

A CHARACTERIZATION OF PDMS PERVAPORATION MEMBRANES FOR THE REMOVAL OF TRACE ORGANIC FROM WATER

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Abstract – A new silicone pervaporation membrane for the removal of one of trace organics, 1,2-dichloroethane from water has been developed using polydimethylsiloxane (PDMS) and oligomeric silylstyrene as a crosslinking agent of PDMS. Optimal conditions for fabricating the best membrane were determined from swelling measurements and pervaporation experiments and then the membrane was characterized at different membrane thickness and operating conditions. In the pervaporation separation of 55-70 ppm of 1,2-dichloroethane aqueous mixtures, the developed membrane has flux of 2.5-330 g/(m²·h) and selectivity of 230-1750 depending on membrane thickness, permeate pressure and operating temperature. Water permeation through thin membrane was found to be subjected to significant desorption resistance, while the desorption resistance and thermodynamic factors as well as the concentration polarization of the organic at the boundary layer in feed can affect the organic permeation, depending on membrane thickness. Selectivity change with permeate pressure depends on membrane thickness: at small membrane thickness range, selectivity increases with permeate pressure and at large thickness region it decreases. From the Arrhenius plots of each component fluxes, the permeation activation energies were determined. Through an analysis of the permeation activation energies of each components, the desorption resistance as well as the effects of the thermodynamic factors on permeation was qualitatively characterized.

Key words: Pervaporation, PDMS Membrane, Swelling Measurement, Trace Organic

INTRODUCTION

In recent years, the removal of organic components from water at low concentration level by pervaporation has been a developing field of interest, especially, in recycling processes as well as in environmental and biotechnological applications. Pervaporation is very attractive in that polluting compounds or organic compounds are selectively removed from the feed, and furthermore this membrane process can be integrated into existing other process to enhance a separation efficiency: when a large volume of dilute organic aqueous stream has to be purified by the removal of organic solvents, the pervaporation step can be part of a large hybrid process by which the bulk of the solvent is removed by pervaporation. Usually pervaporation process is most expressed by solution-diffusion mechanism, that is, the separation and permeation of a liquid mixture can be governed by both selective sorption and diffusion of a component. Thus the permeation rate of each component is proportional to the product of solubility and diffusivity of each component of the liquid mixture to be separated. In selecting a membrane material, since separation can be obtained by different transport rates of permeants through a membrane, which is related to both different solubility and diffusivity, the physico-chemical interaction of the membrane material with permeating molecules should be taken into account in terms of their solubilities and diffusivities in membrane. Elastomeric organophilic membranes which preferentially permeate organic

compounds but retain water are widely used to remove organic compounds from water. The most commonly used polymer is polydimethylsiloxane (PDMS) or silicone rubber. However PDMS has poor film-forming property and mechanical strength. These properties have been improved by using crosslinked PDMS [Takegami et al., 1992], block or graft PDMS with a polymer having excellent film-forming and mechanical properties [Ward et al., 1976; Okamoto et al., 1987]. Polytrimethylsilylpropion (PTMSP) and modified PTMSP membranes have been developed [Ward et al., 1976]. In these membranes, selectivities and permeabilities were improved but they were decreased with time because of the conformational change and crystallization of the polymer resulting in more dense and non-permeable structure. Nijhuis et al. [1993] have prepared a wide range of homogeneous elastomeric membranes using dicumyl peroxide as a general crosslinking agent to study the solution-diffusion phenomena in the removal of volatile organic components from aqueous solution: nitril butadiene rubber (NBR) and ethylene-propylene terpolymer (EPDM) showed extremely high pervaporation selectivities but the organic fluxes of these rubbers were lower than that of PDMS. Separation of a dilute organic aqueous solution is governed by the chemical nature of the permeating species and the membrane material, the morphology of the membrane, and the process operation condition.

In this study, a crosslinked silicone pervaporation membrane for the removal of chlorohydrocarbon from water has been developed using a new oligomeric silylstyrene [Brook et al., 1989] which had been prepared from phenylacetylene in the presence of a catalyst. The oligomer was used as the crosslink-

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ing agent of PDMS. The oligomer has pendent chlorine groups as a reactive site which can react with hydroxyl groups in PDMS to produce crosslinked structure. Control of the concentration of oligomer and fabrication conditions determines the permeation properties of the resulting membrane. The swelling ratio (or solubility of the resulting membrane in dichloroethane) was employed as a measure of the nature of the rubber and the suitability of the polymer as a membrane material. Using appropriate techniques, these rubbers have been fabricated into homogeneous membrane and composite membranes on a polysulfone (PS) support. Pervaporation experiments on membranes fabricated with optimal coating solution were performed at different operating conditions to discuss the effects of the operating conditions and membrane thickness on the pervaporation performance.

EXPERIMENTAL

1. Materials

Silanol terminated polydimethylsiloxane (PDMS) with 1800 of m.w. and hexa-methyldisilazane treated silica with 0.16 μm of average particle size were obtained from Huls Petrach Systems, PA, USA. Dibutyltin dilaurate was from Aldrich Chemical Co. Inc. The new oligomeric silylstyrene was synthesized by our group. The basic chemistry of the oligomer was published [Brook et al., 1989]. All other chemicals of reagent grade were used without further purification.

2. Membrane Preparation

Crosslinked silicone membranes were prepared by condensation reaction between the hydroxyl groups in PDMS and chlorine groups in various functionalized silylstyrene oligomers. A silica treated with hexamethyl disilazane was used as a reinforcement to enhance the mechanical strength of the polymer and a catalyst, dibutyltin dilaurate, was added to accelerate the crosslinking reaction. Two types of membrane configuration have been made with this rubber, homogeneous membrane made of the rubber alone and composite membranes with the rubber coated into the PS support membrane. In the both membrane fabrications, membrane thickness was controlled by the concentration and amount of the coating solution introduced on the known coating area. Scanning electron microscopy (SEM) confirmed that this method could provide a good control of membrane coating thickness.

2-1. Composite Membrane Fabrication

The basic polysulfone (PS) ultrafiltration membrane was used as a support layer. The PS support membrane was allowed to soak in propanol for 2 days to remove glycerine inside and then dried. The dried PS support was subsequently pretreated with 1.5 wt% of PDMS/oligomer/hexane solution by dipping for 5 hours and then reacted at 110°C overnight after drying. The purpose of the pretreatment with the dilute solution is to enhance a wetting and bonding between the support and coated silicone rubber of top layer in a subsequent coating step. The pretreated membrane was embedded between two aluminium guide rings which have 40 cm^2 of inside coating area. A certain composition of coating solution, PDMS/oligomer/silica/dibutyltin dilaurate/n-hexane, was introduced onto the dense surface of the PS support membrane restricted by the rings. After

evaporating the solvent, n-hexane, the coated membrane was placed in a heating oven for 20 hours at 110°C.

2-2. Homogeneous Membrane Fabrication

A certain composition of casting solution was poured into a plastic petri dish of which coating area was known and then allowed to dry in a fume hood. The dry film was transferred from the petri dish to a PS membrane for further reaction at 110°C for 20 hours. After reaction, the homogeneous membrane was peeled from the PS membrane.

3. Swelling Measurements

For swelling measurement, homogeneous membranes which were considered as an isotropic material were used and dichloroethane which is the solute of a pervaporation feed mixture in this study was used as a solvent. The homogeneous membranes were cut into a shape of slab with dimension of 10×50-80 (mm). The slab soaked in the solvent for 2 days for an equilibrium swelling. The swelling slab was taken out and put on a paper after equilibrium swelling and then both ends of the slab were marked with a pen as quickly as possible and the distance (L) between the marks was measured with Vernier Caliper with an accuracy of $\pm 10 \mu\text{m}$. After drying, the length (L_0) the dry slab were checked. The solubility of the solvent in the swollen membrane, ϕ , was calculated from [8]

$$\phi = \frac{R_L^3 - 1}{R_L^3}, \quad \left(R_L = \frac{L}{L_0} \right) \quad (1)$$

4. Pervaporation

A schematic automated pervaporation apparatus used in this study is illustrated in Fig. 1. The automated apparatus is designed and built that can control pervaporation process and log experimental data on an unsupervised basis. The software used to interface the computer with the hardware is a process control program called GENESIS (ICONICS Inc., MA, USA). The dot lines in Fig. 1 present the configuration of connections between the computer and units. The pervaporation membrane cell is made of a stainless steel. A feed mixture enters the cell through the centre opening, flows radially through the thin channel and leaves the cell through the side opening, which allows relatively high fluid velocity parallel to a membrane surface. The effective membrane area is 31.7 cm^2 . The feed mixture temperature is controlled by the water bath which is able to heat or cool the feed. The feed mixture from the feed tank having a capacity of 8 liter is circulated through the membrane cell. The permeate pressure is controlled by a PID pressure controller. By on-line gas chromatography (GC) analysis, the compositions of both feed mixture and permeate vapour were determined. The gas chromatography is a 5890A HP GC equipped with a 3392A integrator and 2 separated lines A and B for analysis of the permeate vapour and the feed liquid, respectively. Each line is composed of a sample injector actuated by air, a FID detector and a packed column. The column in line A is a 10% Fluorad FC-431 and that in line B is 4 ft long with 2 mm inside diameter having a Porapak P. Nitrogen gas is used as GC carrier gas. Also, the on-line measurements of flux and permeate pressure can be made by using a mass flow meter and a pressure transducer, respectively. Pervaporation experiments were performed at different operating temperatures and

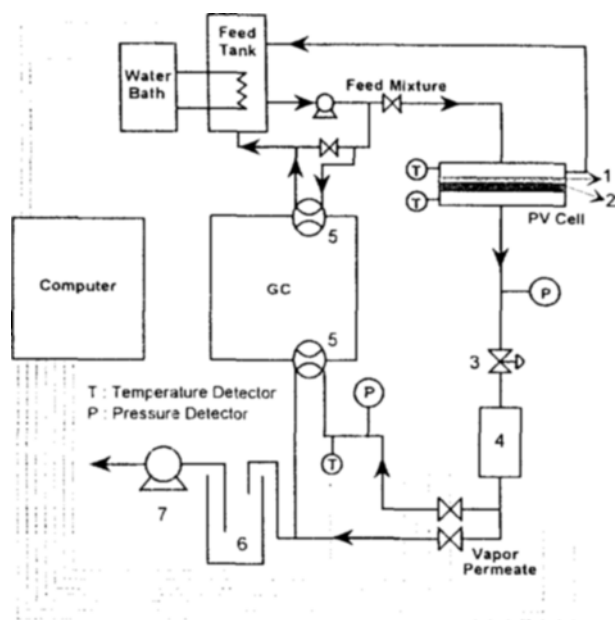


Fig. 1. Schematic presentation of pervaporation apparatus.

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|-------------------------|---------------------|
| 1. Membrane | 5. Sample injectors |
| 2. Sintered metal plate | 6. Cold trap |
| 3. Pressure controller | 7. Vacuum pump |
| 4. Mass flow meter | |

permeate pressures. Feed mixture was dilute 1,2-dichloroethane aqueous solution ranging from 55 to 70 ppm. The hydrodynamic conditions (Reynolds number=5500-6000) of the feed solution flow in the cell were such that the concentration polarization in the liquid mixture could be neglected and the selectivity to organic(1,2-dichloroethane), α , was defined as

$$\alpha = \frac{Y_{\text{organic}}/Y_{\text{water}}}{X_{\text{organic}}/X_{\text{water}}} \quad (2)$$

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

RESULTS AND DISCUSSION

Through the preliminary experiments of swelling and permeation, optimal composition of casting solution to fabricate good membrane in terms of mechanical properties as well as membrane performance was found to be: 0.42 mole fraction of oligomer content, 20 parts of silica content per 100 parts of PDMS and 1.5 parts of catalyst content. According to the result of the swelling measurement of a membrane fabricated with the optimal casting solution, the solubilities of dichloroethane and water in the membrane were 0.335 and 0.076 in volume fraction, respectively. It reflects that the membrane, organophilic material has more affinity toward the organic than water, which could explain why the material was selected, in order to investigate the effects of pervaporation operating conditions on the pervaporation performance of the membrane fabricated with the optimal casting solution, composite and homogeneous membranes with various thicknesses were fabricated. The membrane thickness used in this study ranged from 5 to 60

μm for the top layer of the composite membrane and 100 μm for the homogeneous membrane. Pervaporation experiments with these membranes have been carried out at different operating conditions. Each experiment was repeated once to three times to make sure of the reproducibility of data.

1. Effect of Membrane Thickness

Fig. 2 presents the plots of total flux and selectivity against membrane thickness. This shows a decrease in flux and an increase in selectivity with membrane thickness. In pervaporation, flux is inversely proportional to membrane thickness, assuming that diffusion is the rate-determining step. In Fig. 3, the fluxes of water component at different permeate pressures are presented as a function of reciprocal membrane thickness. The straight lines indicate the variation that would be followed if diffusion is the rate-determining step. In large membrane thickness range, the flux follows the diffusion equation but in small membrane thickness region, more negative deviation of water flux from the straight line is found with decreasing membrane thickness. These observations indicate that there must be other significant resistance in addition to the diffusion resistance contributing to the total permeation. In the permeation of a dilute organic aqueous mixture through an organophilic membrane, total flux consists mainly of water flux so that the concentration polarization of water permeant at the boundary layer adjacent to the upstream membrane interface can be ruled out and the water permeation is independent of the presence of the organic component. Bode et al. [9] found a similar observation that the permeability of pure water through homogeneous polyether block amide (PEBA) decreases with decreasing membrane thickness. They also observed that when membrane is thin, the discrepancy of chemical potential can appear and the permeant concentration is high at the downstream side interface of the membrane while the discrepancy at the upstream side interface of the membrane is negligible, resulting from an equilibrium state across the interface because the exchange fluxes across the upstream side interface is much higher than that across the downstream side interface. From their observations, it can be seen that the other resistance causing the negative deviation of flux from the linearity with decreasing membrane thickness in this study must be from the desorption step at the downstream side interface of the membrane. Two possible resistances in the desorption step can be taken into account;

- Knudsen diffusion in the skin layer (thickness $\approx 3 \mu\text{m}$) of the polysulfone support due to the pore diameter (d) much smaller than the mean free path length (\bar{l}) of a permeant: $\bar{l}/d \gg 1$, possibly causing the reduced flux through the composite membrane.
- Intrinsic downstream interface resistance as described by Bode [Bode et al., 1993].

The former is not likely to be important because it is reported that the skin layer of the PS ultrafiltration support has a porous structure thin enough to have negligible resistance in pervaporation process. The latter can be related to the diffusion of a permeant molecule through the outer layer of the membrane to which the permeant molecules adhere to. It can be significant when membrane thickness is so small that the enhanced net flux could become comparable to the exchange flux across the permeate side interface of membrane, leading to

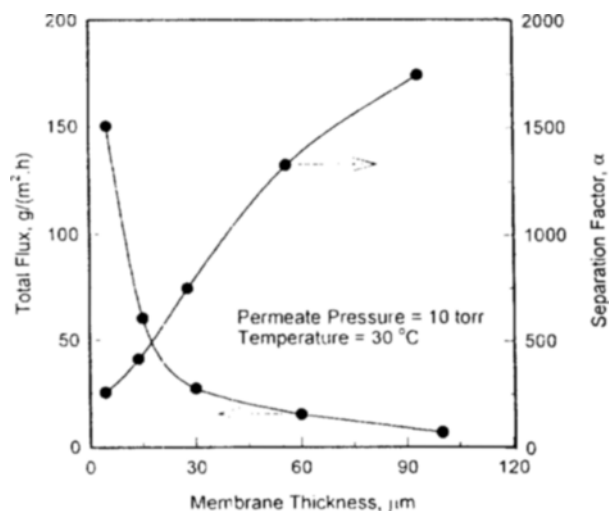


Fig. 2. Plots of total flux and selectivity vs. membrane thickness: operating temperature=30°C, permeate pressure=10 torr.

slow evaporation of the permeant at the membrane surface. Thus, it can be postulated that there is a significant desorption resistance at the downstream side interface of thin membrane. The plots of the fluxes of organic component against inverse membrane thickness at different permeate pressures are shown in Fig. 3. In separation of a dilute aqueous mixture, the organic permeation can be affected significantly by the concentration polarization of the organic component at low Reynolds number of feed flow [Côté and Lipski, 1988]. The Reynolds number (5500-6000) employed in this study is high enough to have little effect on the organic permeation, i.e. small effect of the concentration polarization. Nevertheless, the slope along flux curves in the organic permeation decreases more remarkably with inverse membrane thickness than in the water permeation. This fact can obviously suggest that other factors besides the concentration polarization of the organic component must affect negatively the organic permeation as well. Hence, as in water permeation, the desorption resistance at the downstream interface of the membrane can be taken into account as one of the factors controlling the organic permeation in the light of that the permeant concentration at the downstream interface becomes higher at smaller membrane thickness of high permeate pressure, to such an extent that the evaporation of the permeant can have some contribution to the organic permeation, which will be discussed in next section.

2. Effect of Permeate Pressure

In pressure-controlled pervaporation process, component permeation rates always slow down as permeate pressure is increased while selectivity tends to vary in a more complicated way. Usually, if the faster permeant component is less volatile, such as, in pervaporative dehydration of organic aqueous mixture through a hydrophilic membrane, a selectivity declines as permeate pressure is increased, while in the case of the faster permeant being the more volatile, increasing the permeate pressure may make a selectivity increased as demonstrated by pervaporation of organic aqueous mixture through an organophilic membrane [Neel et al., 1985]. As permeate pressure increases to the saturated vapor pressure of permeants, the permeant con-

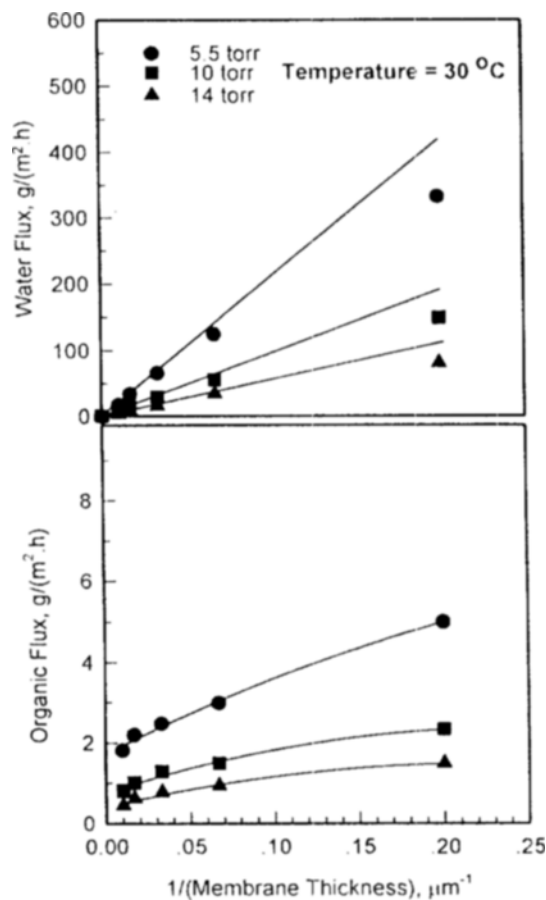


Fig. 3. Component fluxes vs. inverse membrane thickness at different permeate pressure: operating temperature=30°C.

centrations at the permeate-side interface of membrane increases due to slow evaporation of permeants and the desorption resistance becomes significant correspondingly so that the relative volatilities of permeants can affect the separation factor. Fig. 4 shows the effect of permeate pressure on the fluxes of water and organic components. These data show the tendency for both component fluxes to decrease with permeate pressure as the result of decreasing the driving force of permeation. Water flux shows a rapid decrease at low temperature while organic flux is very small and the flux change with permeate pressure is less remarkable. Fig. 5 is the schematic flux profiles of components in which each permeation is schematically depicted to explain the sensitivity of each flux to permeate pressure. The flux change of organic (more volatile component) with permeate pressure is not significant for a given range of permeate pressure regardless of operating temperature, while water flux (less volatile component) is more sensitive to permeate pressure and the sensitivity is more significant at lower temperature. Therefore, as can be seen in Fig. 6, selectivity is little changed with permeate pressure at high temperature and as temperature decreases, selectivity is more remarkably increases with permeate pressure.

3. Effect of Operating Temperature

It can be seen that lower selectivity and higher permeation rate are obtained at higher operating temperature. Usually, the

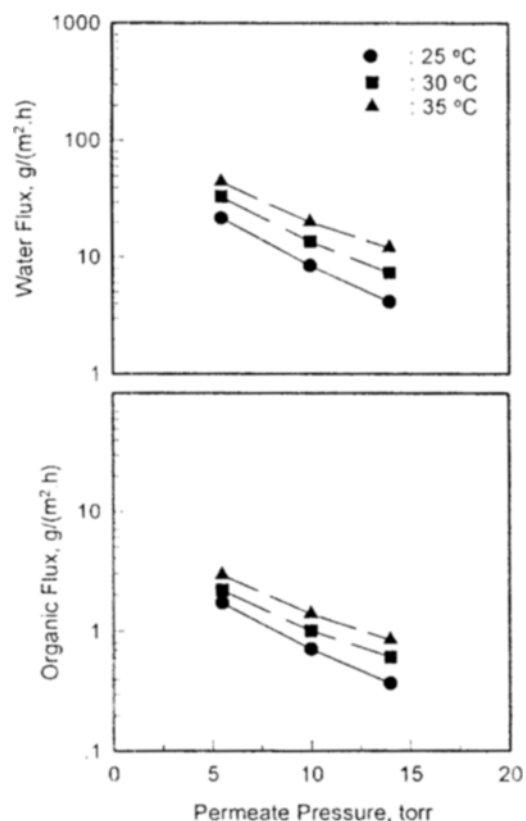


Fig. 4. Plots of component fluxes against permeate pressure at different temperature: membrane thickness=60 μm .

thermal motion of polymer chains in amorphous region randomly produces free volumes. As operating temperature increases, the frequency and amplitude of the polymer chain jumping increase and the resulting free volume become larger. In pervaporation, permeating molecules can diffuse through these free volumes. Thus, when the operating temperature is high, the diffusion rates of associated permeating molecules between different species as well as individual permeating molecules also are high. That is why permeation rate is high and selectivity is low at a high temperature. Flux has an Arrhenius relationship with operating temperature as follows

$$J = A_p \exp\left(\frac{-E_p}{RT}\right) \quad (3)$$

where A_p and E_p are frequency factor and activation energy for permeation, respectively, and T operating temperature. In Arrhenius plots shown in Fig. 7, the slope of each curve stands for the permeation activation energy, E_p . Usually, in a system having diffusion-rate determining step, the activation energy is associated with both interaction between permeant molecules and the plasticization action of the permeants on membrane material. The interaction is a positive factor and the plasticization action is a negative factor on the permeation activation energy. For an example, small activation energy can result from weak interaction between permeant molecules or/and large plasticization action of permeants on membrane material, while large activation energy can be the result of strong interaction

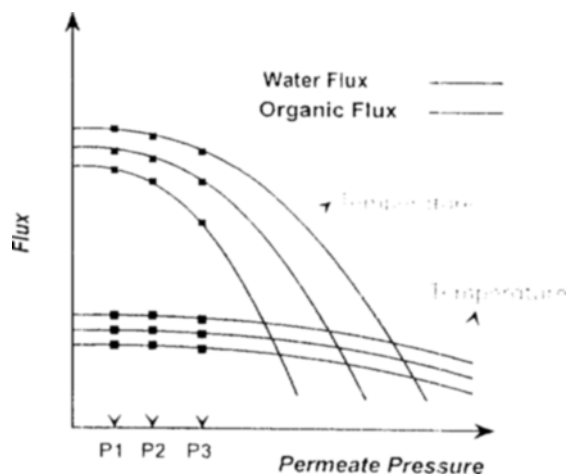


Fig. 5. Schematic component flux profiles with permeate pressure at different operating temperatures.

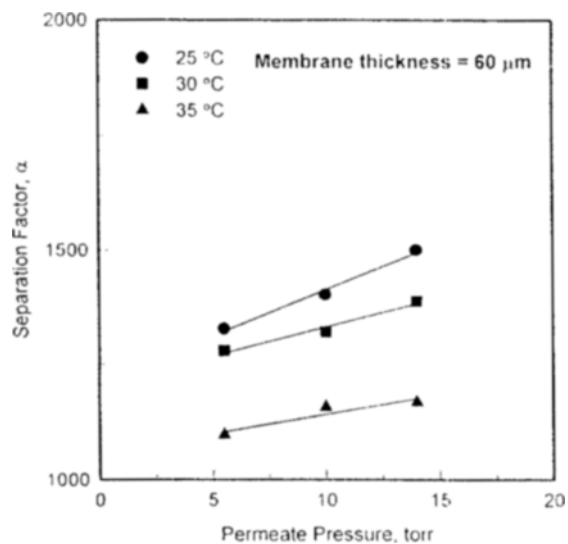


Fig. 6. Selectivity change with permeate pressure at different operating temperatures: membrane thickness=60 μm .

between permeant molecules (causing bigger size of penetrating unit by associated or coupled permeating molecules) or/and small plasticization action. In the solution-diffusion mechanism where desorption step is assumed to have little effect on the overall process, E_p depends on both the apparent activation energy for the diffusion E_d and the heat of sorption H_s :

$$E_p = E_d + H_s \quad (4)$$

However, if the desorption resistance is not negligible as in the case of thin membrane, the desorption step will have a contribution to the overall process as well and thus affect the permeation activation energy such that a term for the heat of desorption (evaporation) can be added in Eq. (4) to increase the value of E_p . In Fig. 8, the E_p of each component determined from Fig. 7 is plotted with membrane thickness at a permeate pressure. The permeation activation energy of organic component is lower than that of water because the membrane is an organophilic material having a good compatibility with

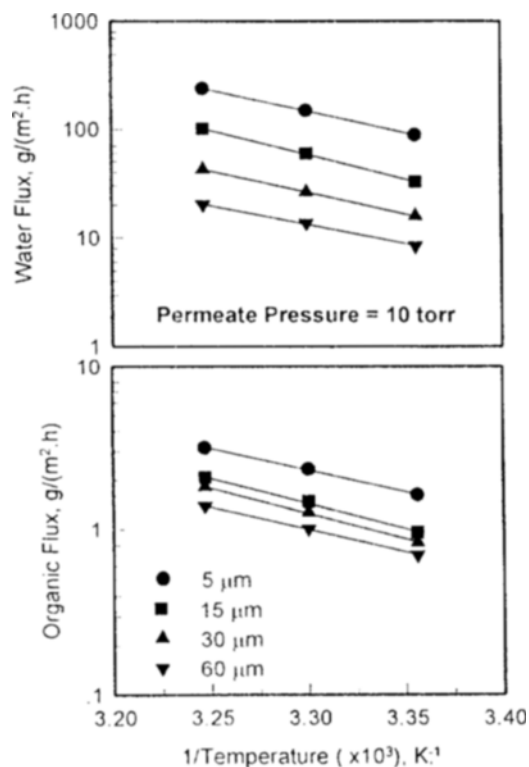


Fig. 7. Arrhenius plots of component fluxes with temperature at different membrane thickness: permeate pressure=10 torr.

the organic component. When membrane material, permeant concentration profile across a membrane and desorption resistance at the permeate-side surface of a membrane are identical, E_p should be almost constant with membrane thickness. In both water and organic permeations, the E_p has the maximum value at 15-30 μm of membrane thickness. The reason for that is not clear but it might be explained in terms of the competitive effects of the plasticization action of the permeant and the desorption resistance on the E_p with membrane thickness. These two factors can compete to influence the E_p value in opposite way; the desorption resistance increases E_p while the plasticization action of permeants decreases E_p by enhancing membrane mobility. As membrane thickness decreases, the flux increases and causes more permeant molecules stick to the outer layer of the membrane at permeate side, so that the diffusion of a permeant molecule through the outer layer of the membrane can slow down and, in addition, more energy should be needed for the evaporation of the more permeant molecules at the membrane surface. As a result, the desorption resistance is not only increased but also the permeant concentration at the downstream interface of the membrane is increased because of slow evaporation of permeants and then the permeant concentration in the membrane is so increased that the plasticization action of permeants on the membrane material can become remarkable because of broader concentration profile developed in thinner membrane. Below 15 μm of membrane thickness, the plasticization action of permeant may be predominant over the effect of the desorption resistance on the E_p value while above 15 μm , the contribution of the desorption resistance to the water

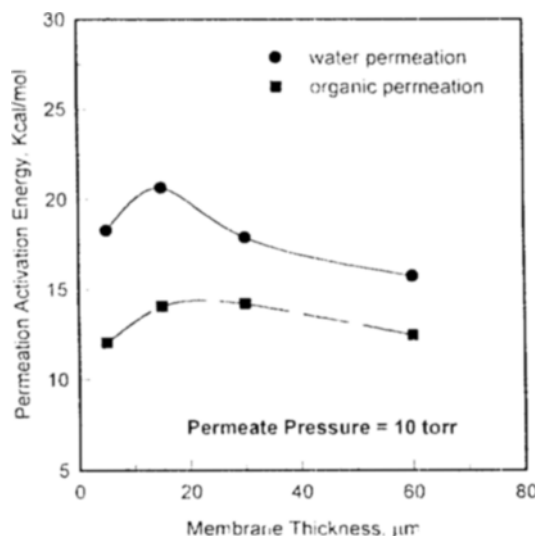


Fig. 8. Permeation activation energies of components vs. membrane thickness at different permeate pressure.

permeation is more prevailing. For the most part, it is found from the water permeation that E_p has a higher value at smaller membrane thickness and higher permeate pressure.

CONCLUSIONS

A crosslinked silicone pervaporation membrane for the removal of chlorohydrocarbons from water has been developed using a new oligomeric silylstyrene as the crosslinking agent of PDMS. Through swelling measurements and pervaporation experiments, optimal casting solution and manufacturing condition were determined for best membrane fabrication. In pervaporation of 55-70 ppm of 1,2-dichloroethane aqueous mixtures, the developed membrane has flux of 2.5-330 $\text{g}/(\text{m}^2\cdot\text{h})$ and selectivity of 230-1750 depending on membrane thickness, permeate pressure and operating temperature. Negative deviation of water flux from the linearity predicted from the Fick's law of diffusion was found with decreasing membrane thickness because of more significant desorption resistance to permeation. Also, the organic flux curve with membrane thickness shows more negative deviation even at high Reynolds number of feed flow at which the concentration polarization effect at feed can not be significant on the permeation. The main cause for that may be significant desorption resistance to the organic permeation. With permeate pressure, the fluxes of each components were decreased due to decreasing driving force to permeation while the selectivity toward volatile component, organic, was increased because the relative volatilities of permeants affect selectivity to some extent. From the Arrhenius plots of each component fluxes against temperature, the permeation activation energy of each component was determined. Through an analysis of the permeation activation energy of each component, the desorption resistance to permeation through thin membrane was qualitatively characterized.

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