the feed, respectively, by using Type 1 membranes at 30°C.

It has been tried to change the crosslinking density. The control of the crosslinking density could arise from the chemical and physical changes of the polymer, i. e., ( i ) changes of the chemical compo-

nent in the polymer depending on the used crosslinking agent, ( ii ) changes of the polymer network; in this case the resulting selectivity depends on the sizes of the mixture to be separated[9]. Fig.

8 shows the permeabilities for the phenol concentration from 500ppm to 5wt% in the feed by using Type 2 membranes. In general, it could be acceptable that more addition of crosslinking agents to the polymer may result in increasing the crosslinking density. Therefore, Type 2 membranes exhibits less polymer chain mobility and have less free volume than Type 1 membranes. As a result, the permeabilities are much less than those by Type 1 membranes.

Fig. 9 and 10 illustrate the separation factors and the phenol concentration in the permeate of Type 2 membranes, respectively. The separation factors decreased with permeate of Type 2 membranes, respectively. The separation factors decreased with increasing the phenol concentration and also the operating temperatures as shown in Fig. 5. The separation factor of ca. 90 can be observed at 30°C and 1wt% phenol concentration in the feed. And the phenol concentration of 70wt% in permeate was obtained at 5wt% phenol concentration in the feed. This result shows slightly lower value of 80wt% phenol concentration in permeate resulted from the PEBA membranes[6]. However, this result shows much better than the phenol concentration of 44wt% obtained by Type 1 membranes at the same operating conditions. This may result mainly in the changes of the polymer network and the changes of the chemical component in the polymer mentioned previously. Therefore, we have tried to prepare the membranes with higher crosslinking density to obtain higher phenol concentration of 70wt% in the permeate, however, it has been observed that more addition of the crosslinking agent to the PDMS polymer than 0.35 made the PDMS polymer gel-like.

#### 4. Conclusions

The 1st stage of the organic-selective process presented in this paper was investigated in more detail. The separation experiments of phenol-water mixtures were carried out by using silicone rubber

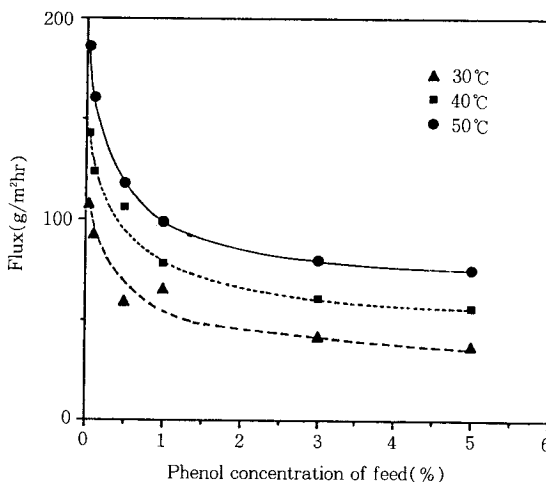


Fig. 8. Permeabilities by Type 2 membranes at at 30, 40, 50°C for phenol concentration of 500ppm to 5wt% in feed mixtures.

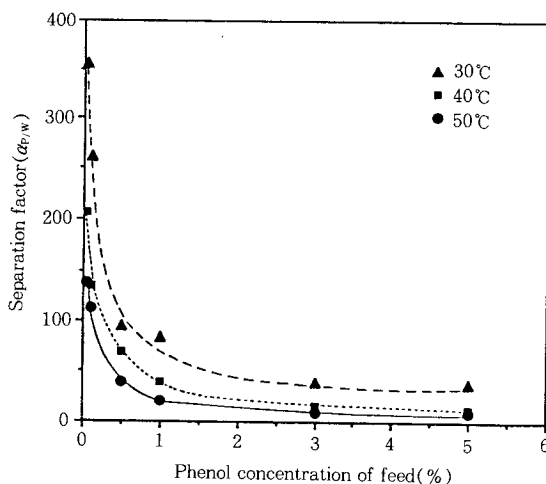


Fig. 9. Separation factors by Type 2 membranes at 30, 40, 50°C for phenol concentration of 500ppm to 5wt% in feed mixtures.

membranes with different crosslinking degrees, i. e., the ratio of crosslinking agent and PDMS, 0.25 (Type 1) and 0.35 (Type 2) at 30, 40 and 50°C. The phenol concentrations in the feed to be separated were ( i ) high concentration (1, 3, 5wt%) ( ii ) low concentration (500, 1000, 5000ppm). Type 2 membranes were more efficient than Type 1 membranes for the separation of phenol-water mixtures.

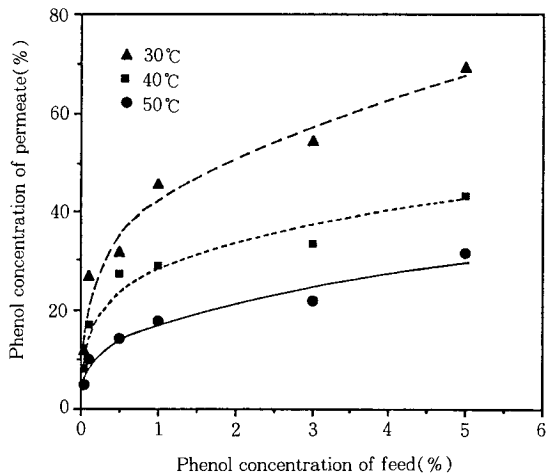


Fig. 10. Phenol concentrations of the permeate by Type 2 membranes at 30, 40, 50°C for phenol concentration of 500ppm to 5wt% in feed mixtures.

The phenol concentration of 70wt% and 11wt% in the permeate were obtained at 30°C and 5wt% of high phenol concentration and 500ppm of low phenol concentration in the feed, respectively. And also, at 5000ppm in the feed, the phenol concentration of 30wt% in the permeate (separation factor = 360) was observed.

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