Improved Measurement Device for Vapor Permeation and Pervaporation

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ABSTRACT: A precision measurement method of vapor permeability through polymer membranes was developed and tested for cellulose acetate membranes. An apparatus with a differential transformer and a float on the liquid source could precisely measure the vapor permeation rate as well as pervaporation flux by sensing the level of the source liquid. The permeation rates with vapor feed and liquid feed of water, alcohols, and organic solvents were measured for silicone rubber and cellulose acetate, cellulose triacetate, and water-soluble cellulose acetate membranes. The measured vapor permeability directly predicted the pervaporation flux through silicone rubber. In the case of swollen material due to the feed liquid, the vapor permeability was not a controlling property of the pervaporation flux, but became an analysis base for it. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 433–438, 1997

Key words: permeability; vapor permeation; pervaporation; cellulose acetate

INTRODUCTION

The permeation and separation mechanism of a pervaporation process is analyzed using a solution-diffusion model. In this model, the driving force that produces permeation is the concentration difference of the permeate in membrane material. Another permeation process, vapor permeation, is treated based on the vapor permeability and partial pressure difference between the feed side and permeate side streams. Pervaporation and vapor permeation are similar as a membrane permeation process, but are different for a basic analysis. The vapor permeation process may be included in the pervaporation process as one step, because the feed liquid during the pervaporation permeates in the vapor state. More study about the relationship between pervaporation and vapor permeation will make the solution-diffusion model for pervaporation more reliable.[1]

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However, there have only been a few reports[2–4] treating the simultaneous measurement of pervaporation and vapor permeation for the same membrane and permeate component. The early study by Stannett and Yasuda[2] pointed out that permeabilities measured during pervaporation and vapor permeation at the saturation vapor pressure were equal. Kataoka et al.[3] reported for the permeation of the ethanol/water system that results using a polyacrylonitrile membrane showed good agreement between pervaporation and vapor permeation, but the results with a cellulose acetate membrane showed a larger permeation flux and a lower separation factor for water during pervaporation than vapor permeation.

Lack of reports from one aspect about pervaporation and vapor permeation is because of difficulties in measuring the permeabilities of condensable vapors through a polymer membrane. The permeability measurement of a condensable vapor needs a vacuum system, and vapor permeation rates through a polymer membrane at a vapor pressure under saturation are generally much smaller than the pervaporation flux. Only for rubbery polymers, through which vapor permeation rates are relatively large, have several measurement methods been reported by varying the feed vapor pressures. Baker et al.[5] applied a Tepler pump system with mercury in glass tubes for the vapor permeability measurement of hydrocarbons through rubbery polymers. Ito et al.[6] reported the vapor permeabilities of acetone and freon through silicone rubber hollow fiber membranes by a measurement method of weighing the vapor source liquid. A new method is needed for the precise measurement of vapor permeability.

The main objective of this study was to develop a precise measurement method of vapor permeability through a polymer membrane. A differential transfer was applied for sensing the level of source liquid. An apparatus with a differential transformer and a float on the liquid source could precisely measure the vapor permeation rate as well as the pervaporation flux. The permeation rates with vapor feed and liquid feed of water, alcohol, and organic solvents were measured using silicone rubber and cellulose acetate membranes. The results were compared with each other and discussed from the view point based on vapor permeability.

EXPERIMENTAL

The membranes used in this work were silicone rubber, cellulose acetate (CA, DS = 2.45), water-soluble cellulose acetate (WSCA, DS = 0.79), and cellulose triacetate (CTA, DS = 2.92) (Daisel Chem. Ind. Led.). A silicone rubber film of 100 μm was purchased by Sinetu Chemical Co., Japan. Polymer solutions of the cellulose acetates were prepared by dissolving CA, WSCA, and CTA in acetone, water, and chloroform, respectively. The polymer solutions were cast and dried on a glass plate to prepare the dense membranes. The thicknesses of the membranes ranged from 10–20 μm. Detailed descriptions of the membrane preparations are given in a previous report.[7] Permeate species were chosen from the aspect of a wide range of solubility parameters,[8] $\delta[(\text{MPa})^{1/2}]$. Water ($\delta$ = 49.7), methanol (δ = 29.7), ethanol (δ = 26.0), isopropyl alcohol (δ = 23.5), benzene (δ = 18.8), and toluene (δ = 18.2) were tested as permeates in this study.

The test apparatus shown in Figure 1 was used to measure the vapor permeabilities and pervaporation fluxes. The membrane permeation apparatus consists of a 9 × 12 mm glass tube vessel for the liquid source, a permeation cell for a flat membrane with a 19.6 cm^2 permeation area, a cold trap, and a vacuum pump. A small glass-tube float with a 6 mm diameter, into which an iron core is sealed, floats on the source liquid in the feed vessel. The position of the float is precisely recorded using a differential transformer placed outside the liquid vessel and a displacement meter. The precision of the displacement meter is 5 μm. The decreasing rate of a liquid surface is precisely measured by the changing position of the float. The precision of the liquid surface's decreasing rate was under 0.15 mm/h and that of the liquid evaporation or permeation rate was under 0.01 cm^3 liquid/h.

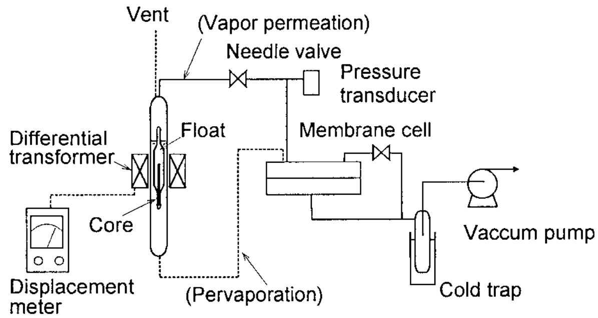

Figure 1 Permeation rate measurement apparatus with a displacement meter.

Another feature of the present method is its short time for a measurement. A common method of a measurement of permeation flux is trapping of a permeated vapor for a period of time and weighing the condensate. This trapping-weighing method needs a considerable period of time to collect a measurable amount of a permeate, for example, of 5 h or more. The present method, using a differential transformer, needs a shorter time of a measurement, say, half an hour, which includes a transition period to a steady-state permeation under a prescribed condition.

The application of the differential transformer afforded an accurate measurement method for vapor permeability as well as the pervaporation flux for a pure permeate component. In all the measurements, a vacuum at the downstream side was maintained at a pressure of 1–3 mmHg. The experiment was carried out at room temperature, 20–24°C. In the case of the vapor permeation measurement, the vapor phase of the liquid vessel was connected with the feed side of the membrane

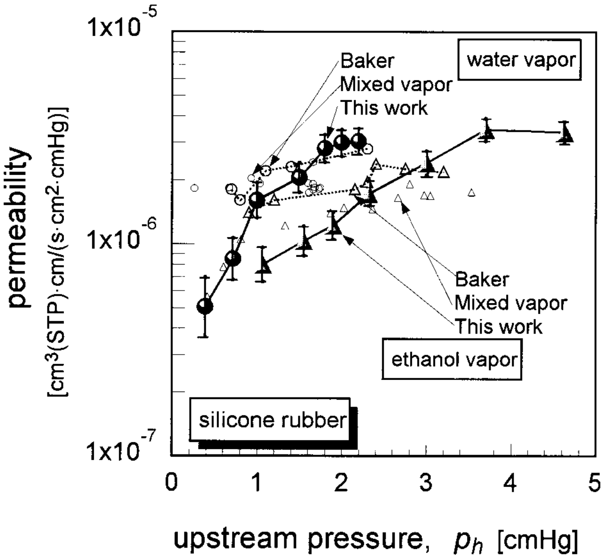

Figure 2 Vapor permeabilities of water and ethanol through a silicone rubber membrane.

cell. After the system was degassed, the pressure of a feed vapor was adjusted by a needle value. The vapor permeation rate was evaluated based on the decreasing rate of the liquid level in the vapor source. In another measurement of pervaporation, the bottom of the liquid vessel was connected with the feed side of the membrane cell and the top was opened to the atmosphere. So, in the pervaporation run, the feed side of the membrane cell was at atmospheric pressure. The pervaporation flux was evaluated from the decreasing rate of the liquid level in the vessel.

RESULTS AND DISCUSSION

The permeation of water and the alcohols through a silicone rubber membrane was first tested as an example of a small interaction or nonswollen membrane material with the permeate. Watson and Payne[9] reported that the swelling ratio of silicone rubber with water and alcohols was less than 12%. In Figure 2, the resulted permeabilities of water vapor and ethanol vapor are compared with the published data by other measurement methods. The feed vapor pressures in the measurements, p_h, were shown as the abscissa in the figure. Baker et al.[5] originally studied the permeability of condensable solvent vapors. They reported vapor permeabilities through various rubbery membranes by measuring the rate of volume loss from feed side by using of a Toepler pump. Their data in the figure are measured at 40°C. This permeability measurement with the Toepler pump is accurate in principle, but it needs a delicate experimental technique and a special experimental setup. In most studies, vapor permeability could be measured by the trapping of permeate vapor. In our pervious report,[10] the permeabilities of this system were reported by the permeation of ethanol–water mixed vapor. The permeate vapors were collected and analyzed in concentration to evaluate permeabilities of the components. This method of collecting permeate needs a long time run and has poor accuracy. Although the temperatures are different in these measurements, the above three methods show comparable results. The features of the present method are a short measurement period compared with the permeate-collecting method, and a simple operation compared with the Toepler pump method.

Figure 2 also shows an error analysis result of the present measurement. The error bars on the data show the uncertainty introduced into permeability data. The accuracy of the measurement of vapor permeation rate was ±10%. It mainly depends on the reading of the recorder charts. There was another error due to uncertainty in the measurement of the pressure of feed side. The error caused by it was ±1 mmHg. Including these effects, we estimated that the experimental error for the permeability was ±21% at $p_h = 1$ cmHg, and ±13% at $p_h = 4$ cmHg.

Figure 3 shows a comparison between the vapor permeabilities and the pervaporation fluxes of water and the alcohols through the silicone rubber membrane. The data series of open keys are the results for the vapor permeability measurements. The feed vapor pressures, p_h, were reduced by the saturated vapor pressures of the pure permeate liquids, p^*, at the operating temperature. This reduced pressure, p_h/p^*, is often referred to as the vapor activity and is shown as the abscissa in the figure. The closed keys at $p_h/p^* = 0$ are apparent permeabilities, Q_{PV}, for the pervaporation run. The apparent permeabilities were calculated by dividing the thickness-normalized fluxes, $N\,\delta$, by the saturated vapor pressure.

$$Q_{PV} = N\delta/p_h \qquad (1)$$

The extrapolated vapor permeabilities of all permeates correspond well with the apparent per-

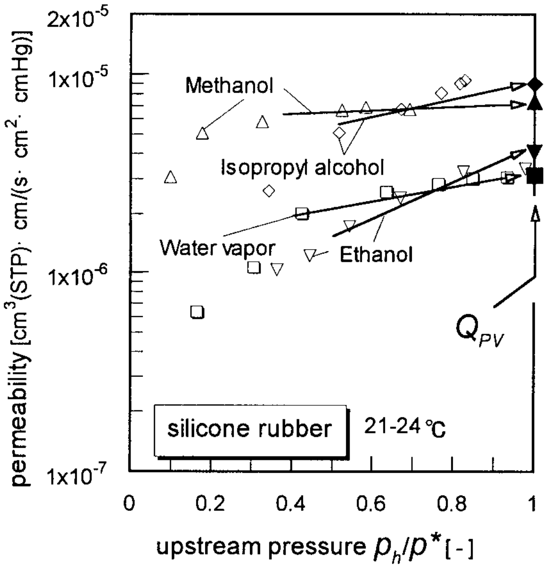

Figure 3 Vapor permeabilities and preparation flux through a silicone rubber membrane.

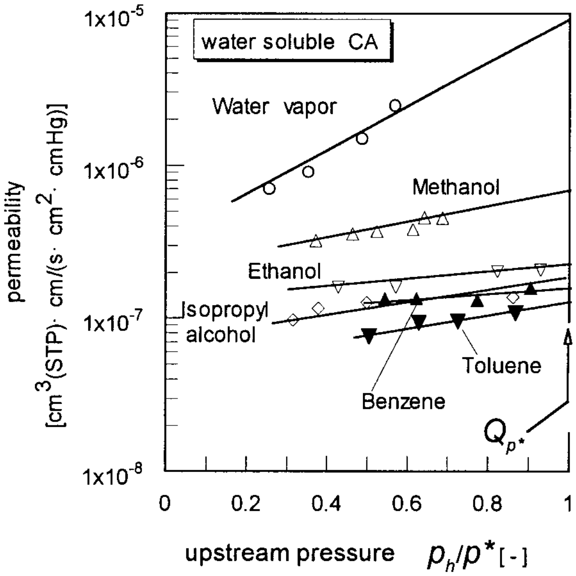

Figure 4 Vapor permeabilities through a water-soluble cellulose acetate membrane.

meabilities for pervaporation. That is, the pervaporation flux of the system could be predicted from the vapor permeability at saturation and the saturation vapor pressure of the feed liquid. From the view point of the conventional solution–diffusion theory, Sun and Chen[11] rigorously analyzed the permeation mechanism through the silicone rubber membrane using the adsorption and desorption rate of the vapors. The present comparison in Figure 2 may prove an alternate and simple view point that vapor permeability becomes a controlling property of the pervaporation for a weak interaction or nonswelling permeate/membrane system.

Figure 4 shows the vapor permeabilities of water, alcohols, and solvents for a water-soluble cellulose acetate membrane. The vapor permeabilities of water and alcohols were large and the order of these magnitudes corresponded to the solubility parameters of these permeates.

The large dependency of the vapor permeability on vapor activity makes it difficult to compare primary data between various systems of permeates and membrane material. In this study, the extrapolated values to $p_h/p^* = 1$, which are shown in the figure, were used in the following comparison.

The evaluated permeabilities at the saturation vapor pressures, $Q_p{}^*$, through cellulose acetate membranes, are shown in Figure 5. The permeabilities of water and ethanol are large for the water-soluble cellulose acetate membrane of highly hydrophilic. On the other hand, the vapor permeabilities for all permeates through the cellulose triacetate membrane are on the same order of magnitude. The cellulose acetate membrane with a hydrophilicity between the water-soluble cellulose acetate and cellulose triacetate showed an intermediate permeation trend. The vapor permeability appears to be affected by an interrelation between the hydrophilicity of the membrane material and the solubility parameters of the permeate, especially for the water or alcohol's vapor permeability.

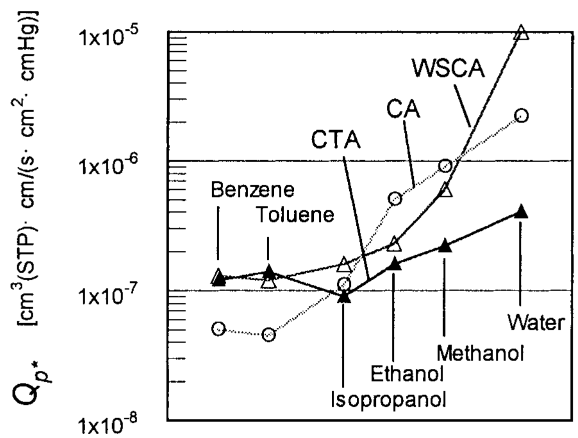

Figure 5 Vapor permeabilities through cellulose acetate membranes.

The pervaporation measurements for the cellulosic membranes were also analyzed in terms of the apparent vapor permeability by eq. (1). Figure 6 shows the results on the same coordinates as Figure 5 for vapor permeability. The apparent permeabilities, or the reduced pervaporation fluxes based on the saturation vapor pressure of the permeates, exhibit large values for water and alcohols and small values for the solvents. As is distinct from the vapor permeability, there is a small effect of the hydrophlicitic properties of the cellulosic membranes on the reduced pervaporation fluxes.

We can compare these two permeation modes of vapor permeation and pervaporation using the terms of the vapor permeability at the saturation vapor pressure and the apparent permeability, respectively. Figure 7 shows the ratio of the apparent vapor permeability of the pervaporation to the vapor permeability at saturation pressure. These ratios for water and alcohols were larger than unity for any membrane. That is to say, the absolute values of the pervaporation fluxes are larger than those of the vapor permeation. These results have been common for the permeation of the water–alcohol mixed vapor or liquid.[3,4] The increasing of the permeation flux in the pervaporation mode is attributed to the swelling of the membrane surface by the feed liquid.[3,10] Also, some ratios for benzene and cyclohexane were smaller than unity. There have been no reports about this phenomena of a lower flux of the vapor permeation than pervaporation. This may be caused by some rejection effect between the polymer material and the feed liquid. We need to further study this decreasing phenomena in the vapor state permeation.

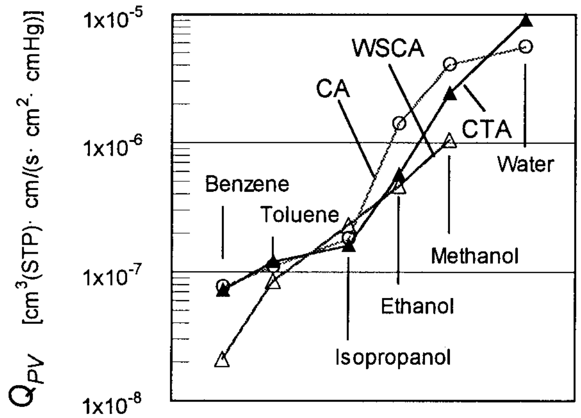

Figure 6 Apparent permeabilities in a pervaporation run.

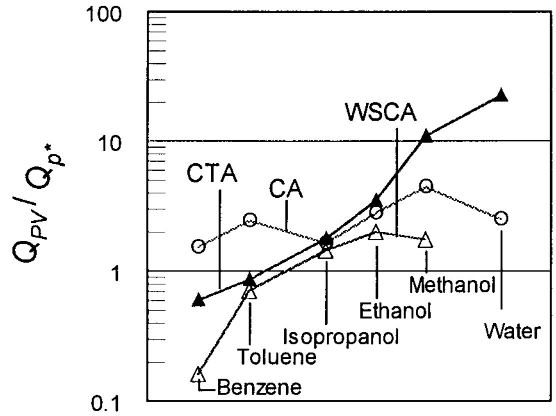

Figure 7 Comparison between apparent permeabilities in pervaporation and vapor permeabilities.

CONCLUSIONS

A differential transfer was applied for sensing the level of a source liquid to develop a precision measurement method of vapor permeability and pervaporation flux through a polymer membrane. The permeation rates with vapor feed and liquid feed of water, alcohols, and organic solvents were measured for silicone rubber and cellulose acetate membranes. The measured vapor permeability directly predicted the pervaporation flux through the silicone rubber. In the case of material swollen by the feed liquid, the vapor permeability was not a controlling property of the pervaporation flux but an analysis base for it. The present precise measurement of the vapor permeability and direct comparison of the pervaporation and vapor permeation in one apparatus will make vapor permeability an analysis base of pervaporation. The mechanism of pervaporation may be analyzed by vapor permeability as well as by the swelling property of the membrane material as a different point of view from the solution–diffusion model.

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