

# Pervaporation Separation of Binary Organic–Aqueous Liquid Mixtures Using Cross-Linked PVA Membranes.

## II. Phenol–Water Mixtures

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### SYNOPSIS

The pervaporation separation of water–phenol mixtures was carried out using poly(vinyl alcohol) (PVA) cross-linked membranes with low molecular weight poly(acrylic acid) (PAA) at 30, 40, and 50°C. The separation was concentrated on the second stage of the water-selective process at which the phenol concentration could be 80 wt % of phenol. The high separation factor of  $\alpha_{w/p}$ , = 3580 for the PVA/PAA = 80/20 membrane was obtained for the phenol : water = 80 : 20 solution at 30°C. © 1994 John Wiley & Sons, Inc.

### INTRODUCTION

The separation processes of liquid mixtures containing organic chemicals by using polymeric membranes are widely used in industry. The membrane separation processes provide several advantages: (1) easy process design; (2) higher product recovery than in the conventional processes; and (3) low-energy consumptions.

Nowadays, the most widely used membrane separation processes for wastewater treatment are reverse osmosis and ultrafiltration. It was reported that the separation efficiencies of the reverse osmosis process are relatively low in the organic compound<sup>1,2</sup> and could be lower than the pervaporation separation process.<sup>3,4</sup> In the reverse osmosis process, there are several developed membranes for the separation of phenol mixtures.<sup>5,6</sup> Since the separation characteristics of pervaporation in terms of the flux and the separation factors are both theoretically and experimentally better than those of reverse osmosis,

the pervaporation separation technique for the aqueous phenol mixtures was chosen in this study.<sup>3,4</sup>

Also, the investigation was concentrated on the water–phenol system using the pervaporation separation technique because of the relatively wide miscible range compared to the other aromatic derivatives and the practical significance of this system. The water–phenol system is known as being one of the azeotropic mixtures, which has a normal boiling point of 94.5°C at 9.2 wt % of phenol. The miscible phases occurs at somewhat higher than room temperature and its compositions are approximately < 10 wt % phenol and > 70 wt % phenol.<sup>7</sup>

Depending on the membrane material used, the pervaporation of aqueous–organic binary mixtures may be directed at the selective removal of water or at the selective removal of the organic compound in the feed. The pervaporation separation of the organic compound from the binary mixtures containing the organic compound or from the wastewater, in general, requires elastomeric (rubbery) polymers, whereas the glassy (amorphous) polymers preferentially permeate water. In the former case, among the most widely used membrane materials are polydimethylsiloxane (PDMS), its copolymers, copolymers of styrene and styrene derivatives, and polyether block amides (PEBA).<sup>7–11</sup>

Pervaporation of 5 wt % phenol aqueous solution

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using PEBA membranes at 40°C showed an enrichment factor of 75 ( $\beta$ , defined as [phenol mass concentration at permeate/phenol mass concentration at feed]), yielding a permeate of 80 wt % phenol.<sup>7-9</sup> The silicone rubber membranes prepared in our laboratory showed the 70 wt % of phenol in the permeate at the same composition of water : phenol = 95 : 5 and 30°C.<sup>12</sup> Therefore, to produce pure water from the wastewater containing the organic compounds, the following concepts could be introduced: This is illustrated in Figure 1. As can be seen, the industry wastewater containing the phenol compound could be concentrated up to 70–80 wt % phenol at the organic-selective process (first stage), and then these concentrated phenol solutions flow into the water-selective process of the second stage. The pure water at the down compartment of this stage could be produced and circulated for reuse.

In this article, the second-stage, water-selective process was investigated in more detail. The experiments were carried out by using developed cross-linked poly(vinyl alcohol) (PVA) membranes with low molecular weight of poly(acrylic acid) (PAA) for 80 wt % phenol solutions at 30, 40, and 50°C.<sup>13</sup> For the first stage, the silicone rubber membranes were used to concentrate the phenol from the water-phenol mixtures and this will be published separately.<sup>12</sup>

## EXPERIMENTAL

### Materials

Fully hydrolyzed PVA with a molecular weight of 50,000 and PAA with a molecular weight of 2000 (25 wt % in water) were purchased from Showa Chemical Co. and Aldrich Co., respectively. The phenol was analytical grade from Junsei Chemical Co. Used water was the ultrapure water produced from the MPI system.

### Membrane Preparation

Aqueous 10 wt % PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ultrapure water and heating them at 90°C for at least 6 h. Also, aqueous 25 wt % PAA solutions were diluted to 10 wt % solutions. Then, two polymer solutions were mixed together by varying each component composition to form a homogeneous solution for at least 1 day at room temperature. Homogeneous membranes were cast onto a plexiglass plate using a Gardner knife with predetermined drawdown thickness. The membranes were allowed to dry in the air at room temperature, and completely dried membranes were then peeled off. The dried blended membranes were heated in a thermosetted oven for desired reaction times and temperatures. The re-

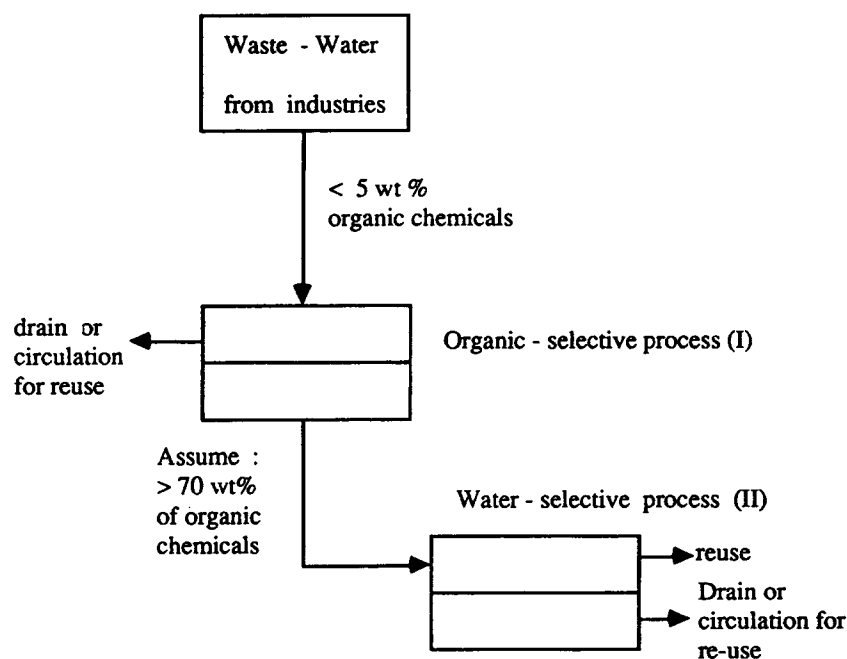
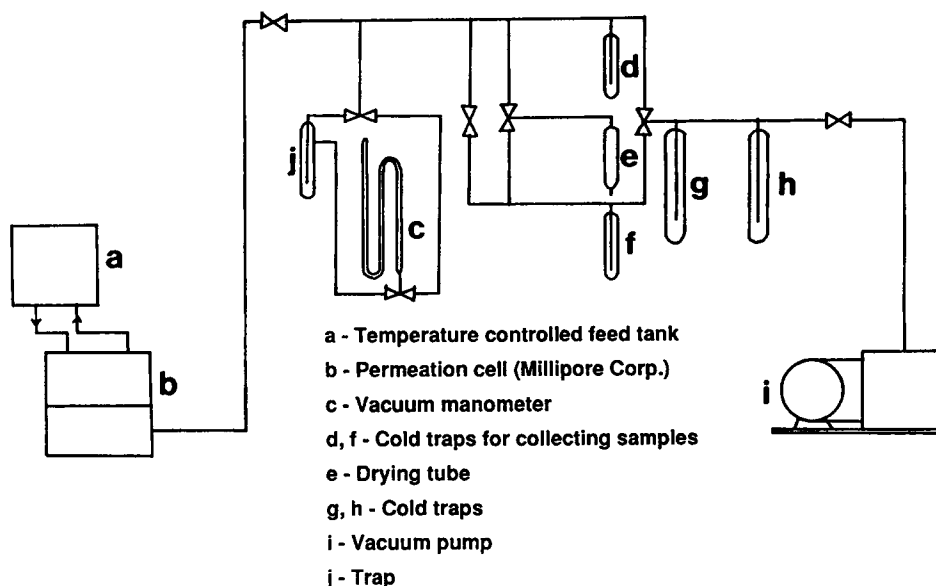


Figure 1 Schematic diagram of basic concepts in this study.



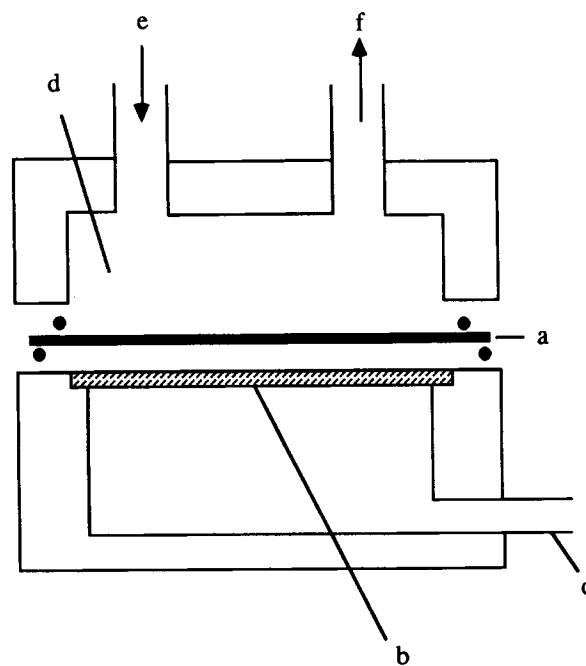
**Figure 2** Schematic diagram of pervaporation apparatus used in this study.

sulting membranes were then stored in solutions to be separated for further use.<sup>13</sup>

### Pervaporation

The apparatus used in this study is illustrated in Figure 2. The permeation cell (Fig. 3) purchased from the Millipore Corp. was constructed of two stainless-steel disks with an effective membrane diameter of 4.7 cm (effective membrane area: 13.8 cm<sup>2</sup>). The bottom disk was fitted with a porous steel plate. The membrane, already put in the solution mixture to be separated, was placed on 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. The feed mixture was then continuously circulated to the membrane cell using the circulator. The cold traps were immersed in liquid nitrogen on the vacuum side of the equipment to collect and condense the vapors. The flux was obtained by weighing the trapped permeate. The necessary vacuum in the downstream side was maintained by a vacuum pump. The vacuum was always kept below 4 mmHg.

The composition analysis of the permeate was done using high-pressure liquid chromatography (HPLC, Waters Co.) and a UV spectrophotometer (Shimadzu Co., Model UV-240). A calibration curve of water-phenol mixtures was prepared using known quantities of the two compounds.



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

**Figure 3** Configuration of the membrane cell used in this study.

## RESULTS AND DISCUSSION

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

$$\alpha = (Y_{\text{water}}/Y_{\text{phenol}})/(X_{\text{water}}/X_{\text{phenol}})$$

where  $Y$  is the weight fraction of the permeate and  $X$  is the weight fraction of the feed.

Figure 4 shows the permeabilities of pure water through the cross-linked PVA membranes varying the cross-linking agents of low molecular weight PAA at 30, 40, and 50°C. As expected, the permeabilities increase with increasing the operating temperatures. Since the  $T_g$  of the wet membranes is much lower than that of the dry membranes,<sup>13</sup> it could be considered that the free volumes in the wetted membranes increase with increasing the operating temperatures, so that the water molecules pass smoothly through the free volumes. Also, the permeabilities decrease with increasing PAA con-

tent; in other words, the flux decreases with increasing the cross-linking portions in the membranes. This tendency could be other evidence that the cross-linking reactions were well progressed and that the cross-linking portion (or cross-linking degree) in the membranes increased with increasing cross-linking agents since  $T_g$  values increased.<sup>14</sup>

Figure 5 shows the permeabilities for phenol:water = 80:20 wt % mixtures at the same temperatures. Unfortunately, the pervaporation experiment for the membrane containing 25 wt % PAA could not be carried out since this membrane was quite brittle, rather than it degrading as in the phenol solution. As can be seen, the permeabilities for the aqueous phenol solution are higher than the pure water permeabilities. This could be the well-known coupling effect in the pervaporation field. In other words, both water and phenol might swell the membrane together, i.e., the swelling degree of both solutions on the membrane could be larger than that of pure water. Therefore, more water molecules can pass

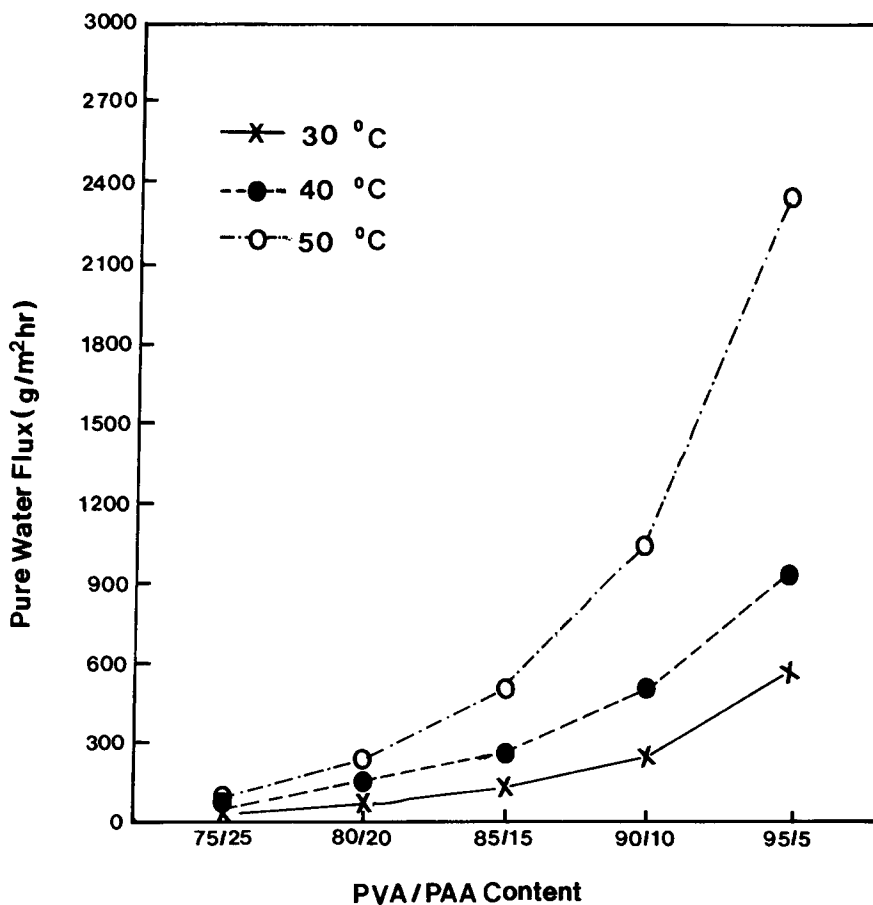
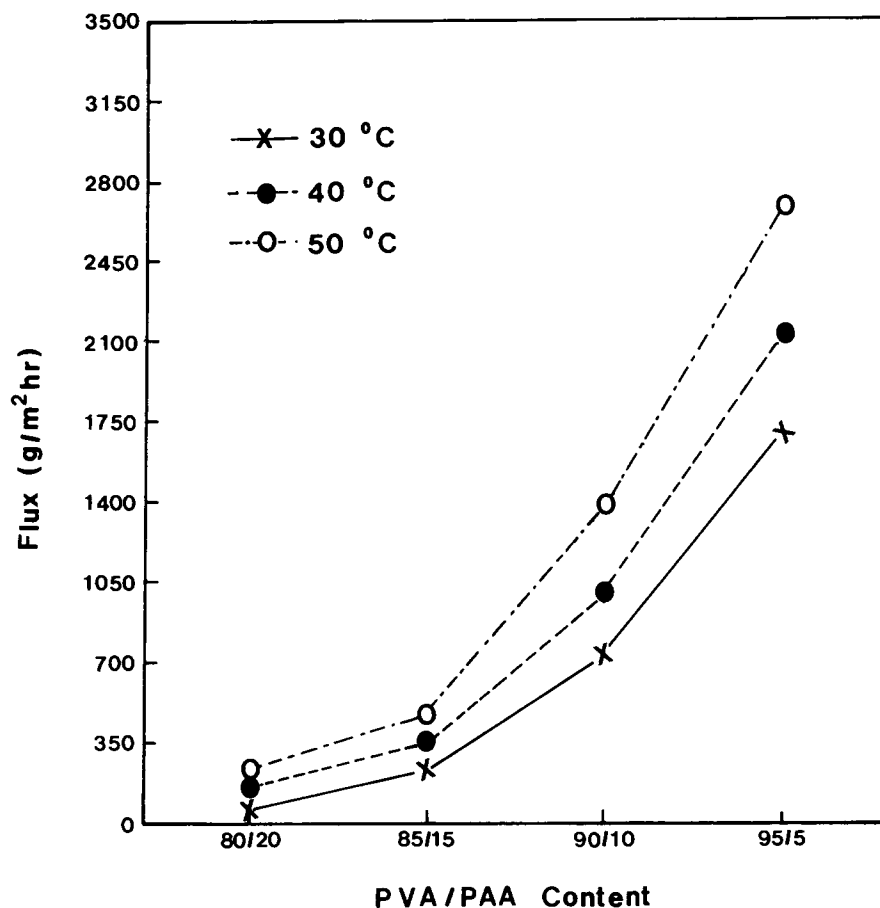


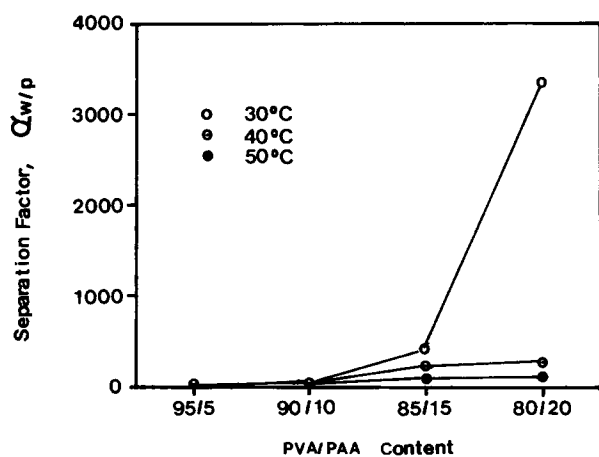
Figure 4 Pure water flux with varying PAA contents at 30, 40, and 50°C.



**Figure 5** Total flux for water : phenol = 20 : 80 mixtures with varying PAA contents at 30, 40, and 50°C.

through the membrane easily during the phenol molecule phase.

The separation factors for the phenol-water so-

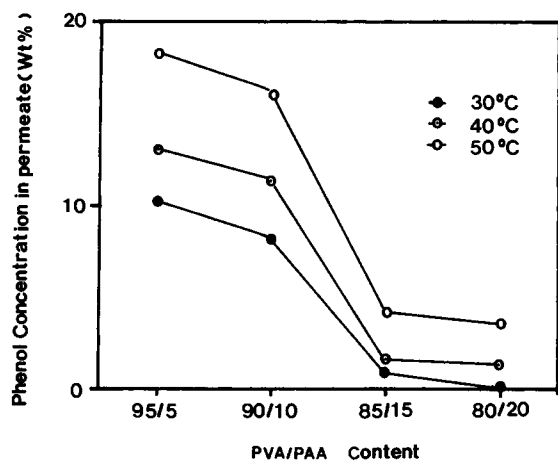


**Figure 6** Separation factor for water : phenol = 20 : 80 mixtures with varying PAA contents at 30, 40, and 50°C.

lution are shown in Figure 6. The separation factors increase with increasing cross-linking agents and decreasing operating temperatures, as expected. The highest separation factor,  $\alpha_{w/p}$ , of 3580 for the PVA/PAA = 80/20 membrane was obtained for the phenol : water = 80 : 20 solution at 30°C. Figure 7 shows the phenol concentrations in permeate with varying PAA contents at 30, 40, and 50°C.

## CONCLUSIONS

The pervaporation separation of phenol-water mixtures was carried out using cross-linked PVA membranes with low molecular weight PAA. The resulting PVA membranes were quite resistant to the phenol aqueous solution during the experiment. The separation results were consistent with previous studies of cross-linked PVA membrane preparation. The highest separation factor,  $\alpha_{w/p}$ , of 3580 for the



**Figure 7** Phenol concentration in permeate for water : phenol = 20 : 80 mixtures with varying PAA contents at 30, 40, and 50°C.

PVA/PAA = 80/20 membrane was obtained for the phenol : water = 80 : 20 solution at 30°C.

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