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Vapor Permeation and Pervaporation of Aqueous 2-Propanol Solutions through the Torlon® Poly(amide imide) Membrane

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Abstract: In the present study, vapor permeation and pervaporation of aqueous 2-propanol mixtures were investigated using Torlon® poly(amide imide) as a membrane material. Torlon membranes preferentially permeated H_2O from aqueous 2-PrOH mixtures both by vapor permeation and pervaporation. Diffusion experiments led to the conclusion that both solubility selectivity and diffusivity selectivity showed a preference for H_2O. Solubility selectivity is by far the dominant factor governing permselectivity, and as a result, Torlon membranes showed permselectivity toward water in vapor permeation and pervaporation. The present study showed that Torlon® poly(amide imide) is a membrane material potentially applicable to the dehydration of water miscible organics.

Keywords: Diffusion coefficients, diffusivity selectivity, permselectivity, pervaporation, solubility selectivity, Torlon, vapor permeation

INTRODUCTION

Torlon® poly(amide imide) thermoplastic has been utilized in many engineering applications such as molded parts for the space shuttle, engine parts of

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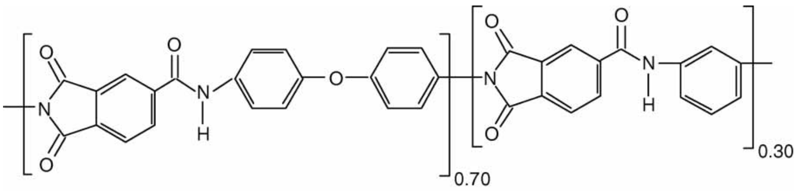
world-class racing cars, and many other critical components. From the high performance of Torlon, the authors investigated this thermoplastic as a membrane material for vapor permeation and pervaporation (1, 2). From a part of those studies, Torlon has emerged as a promising membrane material for the selective permeation of water from aqueous organic mixtures by vapor permeation and pervaporation.

In the present paper, the separation of water and 2-propanol mixtures was adopted as a model separation system, and the vapor permeation and pervaporation performance of Torlon® poly(amide imide) membrane were studied.

EXPERIMENTAL

Materials

Torlon grade® 4000T poly(amide imide) was obtained from BP Amoco Polymers Inc. (now Solvay Advanced Polymers). Dimethyl sulfoxide (DMSO) and 2-propanol (2-PrOH) were purified by the usual method (3). Deionized water was employed throughout the experiments.



Membrane Preparation

A 0.50 g of Torlon was dissolved in 5.0 cm^3 of DMSO. The solution was cast onto a glass plate with an applicator (casting thickness, 0.254 mm), and the solvent was allowed to evaporate at 50°C for 24 h. The thickness of the resulting membranes was in the range of 16–19 μm.

Vapor Permeation (VP) and Pervaporation (PV)

VP experiments were carried out at a reflux temperature of each aqueous 2-PrOH mixture, under atmospheric pressure [ca. 0.101 MPa (ca. 1.0 atm)]. The schematic diagram of the VP apparatus is shown in Fig. 1. The apparatus was connected to a vacuum line and the permeate was condensed and trapped by liquid nitrogen in the same manner as in PV experiments (4). The effective membrane area was 17.3 cm^2 and the downstream pressure was maintained at around 133.3 Pa (1.0 mmHg) in both VP and PV.

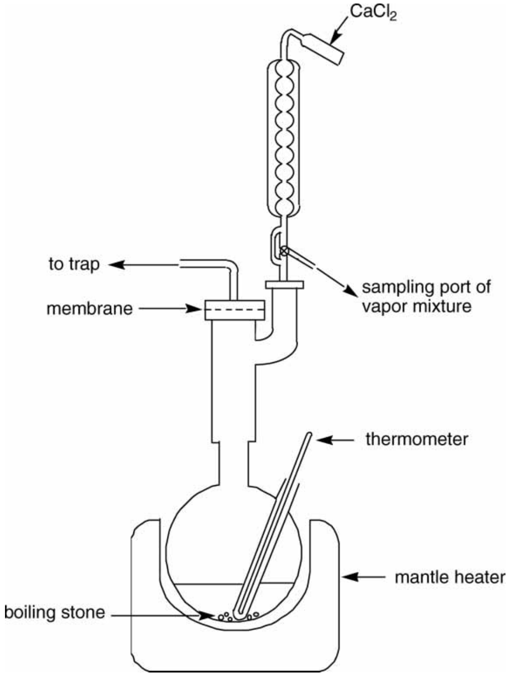


Figure 1. Schematic diagram of apparatus for vapor permeation.

PV was performed using the typical pervaporation technique (4) at a constant temperature of 82°C.

Separation analysis was carried out on a Shimadzu GC-7APT gas chromatography instrument with a 3.0-m-long column packed with polyethyleneglycol 6000 (Shimalite TPA).

The separation factor, α, is defined as

$$\alpha = (Y_{H2O}/Y_{2\text{-}PrOH})/(X_{H2O}/X_{2\text{-}PrOH})$$

In vapor permeation, Y_is are the weight fractions in permeate and X_is are those in vapors in feed, respectively. In pervaporation, Y_is are the weight fractions in permeate and X_is are those in feed, respectively.

Measurement of Diffusion Coefficient

The permeation of H_2O or 2-PrOH vapor through the Torlon membrane in the present study, was measured at 82°C, which corresponds to the reflux temperature for a weight fraction of H_2O in vapor feed of ca. 3.0×10^{-3}. From the time-transport curve for each vapor, the diffusion coefficient was determined by applying the time-lag method (5).

RESULTS AND DISCUSSIONS

Vapor Permeation and Pervaporation

In a previous vapor permeation study (1), the Torlon membrane preferentially permeated water from $H_2O/2$-PrOH at a weight fraction of H_2O of 0.0028 in vapor feed mixture.

First the vapor permeation performance of Torlon membrane was investigated by changing the weight fraction of vapor in feed. The results are shown in Fig. 2. As expected from the previous results (1), the membrane permeated water in preference to 2-PrOH. For all weight fractions of water in the feed solutions, water was permeated in preference to 2-PrOH. Permselectivity toward water ranged from ca. 70 to 160. In some cases, permselectivity

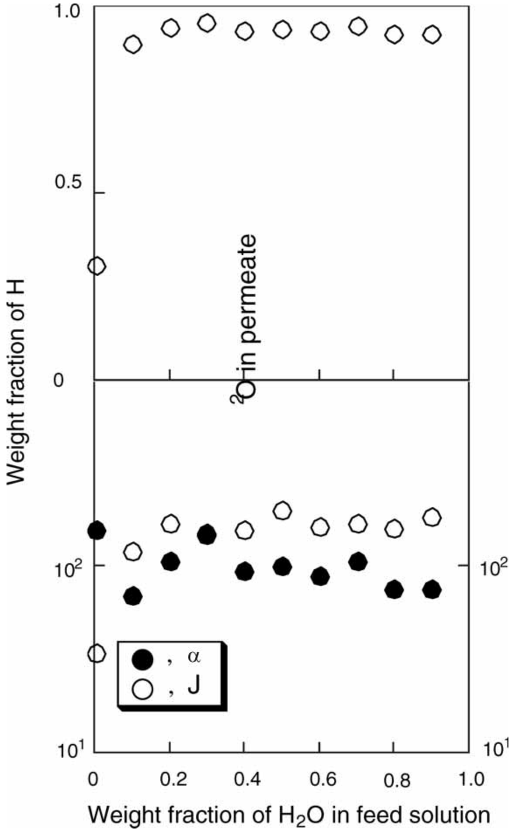


Figure 2. Effect of feed composition on the vapor permeation of H_2O\2-PrOH mixtures through the Torlon membrane. [Downstream pressure, 133.3 Pa (1.0 mmHg); operating temperature, each reflux temperature.]

toward water decreased with the increase in the weight fraction of water vapor in feed due to membrane swelling by water (6–8). In general, the Torlon membrane showed stable permselectivity toward water and also gave stable flux values.

It is of interest to conduct a comparative study of vapor permeation and pervaporation. The effect of feed concentration on pervaporation of aqueous 2-PrOH mixtures through the Torlon membrane is shown in Fig. 3. Water is selectively permeated through the membrane. It can be said that the present membranes selectively permeated water from aqueous 2-PrOH mixture by both VP and PV methods, the selectivity being $\sim 10^2$ and above for •0.1 weight fraction of water in the feed solution.

It is difficult to compare VP and PV performance of the Torlon membrane in the present study, because each VP experiment was carried out at a reflux

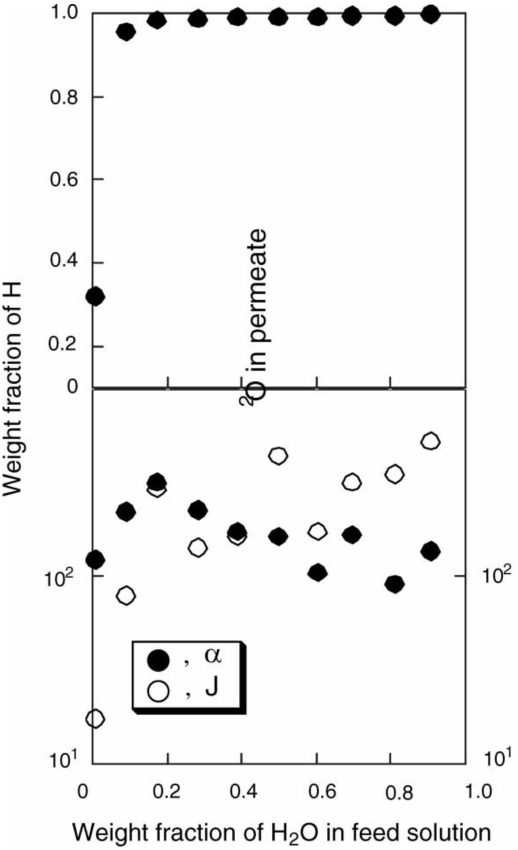


Figure 3. Effect of feed composition on the pavaporation H_2O\2-PrOH mixtures through the Torlon membrane. [Downstream pressure, 133.3 Pa (1.0 mmHg); operating temperature, ca. 82°C.]

temperature, while PV experiments were done at a constant operating temperature of 82°C. But it is expected that equal membrane performance in VP and PV would be observed under the condition that an initial swelling condition of membranes is kept constant in both methods (9).

Diffusivity of Permeant in the Torlon Membrane

There are two methods to elucidate the factors governing the permselectivity in VP and PV. One is as follows: for either VP or PV, diffusivity selectivity ($S_D = D_{H_2O}/D_{2\text{-PrOH}}$, where D_{H_2O} and $D_{2\text{-PrOH}}$ are the diffusion coefficients of H_2O and 2-PrOH, respectively) is estimated from the separation factor (α) and solubility selectivity ($S_S = S_{H_2O}/S_{2\text{-PrOH}}$, where S_{H_2O} and $S_{2\text{-PrOH}}$ are the solubility coefficients of H_2O and 2-PrOH, respectively) (10), obeying the solution-diffusion theory. In this case, S_S is obtained by conducting sorption experiments. The other method is a reverse way, that is, S_S is estimated from α and S_D, where S_D is determined by the time-transport curve (5).

As often suggested in PV (11), the distribution of permeants in a given membrane for VP or PV and that for a sorption experiment might be considerably different. In the distribution for VP or PV, one surface of the membrane, the one in contact with the feed mixture, is swollen. The state of the membrane in contact with the feed solution may be considered to resemble that of the membrane for the sorption experiment. The other surface of the membrane, which is in contact with vacuum in VP or PV, maintains its dry state and contributes to permselectivity. The state of the membrane on the downstream side is considerably different from that of the upstream side. In other words, the state of the membrane surface in contact with vacuum, which plays an important role for permselectivity, is different from that of the sorption experiment even though the sorption experiment is carried out in a vapor phase. From this, the actual solubility selectivity should be higher than the estimated value using sorption data for both VP and PV. That is, the values of solubility selectivity obtained by sorption experiment can be considered to be minimum values. In contrast, the diffusivity selectivities calculated by using separation factor (α) and solubility selectivity (S_S) can be considered to be maximum values; in other words, the actual diffusivity selectivity should be lower than that estimated by using both α and S_S.

From this, the governing factors obtained by the latter method might have a greater accuracy than that by the former method. Consequently, diffusivity selectivity was determined so that the factors governing the permselectivity toward water could be elucidated. A typical time-transport curve obtained experimentally of H_2O vapor through the Torlon membrane at 82°C is shown in Fig. 4. In the present study, VP experiments were carried out at each reflux temperature, which was not equal to 82°C. But diffusivity was measured at that temperature in the present study. Diffusion coefficients of

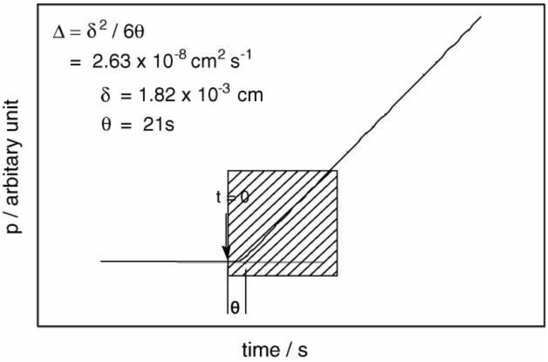


Figure 4. Time-transport curve of H_2O vapor through the Torlon membrane at 82°C. [(H_2O vapor pressure in upstream, 1266 Pa (9.50 mmHg).]

H_2O and 2-PrOH were determined by the time-lag method (5) from the permeation data of pure vapor at a prescribed vapor pressure. It is necessary to know the diffusivity selectivity of the active layer, which is thought to govern permselectivity and to be in the dry state. To accomplish this, vapor with a low activity should be in contact with the membrane. In the present study, each vapor, of which activity was below 0.04 at 82°C, was in contact with the membrane. This enabled the diffusion coefficient to be estimated for a given vapor in the active layer of the membrane in both VP and PV. The resulting determined diffusion coefficients for H_2O and 2-PrOH are summarized in Tables 1 and 2, respectively. The diffusion coefficients for H_2O and 2-PrOH are plotted as a function of activity of vapor in Figs. 5 and 6, respectively. For permeation, the diffusion coefficient D often depends on the local concentration of permeant itself (12–21). In some cases, the concentration dependence of the diffusion coefficient has been reported to be linear (16):

$$D = D_0(1 + \gamma C)$$

Table 1. Diffusion coefficients of H_2O through Torlon membrane[a]

p/Pa	p/mmHg	a (=p/p_0^b)	θ/s	D/($cm^2\ s^{-1}$)[c]
999.9	7.50	0.020	24.0	2.30×10^{-8}
1266	9.50	0.025	21.0	2.63×10^{-8}
1666	12.5	0.033	15.0	3.68×10^{-8}
1933	14.5	0.038	12.9	4.28×10^{-8}

[a] Measurements were carried out at the constant temperature of 82°C.
[b] p_0 = 51320 Pa (385.0 mmHg).
[c] The thickness of the membrane was 18.2 μm.

Table 2. Diffusion coefficients of 2-PrOH through Torlon membrane[a]

p/Pa	p/mmHg	a (=p/p_0^b)	θ/s	D/($cm^2\ s^{-1}$)[c]
666.6	5.00	0.0066	66.6	8.29×10^{-9}
866.6	6.50	0.0086	63.6	8.68×10^{-9}
1066	8.00	0.011	57.9	9.53×10^{-9}
1999	15.0	0.020	35.4	1.56×10^{-9}

[a] Measurements were carried out at the constant temperature of 82°C.
[b] $p_0 = 1.006 \times 10^5$ Pa (754.7 mmHg).
[c] The thickness of the membrane was 18.2 μm.

and in other cases, an exponential form was observed (16):

$$D = D_0 \exp(\beta C)$$

In these two equations, D_0 is the D value as the permeant concentration approaches 0; γ and β are the coefficients characteristic of the membrane/permeant interaction and C denotes the permeant concentration in the membrane. The latter equation is used to simulate the concentration dependence of both H_2O and 2-PrOH diffusion in the present study. D_0 and β were determined to be 1.13×10^{-8} $cm^2\ s^{-1}$ and 35.6, respectively, for H_2O and 5.78×10^{-9} $cm^2\ s^{-1}$ and 49.3, respectively, for 2-PrOH. Adopting

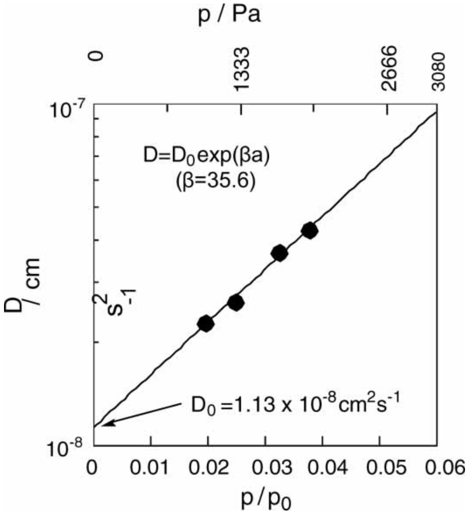


Figure 5. Concentration dependence of diffusion coefficient of water vapor through the Torlon membrane at 82°C. [The saturation vapor pressure, p_0, of water at 82°C is 51.3 kPa (385 mmHg).]

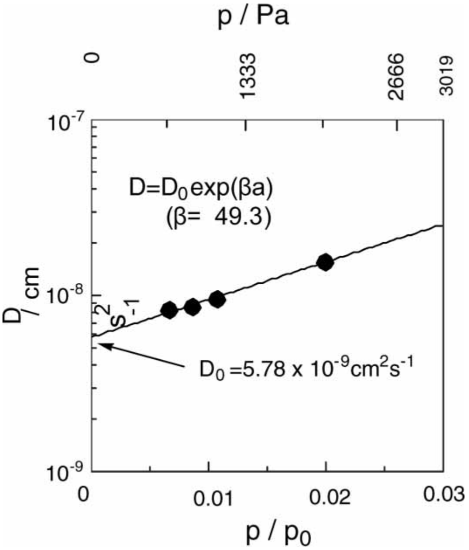


Figure 6. Concentration dependence of diffusion coefficient of water 2-PrOH vapor through the Torlon membrane at 82°C. [The saturation vapor pressure, p_0, of water at 82°C is 101 kPa (755 mmHg).]

D_o values for H_2O and 2-PrOH, the diffusivity selectivity S_D $(=D_{H_2O}/D_{2\text{-PrOH}})$ was determined to be 1.96.

Assuming that the effective diameter of the diffusing permeant is approximately inversely proportional to the diffusion coefficient, it follows that

$$r_{2\text{-PrOH}}/r_{H_2O} = D_{H_2O}/D_{2\text{-PrOH}} = 1.96$$

Therefore the ratio of volume of 2-PrOH to that of H_2O was calculated to be

$$V_{2\text{-PrOH}}/V_{H_2O} = (1.96)^3 = 7.53$$

Assuming that 2-PrOH diffused in and through the membrane unimolecularly, the apparent volume of H_2O (V_{H_2O}) diffusing in the membrane was estimated by using $18.0\,cm^3\,mol^{-1}$ for the molar volume of H_2O and $76.9\,cm^3\,mol^{-1}$ for that of 2-PrOH (2):

$$V_{H_2O} = V_{2\text{-PrOH}}/7.5 = 10.2\,cm^3$$

Permeants do not always migrate in a polymeric membrane unimolecularly. There are cases in which some permeants form clusters, which move in and through the membrane. In the present study, the apparent volume of H_2O moving in the membrane was estimated to be $10.2\,cm^3$. The $10.2\,cm^3$ of H_2O diffusing in the membrane roughly corresponds to around one water molecule. That is, one water molecule diffused unimolecularly through the membrane in the present study.

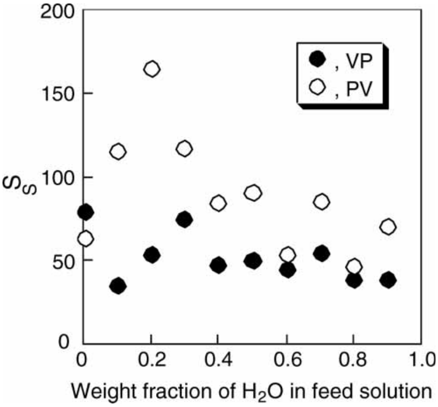


Figure 7. Effect of feed composition on solubility selectivity, S_s, of the Torlon membrane in VP and PV.

In the case that the diffusivity selectivity of 1.96 is adopted in the present study, the solubility selectivities ($S_S = \alpha/S_D = \alpha/1.96$) in VP and PV are estimated, and they are shown in Fig. 7. This led to the conclusion that the permselectivity toward water for the present membrane was mostly dependent on solubility selectivity.

CONCLUSIONS

In the present study, Torlon® poly(amide imide) was adopted as a membrane material. Transport of aqueous 2-propanol mixtures through the present membrane was investigated by vapor permeation and pervaporation. The Torlon membrane preferentially permeated H_2O from aqueous 2-PrOH mixtures by both methods. Diffusion experiments led to the conclusion that both solubility selectivity and diffusivity selectivity showed a preference for H_2O. Among them, the solubility selectivity is by far the dominant factor governing permselectivity. Thus, the present membranes showed permselectivity toward water in vapor permeation and pervaporation, suggesting that Torlon® poly(amide imide) is a membrane material that can be utilized for the dehydration of water miscible organics.

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