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Pervaporation Characteristics of Polyetherimide/γ-Alumina Composite Membrane for a Quaternary Equilibrium Mixture of Acetic Acid-Ethanol-Ethyl Acetate-Water

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Abstract−Polyetherimide/γ-alumina composite membrane has been prepared by dipping method for further reactor application. Separation factors and permeances for a quaternary acetic acid-ethanol-ethyl acetate-water equilibrium feed mixture have been measured on the composite membrane in the range of temperature from 303 K up to 343 K and space time from 27 sec to 27,000 sec at a permeate-side pressure of 2.67×10^{-3} bar. Fluxes for the all four components increase as temperature inicreases due to the increase of free volume within polymer chains. Apparent activation energies have been measured for the four components. The flux change for acetic acid is the most sensitive on the temperature change. The composite membrane shows a good dehydration capability with reasonable separation characteristics, as well as thermal and mechanical stability in desired conditions.

Key words: Composite Membrane, Pervaporation, Polyetherimide/γ-Alumina Membrane, Esterification, Membrane Separation

INTRODUCTION

Pervaporation is a membrane process, which is appropriate for the separations of liquid mixtures containing molecules with sizes less than 3 nm. In general, due to the size limitation on the feed molecules to be separated, developing a defect-free dense polymeric membrane has drawn research interest in this pervaporation process. In the polymeric membrane, intra-molecular distance of the polymer chains is satisfactory to circumvent the size limitation of pervaporation. Moreover, its own solubility may differ from molecules to molecules, which characteristics provide sufficient perm-selective separation capability. However, problems that one openly encounters with the dense polymeric membranes for pervaporation are their low mass flow rate and poor chemical, mechanical and/or thermal stability [Mulder, 1996; Waldburger and Widmer, 1996].

Nowadays, adapting dense polymeric pervaporation membranes into reactors for reversible reactions, i.e., esterification, reforming, has been considered as one of the most important application areas of the membrane process to overcome equilibrium limitation. These are a membrane reactor, which combines a reaction and membrane separation [Park and Geng, 1996; Zhu et al., 1996; Park et al., 1998; Lim et al., 2002], and more recently a hybrid adsorbent-membrane reactor [Park and Tsotsis, 2004]. In such a reactor application area for practical purposes, mass transfer characteristics for the polymeric membranes are better to be measured near reaction conditions, e.g., composition for multi-component and/or equilibrium mixture, temperature, pressure. However, almost all of separation studies of the polymeric or polymeric/ceramic composite pervaporation membranes have been done on the dehydration for binary azeotropic water-ethanol or rarely water-acetic acid systems, while results of separation studies for multi-component equilibrium mixtures have not yet been disclosed [Okamoto et al., 1992; Won et al., 1996; Yeom et al., 1996; Zhu et al., 1996; Kim et al., 1997; Chang et al., 1998; Qariouh et al., 1999; Wang et al., 1999; Song et al., 2002].

Among the different polymeric membranes, hydrophilic polymeric membranes such as polyetherimide membranes demonstrate the most promising binary separation characteristics, showing relatively high separation factors and water fluxes. This can be attributed to enhanced sorption equilibrium by strong hydrogen bonding interaction between water and the polymer surface, which is one of the most important factors influencing mass transfer through the membrane used for pervaporation. The polyetherimide membrane shows water-ethanol binary separation factors in the range of 10 to 400, and fluxes of water in the range of 3.1×10^{-4}-2.2×10^{-2} moles/m^2/sec fluxes [Zhu et al., 1996; Quriouh et al., 1999; Wang et al., 1999].

Even the polyetherimide membrane with good separation characteristics, particularly in reactor application of the polymeric membrane, it can be noted that the polymeric membrane is thermally, mechanically, and chemically not very stable when exposed to severe reaction conditions, e.g., strong inorganic acid catalysts, high temperature, high pressure. Therefore, in order to improve the mechanical strength of the polymeric membranes, when the polymeric membranes are being manufactured, the polymeric membranes are laminated with supporter layers. For these reasons, recently, Zhu et al. [1996], Yoshida and Cohen [2003], Chen and Yuan [2004], and Park and Tsotsis [2004] have proposed a polymeric/ceramic composite membrane concept for pervaporation as a solution for overcoming the problems on both the porous ceramic membrane and the dense polymeric membrane. There is a good synergy, in which this composite type membrane, polymer membrane layer is an actual membrane layer providing perm-selectivity, and the ceramic layer acts as a support layer withstanding severe mechanical, thermal, chemical conditions.

In this research, emphasis has been placed on the preparation of asymmetrical cylinder shape polymer/ceramic composite membranes,

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and on the measure of their separation characteristics for quatnery acetic acid-ethanol-ethyl acetate-water equilibrium mixture to be further used for reactor application undergoing esterifications as a reversible reaction catalyzed by strong sulfuric acid. This composite membrane is potentially capable of overcoming not only the inherent problem of poor mechanical, thermal stability but also the size limitation, i.e., less than 3 nm, frequently encountered with the polymeric membranes or ceramic membranes. Through these resolutions of the problems, we expect to use the polymeric/ceramic composite membrane for reactor application.

EXPERIMENTAL

1. Preparation of Polymer-ceramic Composite Membrane

Polyetherimide (Ultem^{R}-1000) was provided by General Electric Plastics. Its glass transition temperature was reported to be 217 °C. An asymmetric porous tubular type ceramic γ-alumina membrane (I.D. of 7.0×10^{-3} m, O.D. of 1.0×10^{-2} m, Membralox^{TM}) was obtained from U. S. Filter and was used for preparing composite membranes. The γ-alumina membrane consists of four different layers. Actual membrane layer is only the inner-most layer and the others are support layers. Pore size and thickness of the inner-most layer is 4.0×10^{-9} m and 5.0×10^{-6} m, respectively. Pore size (thickness) of the second sub-layer next to the inner-most layer, the third sub-layer and the outer-most layer are 0.20×10^{-6} m (30.0×10^{-6} m), 0.8×10^{-6} m (50.0×10^{-6} m), and 15.0×10^{-6} m (1.4×10^{-3} m), correspondingly. The surface of the alumina membrane was cleaned by n-hexane and sulfuric acid. About 1.50×10^{-2} m of each end of the porous alumina membrane was coated with a commercial glaze (Ultra-clear, GL 611A, Duncan) for sealing. A 3 wt% polyetherimide solution in 1,2-dichloroethane (99.9%, analytical, Mallinckrodf) was prepared to be used for coating. A 2.50×10^{-2} m^{-4} 3-neck round flask with an installed magnetic stirrer was used for dissolving the resin under reflux conditions. After preparation, the solution was filtered to remove any un-dissolved particles. Coating of the ceramic support with the polymer solution was carried-out by dipping the alumina substrate into the 3 wt% polyetherimide solution for 1 hour. The membrane was then dried overnight at room temperature, and then vacuum dried for one more day to remove the remaining solvent from the bulk of the polymer film. The effective length of the polymer membrane was 0.170 m, which corresponds to the space time of 2,700 sec. In order to ensure that the prepared polymeric/ceramic composite membranes were defect-free, the dried membrane was tested by permeation with argon gas in a dead-end membrane permeation module as seen in Fig. 1. The criterion of selection for the defect-free membrane was its measured permeance, which for such a membrane was chosen to be less than 40 gas permeation unit (GPU) of argon (one GPU corresponds to 7.50×10^{-7} m^3-Ar(STP)/m^2/sec/bar). For the membranes whose permeances exceed 40 GPU, we applied a second or even a third coating until the argon permeance decreased below 40 GPU. Fig. 2 schematically describes the procedure of preparing the defect-free polymeric/ceramic composite membranes. The defect-free membranes were subsequently used

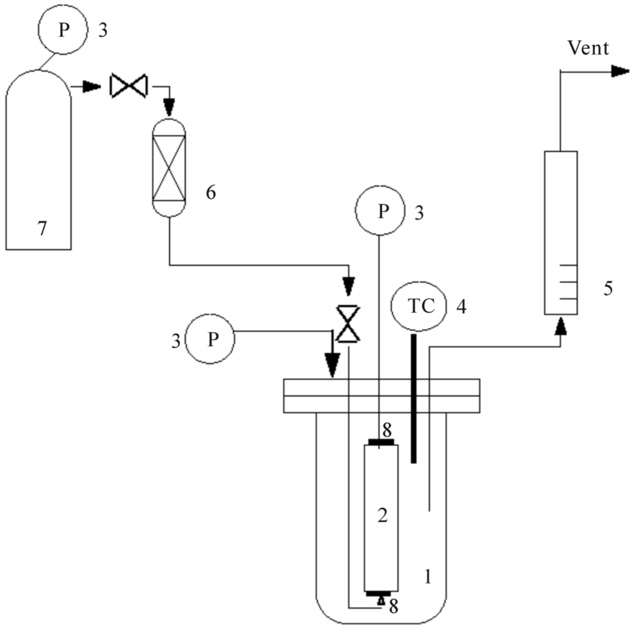

Fig. 1. Dead-end gas permeation test module.

1. Test module
2. Membrane
3. Pressure gauge
4. Thermocouple
5. Bubble flow meter
6. Gas purifying trap
7. Argon gas cylinder
8. Carbon sealing

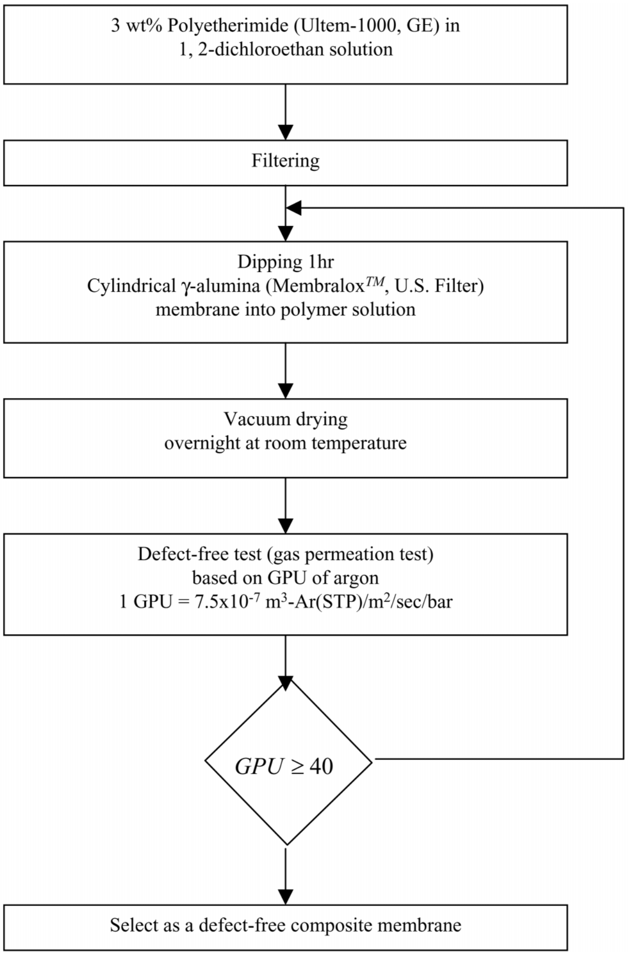

Fig. 2. A schematic diagram of the procedure of preparing polymer/ceramic composite membranes for pervaporation.

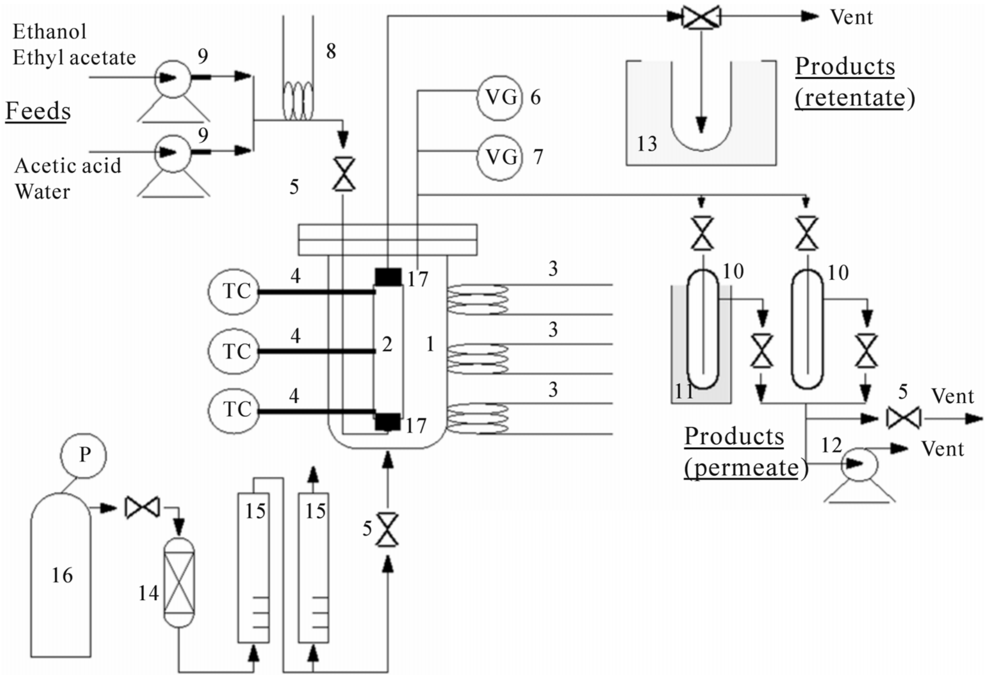

Fig. 3. A schematic design of a membrane separation by pervaporation system.

1. Module
2. Membrane
3. Heater
4. Thermocouple
5. Needle valve
6. Vacuum gauge (>0.0040 bar, abs.)
7. Vacuum gauge (<0.0040 bar, abs.)
8. Pre-heater
9. Syringe pump
10. Liquid N_2 trap
11. Liquid N_2
12. Vacuum pump
13. Ice bath
14. Gas cleaning trap
15. Flow-meter
16. Cleaning gas
17. Carbon sealing

for pervaporation experiments.

2. Pervaporation Experiments

A membrane module with a polymeric/ceramic composite membrane placed at its center was constructed as shown in Fig. 3. It was used to measure the separation characteristics of the composite membrane. During the pervaporation separation experiments, two separate feed streams were introduced into the membrane inside in order to prevent unnecessary reaction between acetic acid and ethanol catalyzed by acetic acid as a self-catalyst for esterification. The first one consisted of 14 mole% of ethanol (dehydrated, 200 prof., Quantum Chemical Corp.) and 36 mole% of ethyl acetate (99%, Fisher Chemical), and another one contained 14 mole% of acetic acid (glacial, 99.7%, EM Science) and 36 mole% of water. This feed composition is near an equilibrium composition produced from an equimolar ethanol and acetic acid mixture at room temperature. We chose this particular composition since this equilibrium composition was more appropriate for the reactor applications, which is generally product composition of conventional reactors.

This mixture was delivered by a syringe pump (ATI, Sage). The inside of the membrane was packed with spherical inert nonporous glass beads (60/80 mesh, Alltech Associates, Inc.). The observed external bed porosity equals 0.3. The space time, τ, equals the reactor pore volume of 1.77×10^{-6} m^3 divided by the total volumetric flow rate of the inlet, ranged from 27.0 to 27,000 sec. To maintain isothermal conditions along the membrane tube length, the reactor was heated by three different heaters controlled by Omega CN9000A digital PID temperature controllers connected to Omega *J*-type thermocouples. Vacuum on the permeate-side was maintained by using an Alcatel 2004A mechanical vacuum pump. Over the entire range of conditions for the pervaporation experiments, the permeate-side pressure was kept at a constant value of 2.67×10^{-3} bar (i.e., 2.0 torr). Pressure for the permeate-side was monitored by a Varian 801 digital vacuum gauge and another analogue type vacuum gauge in order to cover a broad range of pressure. The pressure was controlled by a metering needle valve attached between the liquid nitrogen traps to the vacuum pump. The system reached steady state conditions after 2 to 6 hours from the start of the experiments depending on the experimental conditions. After steady state conditions were attained, the permeate products were collected by two liquid nitrogen traps for 6 hours. To measure compositions of the retentate-side products, samples were regularly collected by a syringe through a rubber septum installed on the top of the outlet for the membrane module. The samples were analyzed by GC. The two liquid nitrogen traps were switched to discharge the collected frozen product from time to time. At relatively higher temperature, the membrane allows more ethyl acetate permeation together with the water. Under such experimental conditions, the permeate products frequently showed phase separation between the water and the ethyl acetate. For the GC analysis, in this case, a 10 vol% of *sec*-butyl alcohol (99.8%, Fisher Scientific) was added to homogenize the samples before the sample was injected into the GC.

3. Separation Characteristics

For measuring of the pervaporation membrane separation, fluxes and separation factors for the quaternary mixture were experimentally measured, and subsequently permeances were calculated by using the estimated activity and fugacity assisted by appropriate thermodynamic properties.

The permeances and the separation factors are two major mass transfer characteristics for pervaporation membrane separation. The permeances are overall mass-transport coefficients encompassing a variety of phenomena that occur during pervaporation through the membranes. They include sorption between the molecules and the surface of the membranes, diffusion through the membrane, desorption from the permeate-side, and bulk mass-transport on both interfaces of retentate-side and permeate-side of the membrane [Mulder, 1996]. The permeances are defined by dividing the fluxes of each component i by the activity in retentate-side and fugacity in permeate-side difference for non-ideal solutions, and have units of moles/m^2/sec/bar. If the membrane is very thin, it can be assumed that its morphology does not change, i.e., no swelling, substantially by sorption, and its permeance no longer depends on the thickness of the membrane. The permeance, U_i, is conventionally defined by Eq. (1), Eq. (2) and Eq. (3):

$$U_i = \frac{H_i}{l} \equiv \frac{J_i^{PV}}{f_i^R - f_i^P} \tag{1}$$

where,

$$f_i^R = \gamma_i^L x_i P_i^{SAT} \tag{2}$$

$$f_i^P = y_i P^V \Phi_i^V \tag{3}$$

in the above expression, H_i is the normalized permeability, which is a more appropriate transport parameter to use when the swelling due to sorption is significant, l, is the thickness of the membrane, f_i the fugacity, and superscripts R, P, L, V, SAT and PV represent retentate-side, permeate-side, liquid phase, vapor phase, saturation and pervaporation, respectively. The γ_i is activity coefficient and the Φ_i is fugacity coefficient of molecules in liquid phase and vapor phase, respectively. The activity coefficient was estimated by using the UNIQUAC equation with appropriate parameter values. The fugacity coefficient was calculated with the so-called Soave modified Redlich-Kwong equation of state with critical values of molecules. The parameter values are summarized elsewhere for both the UNIQUAC equation and the Soave modified Redlich-Kwong equation of state [Prausnitz et al., 1986].

The ability of the pervaporation membrane to separate a feed mixture is commonly determined by binary separation factor, which is a relative value and is very similar to relative volatility in distillation. The separation factor can be defined as Eq. (4):

$$\alpha_{i-j} = \frac{y_i^P / y_j^P}{x_i^R / x_j^R} \tag{4}$$

where, y is a vapor mole fraction of the chemical species on the permeate-side and x is a liquid mole fraction of the feed mixture on the retentate-side.

RESULTS AND DISCUSSIONS

1. Effects of the Space Time for Binary Separation

As a preliminary experiment, in order to find reasonable range of membrane length, we performed binary ethanol-water separation experiments. However, due to limitations, i.e., too short or too long to do experiments, of the length of the membrane, we changed space time instead of the membrane length. Fig. 4 is a plot of the experimental results of the separation experiments involving a binary feed mixture consisting of 36 mole% of water and 64 mole% of ethanol. In these separation experiments, a polymeric/ceramic composite membrane was utilized packed with inert nonporous spherical glass beads. The glass beads provided a mixing effect in the membrane retentate-side. The binary separation experiments took-place at 313 K and a permeate-side pressure of 2.67×10^{-3} bar. The space time ranged from 27 to 27,000 sec, which corresponded to the length of the membrane from 0.0017 m to 1.7 m. The largest space time of the 27,000 sec was the upper experimental limit in this system, for which we were able to maintain a constant volumetric feed flow rate.

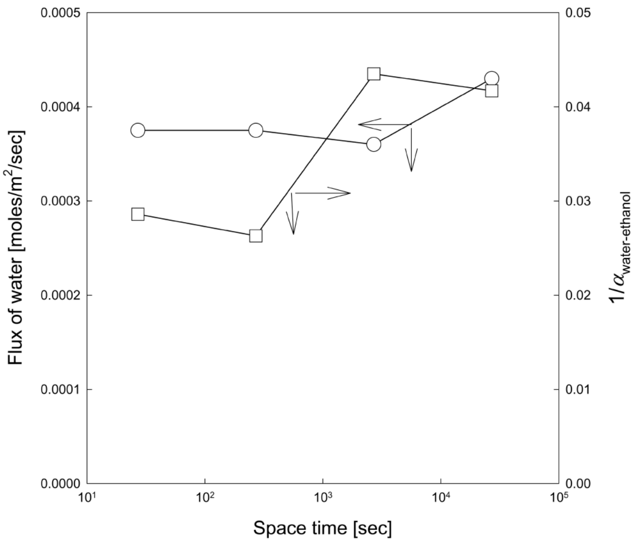

Fig. 4. Flux of water as a function of space time for a binary water-ethanol feed mixture at 313 K, permeate-side pressure of 2.67×10^{-3} bar and mole fraction of water equals to 0.360.

When the system reached steady state conditions, several data points were collected for a single experiment at a fixed value of a space time. In Fig. 4, the points were the averaged value of the experimentally observed data under steady state at a given space times. In Fig. 4, the permeance of water and the binary separation factor were calculated by using Eq. (1), Eq. (2), Eq. (3) and Eq. (4), correspondingly, employing the UNIQUAC equation to calculate the activity coefficients and Soave modified Redlich-Kwong equation of state to estimate the fugacity coefficients. The experimentally observed water flux varied from 3.75×10^{-4} to 4.3×10^{-4} mole/m^2/sec. In the same range of space times from 27 to 27,000 sec, these corresponded to the length of the membrane from 0.0017 m to 1.7 m; the separation factor varied from 24 to 35. Over the entire range of the space time, the water flux seemed fairly constant within the experimental error of measurement; meanwhile, the separation factor slightly decreased between the space time of 270 sec to 2,700 sec. Tentatively, this is because of the effect of the composition change on the water and ethanol along the length of the membrane. As is well known in the membrane separation by pervaporation, the separation factor is influenced by composition of the feed water and ethanol mixture. In the experiment at the space time of 27,000 sec, over the space time of 270 sec, the concentration of water decreased

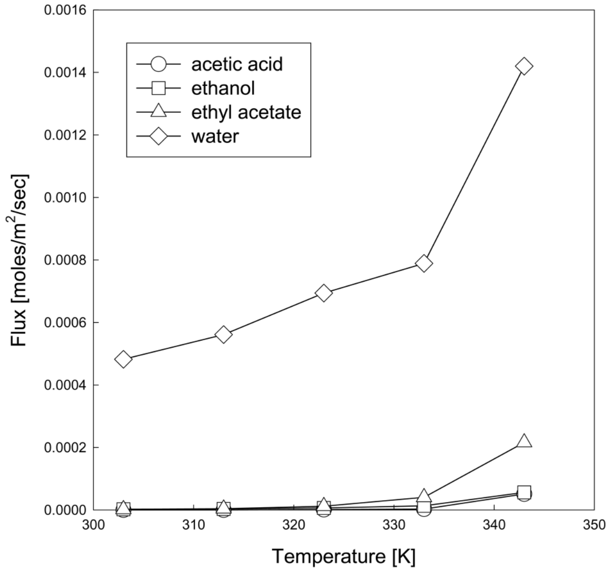

Fig. 5. Fluxes of various chemical species for a quaternary acetic acid-ethanol-ethyl acetate-water equilibrium feed mixture as a function of temperature at the permeate-side pressure of 2.67×10^{-3} bar and a space time 2,700 sec.

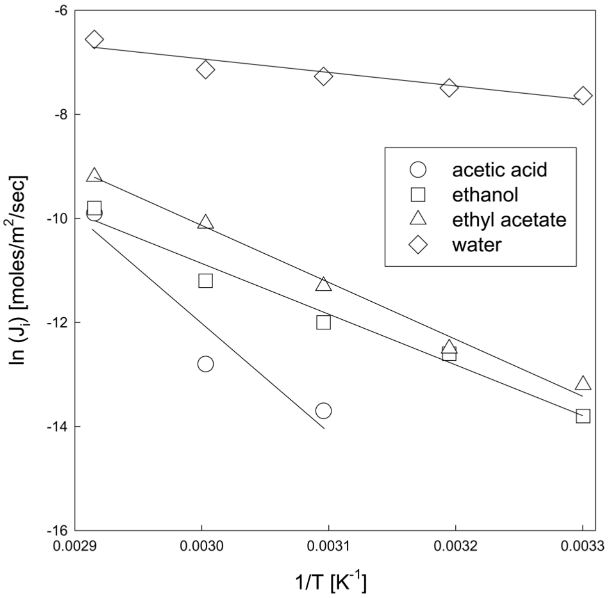

Fig. 6. Linear plots using Arrhenius type empirical correlation for the various chemical species measured from a quaternary acetic acid-ethanol-ethyl acetate-water equilibrium feed mixture at the permeate-side pressure of 2.67×10^{-3} bar and a space time 2,700 sec.

since a certain amount of water already permeated through the membrane within the space time from zero to 270 sec. Therefore, relatively less amount of water remained in the retentate-side to be separated over the space time of 270 sec. Consequently, a relatively high level of ethanol permeation occurred over the space time of 270 sec. This situation led to the decrease of the separation factor, and happened between the space time of 270 sec and 2,700 sec. All water in the retentate-side was eventually being depleted by the pervaporation if the space time was much smaller than 2,700 sec. In the tested range of space time, however, it seems that the system was not significantly influenced by the composition change.

2. Effect of Temperature for Flux Measured from a Quarternary Equilibrium Mixture

Fig. 5 is a plot of flux, experimentally measured with a quaternary equilibrium feed mixture by using the polyetherimide/γ-alumina composite membrane. This feed composition corresponds to the hypothetical conversion of 72% from a conventional reactor with an equimolar ethanol and acetic acid feed mixture. The permeate-side pressure was fixed values of 2.67×10^{-3} bar and the space time 2,700 sec, which was corresponding to the membrane length of 0.17 m, calculated at the entrance condition of the membrane. The observed flux for water was in the range of 4.82×10^{-4} to 1.42×10^{-3} mole/m^2/sec. This level of water flux was similar to what Zhu et al. [1996] has reported for water-ethanol binary separation by pervaporation using polyetherimide/γ-alumina membrane. The fluxes of the various chemical species exponentially increased as a function of increasing temperature. This is because, the polymer chain is going to be loose when the polymer is exposed to elevated temperature. This situation leads to swelling of polyetherimide membrane by increase of free volume within inter-molecular polymer chains, and, as a result, this free volume provides large size of passages for the mass transfer of the feed molecules. According to Muramatsu et al. [2003], the size of the passage produced by the free volume is exponentially proportional to temperature change.

Table 1. Activation energies and preexponential coefficients of fluxes

Components	Activation energies E_a [KJ/mole]	Preexponential coefficients, J_0 [moles/m^2/sec]
Acetic acid	174	1.19×10^{-6}
Ethanol	81	6.33×10^{-6}
Ethyl acetate	90	1.27×10^{-5}
Water	21	7.03×10^{-4}

In order to analyze details of the temperature effect, as shown in Fig. 6, we performed linear regression using an Arrhenius type empirical correlation as follows:

$$J_i = J_{i0} \cdot e^{-\frac{Ea}{RT}} \tag{5}$$

where, J is a flux, J_0 a preexponential coefficient, E_a an apparent activation energy, R an ideal gas constant, and T an absolute temperature. The subscripts i refer to the chemical species i.

Table 1 is a summary of regression results for the activation energies and the preexponential coefficients. According to Table 1, the apparent activation energy of the water flux measured from the quaternary feed mixture was 21 KJ/mole, which was the lowest value among the four components. The highest activation energy value was observed for acetic acid, which was 174 KJ/mole. Ethanol and ethyl acetate showed similar level of activation energies. Therefore, the flux of acetic acid was the most sensitive for temperature change; meanwhile the flux of water was slightly influenced by the temperature change. It appears that acetic acid more strongly swells the polyetherimide membrane than other components at relatively high temperature.

In comparison, the activation energy of the ethanol was 81 KJ/mole, about four times higher than that of water; the activation energy of ethyl acetate was four times higher, and the activation energy of acetic acid was about eight times higher. These differences in the activation energies among the four chemical species were significant for the membrane based pervaporation process. Presumably, affinity and/or solubility differences between each molecules and polymeric membrane surface are counted on the differences in activation energies. For the polyetherimide/g-alumina composite membrane for pervaporation, the activation energies of the fluxes for the pure water and ethanol have also been reported by Qariouh et al. [1999]. They have reported the activation energy of the pure water to be 45 KJ/mole, and the activation energy of the pure ethanol to be 92 KJ/mole. Though these values differ from the value measured by us with the quaternary mixture that is reported in this work, it is interesting to note that the permeation data for the pure ethanol show significantly higher activation energy than that of water.

3. Effect of Temperature for Permeance and Separation Factor Measured from a Quarternary Mixture

Fig. 7 shows the permeances of the four components in the feed mixture. The values ranged from zero to 2.39×10^{-3} mole/m^2/bar/sec for acetic acid, 1.33×10^{-4} to 4.43×10^{-4} mole/m^2/bar/sec for ethanol, 2.07×10^{-5} to 4.64×10^{-4} mole/m^2/bar/sec for ethyl acetate and 2.07×10^{-2} to 7.33×10^{-3} mole/m^2/bar/sec for water, correspondingly. The values are summarized in Table 2. The highest permeance level were observed for water, while the permeance levels for other components are significantly low. The water is a byproduct in esterification, and has to be removed for equilibrium shifting enhancement and purification purposes in membrane reactor application. A good dehydration characteristic for reactor application of the composite membrane can be provided by such permeance level difference. According to Fig. 7, the permeance of water surprisingly slightly decreased, while the flux of the water increased with increasing temperature. It can be explained by a change of activity in the liquid phase, i.e., retentate-side, is greater than the change of the fugacity in vapor phase, i.e., permeate-side, of Eq. (1), Eq. (2) and Eq. (3), which increases with increasing temperatures. The difference between the activity and fugacity is a driving-force of mass transfer for membrane separation by pervaporation. According to the UNIQUAC equation and Soave modified Redlich-Kwong equation of state for non-ideal solution, both the activity, and fugacity are temperature dependent, while only the concentration of liquid phase is temperature independent [Prausnitz et al., 1986]. As seen in Table 2, in a high temperature range, the permeances of acetic acid, ethanol and ethyl acetate are not negligible when compared with the permeance of water. In this relatively high temperature condition, as previously explained, high level of swelling takes-place due to increase of free volume formed in the polyetherimide membrane. Moreover, it seems that this composite membrane seems not applicable for the separation of multi-component mixture. However, only the range of the low temperature condition is interesting in the membrane reactor

Table 2. Permeance of a quaternary acetic acid-ethanol-ethyl acetate-water equilibrium mixture for various temperatures at the permeate-side pressure of 2.67×10^{-3} bar and a space time 2,700 sec

T [K]	Permeance, U_i [moles/m^2/bar/sec]			
	Acetic acid	Ethanol	Ethyl acetate	Water
303	0.0	1.33×10^{-4}	2.07×10^{-5}	2.07×10^{-2}
313	0.0	1.06×10^{-4}	2.66×10^{-5}	1.32×10^{-2}
323	1.41×10^{-4}	1.19×10^{-4}	5.47×10^{-5}	9.43×10^{-3}
333	2.01×10^{-4}	1.61×10^{-4}	1.25×10^{-4}	6.47×10^{-3}
343	2.39×10^{-3}	4.43×10^{-4}	4.64×10^{-4}	7.33×10^{-3}

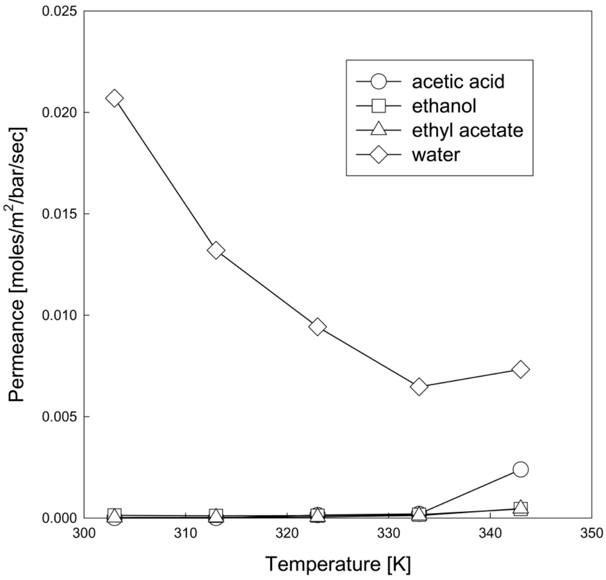

Fig. 7. Permeances of various chemical species for a quaternary acetic acid-ethanol-ethyl acetate-water equilibrium feed mixture as a function of temperature at the permeate-side pressure of 2.67×10^{-3} bar and a space time 2,700 sec.

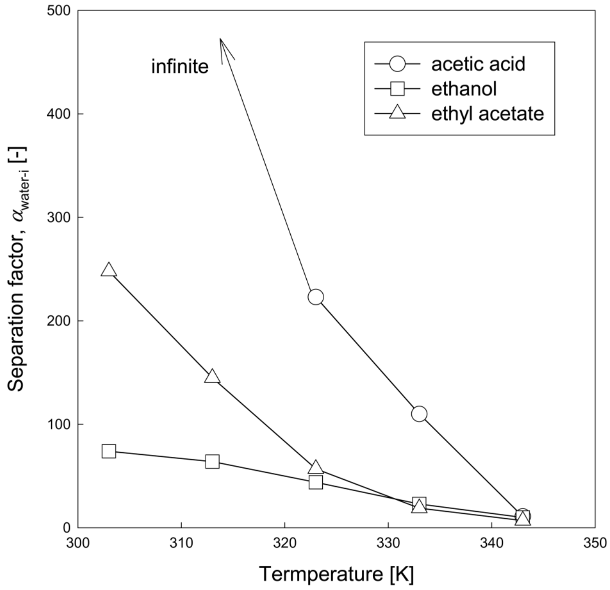

Fig. 8. Separation factors of various chemical species for a quaternary acetic acid-ethanol-ethyl acetate-water equilibrium feed mixture as a function of temperature at the permeate-side pressure of 2.67×10^{-3} bar and a space time 2,700 sec.

Table 3. Separation factors of a quaternary acetic acid-ethanol-ethyl acetate-water equilibrium mixture for various temperatures at the permeate-side pressure of 2.67×10^{-3} bar and a space time 2,700 sec

T [K]	Separation factor, $\alpha_{water-i}$		
	Acetic acid	Ethanol	Ethyl acetate
303	infinite	74	248
313	infinite	64	145
323	223	44	57
333	110	23	19
343	11	10	7

operation as one of the most typical advantages on the membrane reactor [Park and Tsotsis, 2004].

Fig. 8 shows separation factors for all four components as a function of temperature. The separation factors for acetic acid, ethanol and ethyl acetate decreased when temperature increased. Amount of water rapidly accumulated in the permeate-side, and its ratio was much greater than other components upon temperature increasing. As explained earlier, this trend of the separation factors against temperature again seems due to the effect of free volume forming in the polyetherimide membrane. In this circumstance, the membrane showed poor separation factors. The values of the separation factors for all components asymptotically approached more or less 10 at a temperature of 343 K. In the range of temperature condition over 343 K, the size of the passages produced by free volume is tentatively greater than the size of the feed molecules. As a result, the polyetherimide membrane will show no more separation behavior.

The values of the separation factors are summarized in the Table 3. The binary separation factor for water-acetic acid varies from 11 to infinite, for water-ethanol varies from 10 to 74, and water-ethyl acetate varies from 7 to 248 at various temperatures. The highest temperature sensitivity of flux for acetic acid, i.e., high activation energy, led the rapid change of separation factor when the temperature increased. Wang et al. [1999] have also reported that the separation factor for the binary water and ethanol system depends on temperature.

CONCLUSION

Polyetherimide/γ-alumina composite membrane was prepared for further reactor application. The prepared composite membrane was characterized by measuring separation factors and permeances for a quaternary acetic acid-ethanol-ethyl acetate-water equilibrium mixture. The change of flux for acetic acid has been proven as the most sensitive on the change of temperature, and has shown the highest value of apparent activation energy. The highest permeance value has been observed for water over the entire range of experimental conditions. At relatively high temperature conditions, the polyetherimide membrane has shown a certain level of swelling and consequently has shown a poor separation factor. However, from room temperature up to a temperature of about 333 K, this composite membrane shows sufficient separation factors and permeances, and withstands for existing sulfuric acid as a strong inorganic acid and relatively high temperature conditions. This range of the temperature condition is the more interesting range for reactor applications. Moreover, obviously, there is a strong synergy between the good separation characteristics of the polymeric membrane and the physical and chemical stability of the ceramic membrane.

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We thank Prof. Theodore T. Tsotsis of the Department of Chemical Engineering at the University of Southern California for his valuable discussion on this work.

NOMENCLATURE

Ea : activation energy [KJ/mole]
f : activity or fugacity [bar]
H : normalized permeance [moles/m^2/sec/bar/m]
J : flux [moles/m^2/sec]
l : thickness of membrane [m]
P : pressure [bar]
T : absolute temperature [K]
U : permeance [moles/m^2/sec/bar]
x : mole fraction of liquid-phase
y : mole fraction of vapor-phase

Greek Letters

α_{i-j} : binary separation factor
γ : activity coefficient
Φ : fugacity coefficient

Subscripts and Superscripts

i : components, acetic acid, ethanol, ethyl acetate, water
j : components, acetic acid, ethanol, ethyl acetate, water
L : liquid-phase
P : permeate-side
PV : pervaporation
R : retentate-side
V : vapor-phase

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