

Pervaporative Dehydration of Diethylene Glycol Through a Hollow Fiber Membrane

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ABSTRACT: In this study, the pervaporative dehydration of diethylene glycol (DEG) through a commercial hollow fiber membrane was investigated at various feed temperatures in the range of 333–363 K with feeds containing 0.5–2.0 wt % water. Unlike the usual pervaporative dehydration process in which water is less volatile than the organic solvent, the feed mixture used in this study contained the organic component DEG, which is less volatile than water, resulting in unique permeation behaviors. The permeation behaviors of the individual components were investigated as functions of the feed temperature and feed composition. In particular, the effect of the low vapor pressure characteristics of DEG was investigated. Semi-empirical equations for predicting the individual component fluxes and separation factor were quantified directly from actual dehydration pervaporation of DEG. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 499–506, 2013

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INTRODUCTION

Diethylene glycol (DEG) is an industrial chemical with uses that include dehydration of natural gas, production of polyurethanes and unsaturated polyester resins, petroleum solvent extraction, and antifreeze preparations.¹ DEG is commercially made as a by-product of the ethylene glycol (EG) production process, where a large excess of water is used in the hydrolysis reaction. The excess water must later be removed to obtain pure products.² Glycols are difficult and expensive to recover from aqueous solutions because of their high boiling points and affinity to water as the energy utilized in this process constitutes a substantial portion of the cost of recovery. The dewatering processes are therefore critical in the production and recycle processes of glycols.³

Among membrane processes, pervaporation is a technique that allows the separation of liquid mixtures through a polymeric membrane. Since the membrane process has been proven effective for the dehydration separation of organic compounds,^{4–6} attention is now being focused on energy conservation as well as environmentally friendly separation as the process promises much greater benefits especially in an era of skyrocketing oil prices.

A high water perm-selectivity in a membrane can be achieved in two ways, either by increasing the diffusion ratio of water to the organic solvent or by increasing the sorption ratio of water to the organic solvent. Liquid molecules mutually interact

among themselves through three kinds of interactions: dispersion, dipole, and hydrogen bonding. The dispersion interactions of liquid organic molecules are comparable to each other in value, with most of them being in the range of 15–20 MPa^{0.5}. Water has a higher polarity than organic solvents; in particular, it provides the strongest intermolecular hydrogen-bonding interaction followed by glycols, alcohols, esters, and chlorinated hydrocarbons.⁷ For this reason, hydrophilic polymeric membranes are generally selected for the dehydration of organic solvents because they contain hydrophilic functional groups on main polymeric chains; these groups have relatively high polarities and strongly interact with water molecules via hydrogen bonding. As a rule of thumb, for the pervaporative dehydration of a water/organic solvent mixture, a large difference in the hydrogen bonding interactions between water and the organic solvent is recommended. However, DEG, which is in the glycol family, has the second highest hydrogen bonding strength after water, meaning that the dehydration of DEG is not easy compared to that of other solvents. To the best of our knowledge, there have not been any studies of the pervaporative dehydration of DEG even though several publications on the dehydration of other glycols have been reported.^{7–11}

In this study, pervaporative dehydration of DEG through a commercial hollow fiber membrane was investigated. The hollow fiber membrane has a hydrophilic active layer on the inside of the hollow fiber membrane, capable of dehydrating

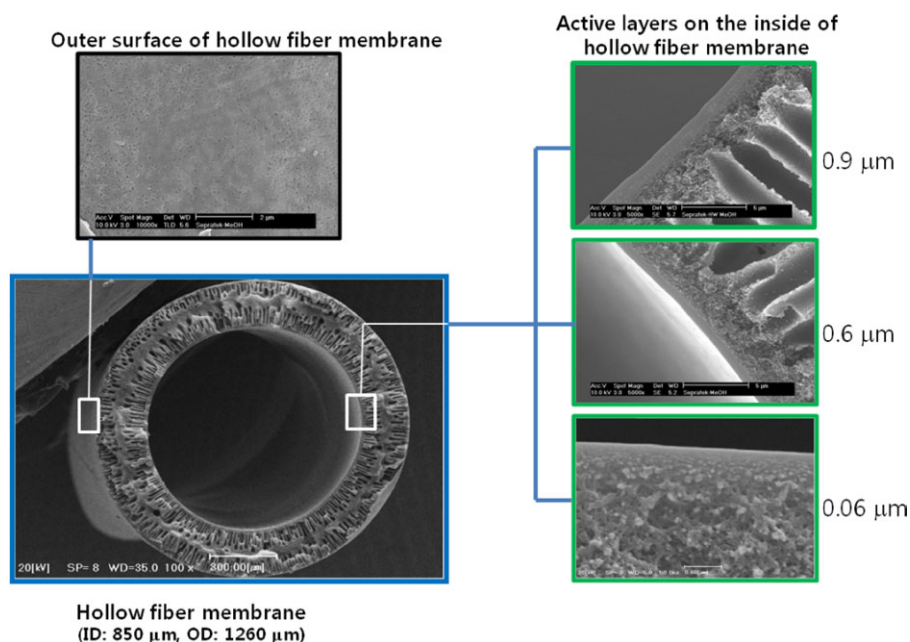


Figure 1. Structure of the pervaporation hollow fiber membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DEG into the bore side and permeating water from the inside to the outside of the hollow fiber membrane. The hollow fiber membrane was reinforced by braiding it with robust polymeric yarns and metal wires such that the membrane exhibited excellent mechanical properties, being very sustainable under harsh circumstances. The investigations were carried out at various temperatures in the range of 333–363 K with feeds containing 0.5–2.0 wt % water. The permeation behaviors of individual components are discussed in terms of the feed temperature and feed composition.

Semiempirical equations for predicting individual component fluxes and the separation factor under given operating

conditions were quantified directly from actual dehydration pervaporation of DEG.

EXPERIMENTAL

Materials

The pervaporation hollow fiber membrane (PVHF-085060BW) was generously supplied by SeptraTek (Incheon, Republic of Korea). Details of the membrane are shown in Figures 1 and 2. The membrane has a hydrophilic active layer with a 0.6 μm thickness on the inside of the hollow fiber, as shown in Figure 1. The active layer is a modified poly(vinyl alcohol)(PVA)/acrylate that is highly crosslinked to ensure stability against harsh

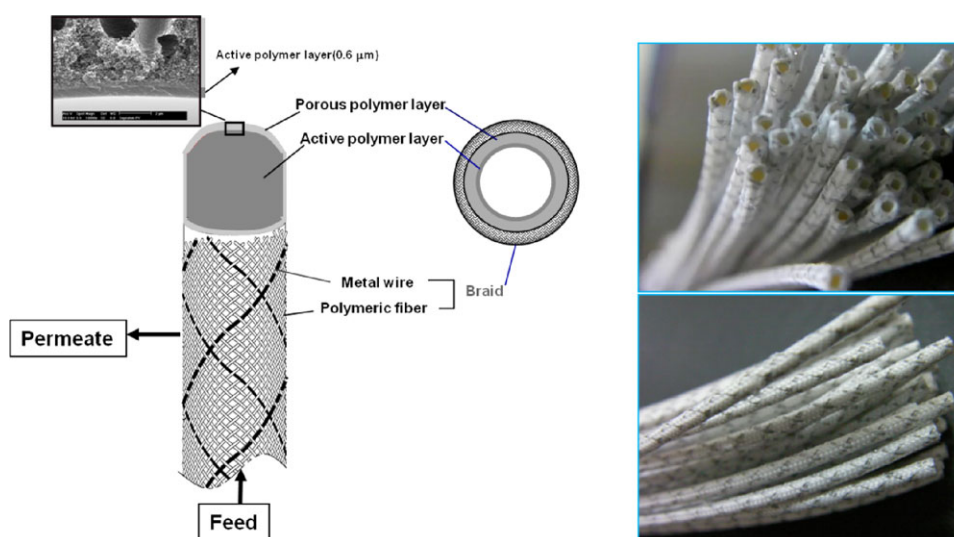


Figure 2. Braid-reinforced pervaporation hollow fiber membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

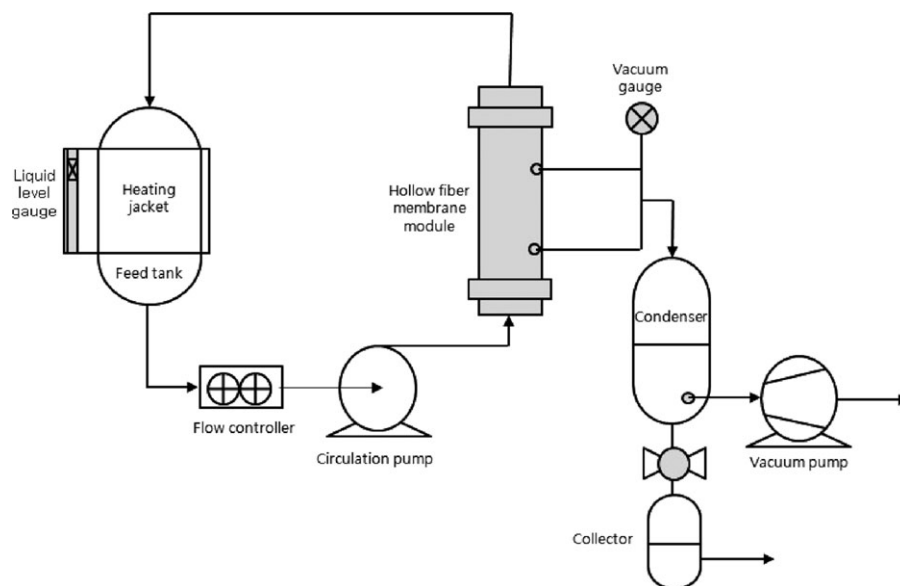


Figure 3. Schematic representation of the pervaporation apparatus.

circumstances, and the support porous layer is made of polyether imide (PEI) with pores 300 K Dalton.

The feed mixture to be dehydrated flows into the bore side, permeating water from the inside to the outside of the hollow fiber membrane. The membrane was reinforced by braiding it with high strength yarns and metal wires, as shown in Figure 2, to achieve excellent pressure resistance (max. service pressure: 40 atm) as well as good dimensional stability in organic solvents even at high temperature (max. service temperature: 373 K). DEG was obtained from OCI Co. Ltd. (Assay > 99.0%). DEG/water mixtures of different compositions were prepared by blending DEG and deionized water.

Membrane Module Preparation

Membrane modules were prepared by inserting a bundle of the hollow fiber membranes (effective length = 0.5 m) into a chlorinated polyvinyl chloride (C-PVC) tube with an inner diameter of 25.4 mm, potting both ends of the tube with epoxy resin, cutting both the potted parts to expose the hollow fiber membrane bundle, and putting C-PVC caps on both ends of the module. The module contained 130 hollow fibers and its effective membrane area was 0.16 m².

Pervaporation

Figure 3 is a schematic diagram of the experimental setup used for the pervaporation testing. The membrane module was installed between the circulation pump and the feed tank so that the feed mixture (2.5 kg) could be circulated from the feed tank through the membrane module by the pump, while the feed flow rate was adjusted by varying the rotation speed of the circulation pump. The permeate pressure was maintained below 0.67 kPa and the feed temperature was controlled by using the tube heater and the heating jacket. The circulation rate of the feed stream was 1000 mL/min and feed temperatures of 333, 343, 353, and 363 K were used.

The permeation rate (J) was determined from both the volumetric and the compositional changes of the liquid feed in the feed tank over a given time period as follows.

$$J = Q/(A \times \Delta t) \quad (1)$$

$$Q = V_1 \rho_1 - V_2 \rho_2 \quad (2)$$

$$\rho_i = \rho_{\text{water}} X_i + \rho_{\text{DEG}} (1 - X_i), \quad i = 1, 2 \quad (3)$$

$$\Delta t = t_2 - t_1 \quad (4)$$

In these equations, Q is the amount (weight) of the permeate through the membrane, Δt is the sampling interval, A is the effective membrane area, and ρ_i is the density of mixture. V_i and X_i are respectively the volume and the water weight fraction of the liquid feed in the feed tank at time t_i . The separation factor (α) can be defined as

$$\alpha = [Y/(1 - Y)]/[X/(1 - X)] \quad (5)$$

where X and Y indicate respectively the weight fractions of water in the feed and permeate streams.

In this study, the permeation rate and separation factor were calculated by measuring the change in volume and water concentration. It was assumed that the feed is a binary mixture of DEG and deionized water. The change in feed volume (V) in the feed tank was measured by using a liquid level gauge and the water weight fraction of the liquid feed (X) was analyzed by means of a volumetric Karl-Fischer system (795 KFT Titrimo, Metrohm, Switzerland). Since the volume change and composition of the feed are known, the weight fraction of water in the permeate (Y) can be calculated as

$$Y = (F_1 X_1 - F_2 X_2)/Q \quad (6)$$

where $F_i (=V_i \rho_i)$ is the weight of the feed. Thus, the individual fluxes are as follows.

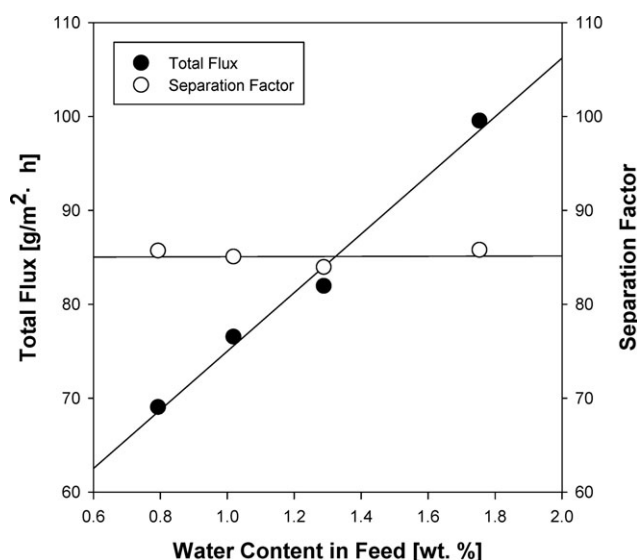


Figure 4. Plots of the total permeation rate and separation factor as a function of the water content in the feed at 353 K.

$$J_{\text{water}} = YJ \quad (7)$$

$$J_{\text{DEG}} = (1 - Y)J \quad (8)$$

In general lab-scale experiments for pervaporation, the permeate is collected in a condenser for a period of time and analyzed to determine its flux and composition. In the case of DEG with its extremely low vapor pressure, however, it would be partially condensed (along with the permeate line) on the way to the condenser if neither high temperature nor a high degree of vacuum is kept in the permeate line. This partial condensation can make it difficult to precisely analyze the membrane performance. Thus, an alternative methodology for the pervaporation of the DEG/water mixture is to indirectly determine the membrane performance from the abovementioned volumetric and compositional changes in the feed.

[Note: the data values reported in this study are the averages of values obtained over a 2–3 h period].

RESULTS AND DISCUSSION

Effect of Feed Composition

The permeation and separation of the binary mixtures were investigated with water concentrations in the range of 0.8–1.8 wt % at 353 K and the results are shown in Figures 4 and 5. It is well known that the feed composition has a strong effect on the permeation and separation of a binary mixture. This is especially true when one of the components is a plasticizing agent for a polymeric membrane, as water is in the case of hydrophilic membranes. Usually, a hydrophilic membrane contains functional groups that have a relatively high polarity and that strongly interact with water molecules via hydrogen bonding. Therefore, the selectivity of the membrane to water can be enhanced.¹² In our experiment, as the water concentration in the feed mixture increased, the total permeation rate increased

proportionally to the water content in the feed while the separation factor remained almost constant, as shown in Figure 4.

The separation behavior of a binary mixture can be discussed in detail by analyzing the permeation of the individual components. If we examine the permeation rates we obtained for the individual components shown in Figure 5, it is very interesting to note that the DEG permeation rate was almost constant over the range of the feed water content while the water permeation rate increased proportionally to the water content in the feed.^{13–15} When the water concentration in the feed is too small to affect the hydrophilic membrane structure, the degree of plasticization of the absorbed water on the membrane will be negligible. In this case, the solubility of the water component in the membrane would mainly contribute to the water permeation rate, rationalizing the proportional relationship of the water flux to the water content in the feed. Figure 6 shows that in our experiment the water flux increased progressively with increasing feed water concentration at the different feed temperatures. The linear relationships of the water flux as a function of the water content at different temperatures obtained from the data in Figure 6 are as follows,

$$\text{Flux}_{\text{Water}} = -2.021 + 25.35C \text{ at } 343 \text{ K} \quad (9)$$

$$\text{Flux}_{\text{Water}} = -1.917 + 36.54C \text{ at } 353 \text{ K} \quad (10)$$

$$\text{Flux}_{\text{Water}} = -1.963 + 41.95C \text{ at } 363 \text{ K} \quad (11)$$

where C denotes the water concentration (wt %) in the feed. The ideal permeation rate for binary liquid permeation is defined as the permeation rate of a component, which is proportional to the concentration of the component in the feed mixture,¹⁶ without coupling of fluxes, i.e. in the absence of

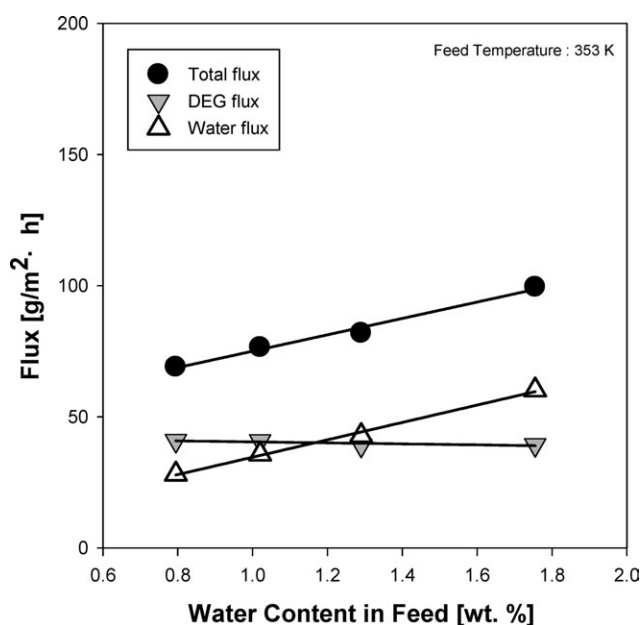


Figure 5. Plots of the permeation rates of individual components as a function of the water content in the feed.

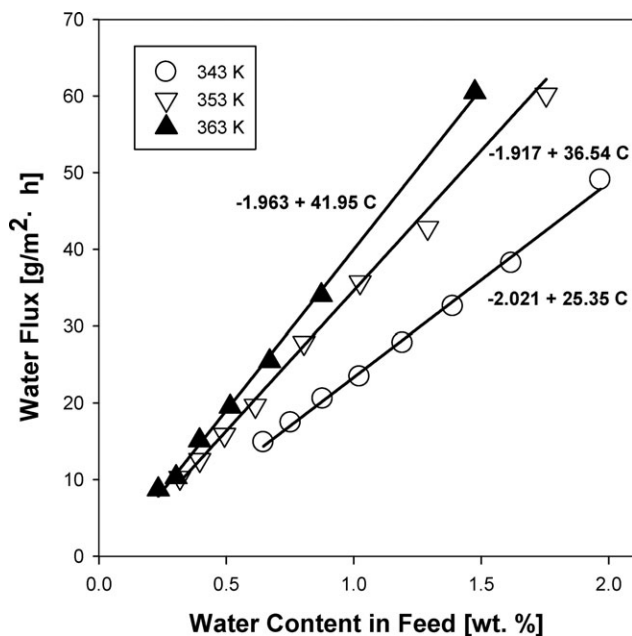


Figure 6. Water flux as a function of the feed composition at different feed temperatures.

effects of the presence of the other component. On the basis of this definition, eqs. (9)–(11) for the water permeation rate represent typical ideal permeation expressions.

On the other hand, in terms of the DEG component, which is the major component in the feed, the feed composition can be considered to be essentially constant, where the permeation rate results are very similar to those obtained for the case of pure DEG. Therefore, if there is no significant change in the membrane structure over a given range of feed composition, it is reasonable that the DEG permeation rate should be constant within that range.

Figure 7 presents the water content in the feed tank as a function of the permeating time at different feed temperatures. The water content decreased with increasing permeating time since the water component is continuously removed as it selectively permeates through the membrane. At higher feed temperature, more water permeated through the membrane, while DEG permeated nearly constant as shown in Figure 5. This is why a more significant decrease in the water content in the feed tank is observed at higher feed temperatures.

Effect of Feed Temperature

We investigated the effect of the feed temperature on the total flux and separation factor for a water content of 1 wt. % in the feed and the results are shown in Figure 8. It can be seen that lower separation factor and permeation rate were obtained at lower feed temperatures. According to the free volume theory,¹⁷ the thermal motion of polymeric chains in the amorphous regions randomly produces free volume. As the temperature is increased, the frequency and amplitude of chain jumping (i.e., thermal agitation) increases and the resulting free volume becomes larger. In pervaporation, the permeating molecules can diffuse through these free volumes. Thus, when the temperature is high, the diffusion rates

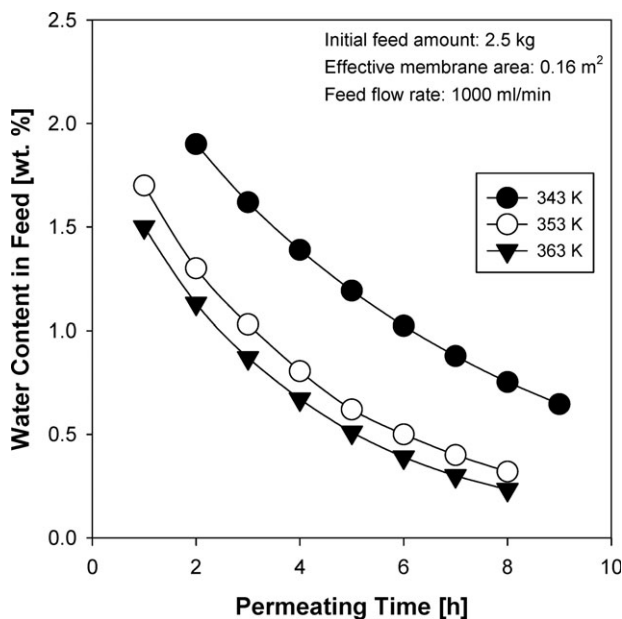


Figure 7. Water content in the feed mixture in the feed tank as a function of the permeating time at different feed temperatures.

of individual permeating molecules and associated permeating molecules are high, so that the total permeation rate is high and the separation factor is low in most cases. In this study, however, the separation factor also increased even though the total flux increased with increasing feed temperature. This opposite tendency of the separation factor with increasing feed temperature is due to the following unique characteristics of the feed mixture, which have rarely been applied in a dehydration process.

In accordance with the solution–diffusion mechanism,¹⁸ both the solution and the diffusion characteristics of a permeant in a membrane affect the selective permeation. Water molecules are

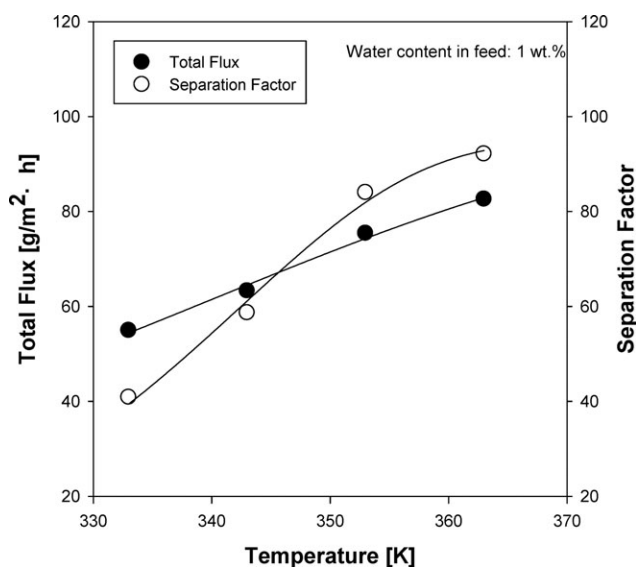


Figure 8. Plots of the total permeation rate and separation factor as a function of the feed temperature with a water content of 1 wt. % in the feed.

smaller in size than diethylene glycol molecules and thus the diffusion step is obviously favorable for the permeation of the water component. On the other hand, the pervaporative dehydration of organic solvents through a hydrophilic membrane is often attributed to the selective sorption of the water component into the membrane from the aqueous organic mixture. It would be of interest to know whether the preferential sorption of water over DEG indeed occurs in the membrane. Unfortunately, there is no information available concerning the hydrophilic active layer in the hollow fiber membrane used in this study from the supplier except that it is made of a polyvinyl alcohol-based hydrophilic polymeric material. Thus, the sorption properties of the individual components of the DEG/water mixture were indirectly obtained from previous publications.^{7–11} These publications reported that the family of glycols is absorbed in a hydrophilic membrane to a great extent, comparable with water sorption in the membrane, revealing that the water component is not preferentially sorbed in the hydrophilic membrane over the glycol component. The sorption characteristics of glycol in the membrane can be explained in terms of molecular structure. The glycol molecule has two hydroxyl groups, which may cause strong intermolecular hydrogen bonding as explained in the previous section. The strong hydrogen bonding interactions of glycol molecules may exhibit a strong affinity to the membrane, leading to competitive sorption. On this basis, it is postulated that the selective permeation of water can arise from the selective diffusion of water molecules or other factors. Considering the physical properties of DEG compared with those of water shown in Table I,^{19,20} we find the DEG molecule is much larger. Thus, water molecules diffuse more selectively than DEG molecules. In addition, boiling point and vapor pressure data lead us to judge that DEG is much less volatile than water and thus DEG molecules permeated into the permeate side of the membrane surface would evaporate slowly and the DEG concentration would increase at the downstream membrane surface. It has also been reported that the desorption resistance of a component increases with increasing component concentration or chemical activity at the permeate side surface

Table I. Comparison of the Physical Properties of Diethylene Glycol and Water^{19,20}

	Diethylene glycol	Water
Formula	C ₄ H ₁₀ O ₃	H ₂ O
Molar mass (g/mol)	106.12	18.02
Density at 273 K (g/cm ³)	1.1182	1.000
Melting point (K)	262.55	273
Boiling point (K)	518.3	373
Vapor pressure at 293K (mmHg)	0.002	20.0
Viscosity at 293K (cP)	35.7	0.97
Molecular volume (cm ³ @ 298K)	94.9	18
Solubility parameters (MPa ^{0.5})		
δ _d	16.6	15.5
δ _p	12.0	16.0
δ _h	20.7	42.3

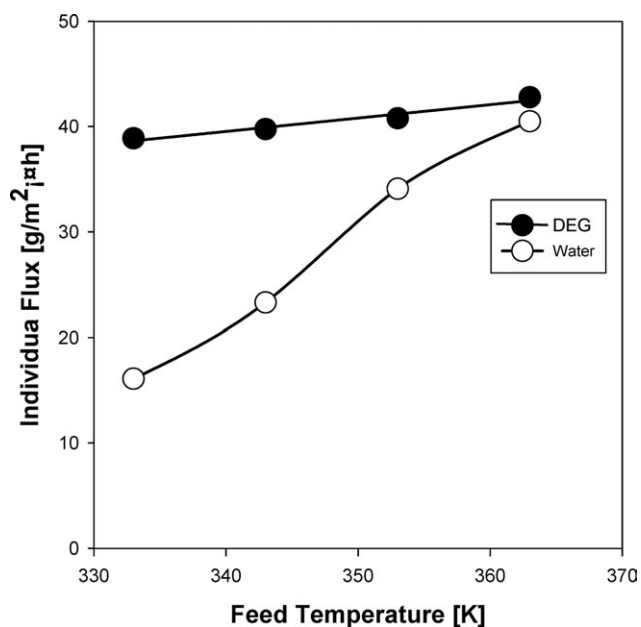


Figure 9. Permeation rates of individual components as a function of the feed temperature with a water content of 1 wt % in the feed.

of the membrane.²¹ As a result, we speculate that DEG permeation was likely suppressed on account of the significant desorptional resistance developed in its permeation and that water molecules thereby permeated selectively through the membrane. Unlike the usual pervaporative dehydration process in which the selectively permeating component is less volatile than the organic solvent, the feed mixture employed in this study contained the organic component DEG, which is less volatile than water and thus causes the unique permeation behaviors. In Figure 9, the DEG permeation rate and permeate concentration are respectively 38 g/(m²h) and 63 wt % DEG at 343 K. Both of these values are seemingly too high for the large molecular size of DEG relative to that of water when considering diffusion as the main factor contributing to permeation. Thus, the high values of the DEG flux and DEG permeate concentration are obviously due to significant sorption of DEG in the membrane. The slight increase in the DEG flux with increasing feed temperature is attributed to the low volatility of DEG as well as to significant desorptional resistance to DEG permeation, as discussed above. This is why the separation factor increases with increasing feed temperature. The flux of the DEG component can be simply expressed by a linear relationship with feed temperature in the given range of feed compositions as

$$\text{Flux}_{\text{DEG}} = -3.743 + 0.1273T \quad (12)$$

where T is the feed temperature (K). It was observed in Figure 6 that the water flux is linear as a function of the feed composition at a given temperature. The parameters including the slopes and intercepts were plotted as a function of the feed temperature in Figure 10. Then, a model equation for the water flux was determined by fitting each plot into a proper function of the feed temperature obtained by regression.

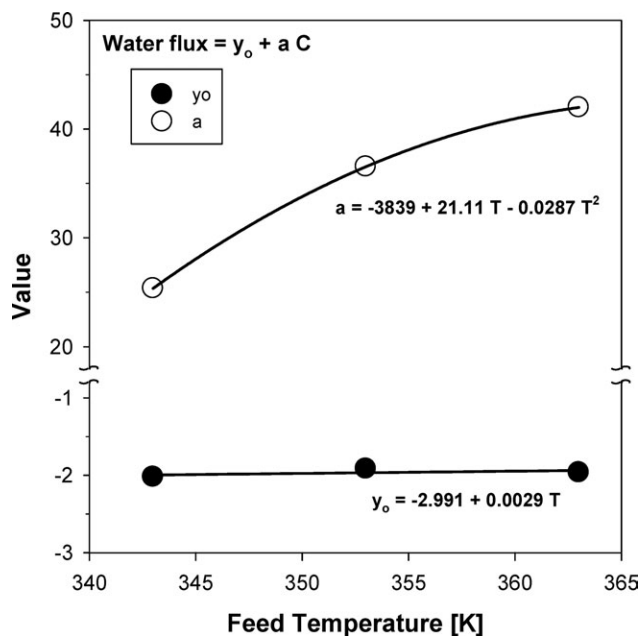


Figure 10. Parameters used in the water flux equation as a function of the feed temperature.

$$Flux_{water} = -2.991 + 0.0029T + (-3839 + 21.11T - 0.0287T^2)C \quad (13)$$

Therefore, the permeation rates of DEG and water can be calculated using respectively eqs. (12) and (13). To confirm that these equations are accurate, the total fluxes and water fluxes were calculated at various feed compositions and feed temperatures

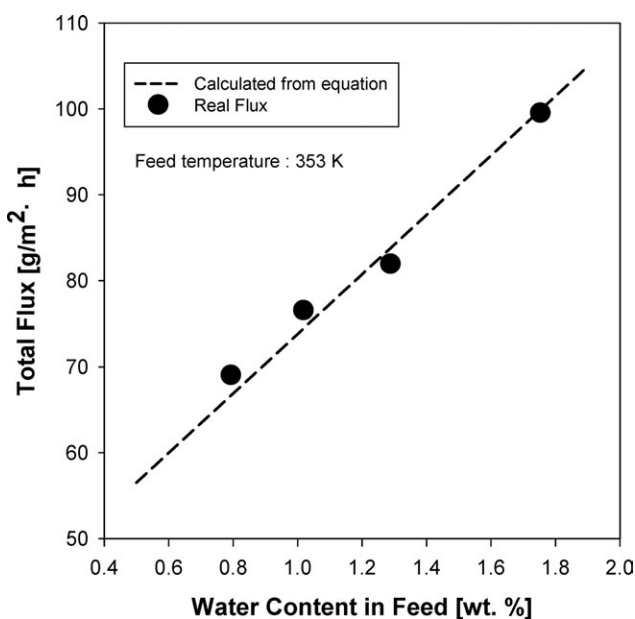


Figure 11. Comparison of the calculated and experimentally obtained total fluxes as a function of the water content in the feed at a feed temperature of 353 K.

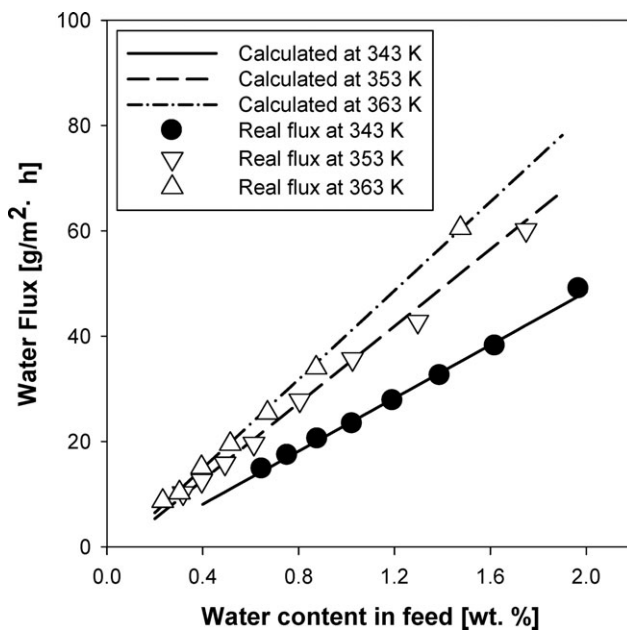


Figure 12. Comparison of the calculated and experimentally obtained permeation rates as a function of the water content in the feed at different feed temperatures

and compared with the experimental values. Figures 11 and 12 show the comparison between the calculated and experimental values we obtained for the various conditions we used. As seen in the figures, excellent agreement (i.e., within $\pm 2\%$ accuracy) was obtained between the calculated values and experimental data. This demonstrates that these developed flux equations provide practical permeation values that can be applied to the pervaporation process. The equations will be used in a simulation of pervaporation dehydration to optimize the process conditions and improve the design of the pervaporation system. The simulation work is underway and the results will be published in the near future.

CONCLUSIONS

The pervaporative dehydration of DEG through a commercial hollow fiber membrane was investigated at various temperatures in the range of 333–363 K with feeds containing 0.5–2.0 wt % water. In this study, it is noteworthy that the water component, which is the selectively permeating component, is more volatile than the organic component DEG, even though water is commonly less volatile than the organic solvent in the general dehydration process.

It was observed that the permeation of water demonstrated ideal permeation behavior where the permeation rate of a component in a binary liquid is proportional to the concentration of the component in the feed mixture, without coupling of fluxes. The permeation rate of DEG was nearly constant with the various feed compositions because the concentration of the DEG component can be considered to be constant as the feed is almost pure DEG. From the discussion of individual component permeation, it was postulated that DEG permeation was depressed due to the significant desorption resistance

developed in its permeation and that water molecules thereby permeated selectively through the membrane. However, because of significant sorption of DEG in the membrane, we observed a higher than expected DEG flux and high DEG permeate concentration based on the large molecular size of DEG relative to water. The slight increase in the DEG flux with increasing feed temperature is attributed to the low volatility of DEG as well as to significant desorptional resistance to DEG permeation.

Semiempirical equations to predict the individual component fluxes and separation factor at given operating conditions were quantified directly from actual dehydration pervaporation of DEG. As we will discuss in a future publication, the equations can be used to provide more practical values in simulations of the pervaporation process.

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