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Pervaporation performance and Transport phenomenon of PVA blend membranes for the separation of THF/water azeotropic mixtures

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Summary

Dense polymer membranes were made by mixing aqueous solutions of hydrophilic polymers poly(vinyl alcohol) (PVA) and polyethyleneimine (PEI) in different ratios for investigating the separation of Tetrahydrofuran (THF)/water azeotropic mixtures by pervaporation (PV). In order to gain a more detailed picture of the molecular transport phenomenon, we have performed sorption gravimetric experiments at 30°C to compute diffusion, swelling, sorption and permeability coefficients of PVA/PEI membranes in the presence of THF and water. The membranes were found to have good potential for breaking the azeotrope of THF at 6% concentration of water. An increase in PVA content in the blend caused a reduction in the flux and an increase in selectivity. Among the blends tested in the study, the 5:1 PVA/PEI blend membrane showed the highest separation factor of 181.5, exhibited a flux of 1.28 kg/m^{2}h for THF respectively at azeotropic feed composition.

Introduction

Pervaporation (PV) is an efficient membrane based process used for the economical separation of liquid mixtures, especially aqueous–organic azeotropes, closely boiling mixtures, isomers, besides heat sensitive and hazardous compounds [1, 2]. PV separation is based on the differences in sorption and diffusion properties of the permeating molecules [3, 4]. Generally hydrophilic polymers are used to prepare membranes for the separation of various solvent-water mixtures in the pervaporation because the water molecule is easily incorporated into the hydrophilic polymeric membrane. Among the hydrophilic polymer membranes, Poly(vinyl alcohol) (PVA) is one of the widely used material in PV due to its excellent film forming capacity, chemical stability and good selectivity towards water inspite of poor physical stability in aqueous medium. The films must be insolubilized by crosslinking or blending with other polymers to improve the stability in aqueous solutions, for the crosslinked polymers have a netlike structure as compared to linear polymers [5-12].

THF is a relatively expensive solvent and thus being able to recover used solvent by dehydration can offer significant savings whilst also being environmentally beneficial. THF is soluble in water in all proportions and thus, it cannot be separated by the use of conventional distillation. Therefore, PV would be a better candidate for dehydration of THF since unlike distillation it can be carried out at low temperature and the azeotropic composition encountered in distillation can be separated by PV using a dehydrating membrane without any requirement of a third entrainer. THF forms an azeotrope with water at 5.3 wt% concentration and the mixture of THF–water needs dehydration during manufacture of THF [13].

Poly(ethyleneimine) (PEI) is a branched chain cationic hydrophilic polymer with a lot of amine groups and has been extensively used to modify membrane surfaces [14] Because of its amino functional groups, PEI is used to prepare blend membranes with anionic polymers like cellulose acetate, poly(p-chloro methyl styrene) and poly(methacrylate) [15-19]. Though PVA membranes are proven materials for the dehydration of alcohols, their performance has not been satisfactory for the separation of water from organics such as tetrahydrofuran or 1,4-dioxane, due to low selectivities.

The present investigation is an attempt to enhance the performance of PVA membranes for dehydrating THF–water mixtures by blending the polymer with poly(ethyleneimine) (PEI). This work also explores the effect of varying the blend ratios on the separation performance parameters such as flux and selectivity. In order to gain a more detailed picture of the molecular transport phenomenon, sorption measurements are conducted to explain the mechanism of interaction between the polymers constituting the blend as well as PV results.

Experimental

Materials

PVA, of weight average molecular weight (Mw) 125,000, degree of hydrolysis 98–99%, degree of polymerization 1570±50 and saponification degree 99% was purchased from Loba Chemie, Mumbai, India. The aqueous solution (50 wt%) of PEI (Mn = 70,000) having primary, secondary and tertiary amino groups in the ratio of 1:2:1 were purchased from Aldrich, USA. Solvent THF of purity 99.9% was purchased from S.D. Fine Chemicals, Mumbai. Deionized water of conductivity 0.02 mS/cm for preparation of feed solutions was generated in the laboratory itself.

Membrane preparation

PVA/PEI membranes were prepared by solution casting and solvent evaporation technique. 7g of PVA was dissolved in 93 ml of deionized water to form a 7 wt% solution at 90°C. A 7 wt.% of PEI solution was prepared individually by dissolving 3.5 g of 50% PEI in 23.25 ml water and mixed with 7% PVA solution. PVA and PEI blends were then prepared by mixing the individual solutions in different ratios. The mixture was then stirred for a period of half an hour to form a homogeneous solution. The bubble free blend solution was cast to the desired thickness on a clean glass plate and solvent was allowed to evaporate slowly at room temperature for a period of 24 h.

In order to obtain a uniform dense membrane, the glass plate was placed in the oven. Drying was carried out at a temperature of about 60°C for about an hour in an oven.

Pervaporation Procedure

Experiments were carried out on a 100 ml batch level with an indigenously constructed pervaporation manifold operated at a vacuum as low as 0.25 mmHg in the permeate line. The membrane area in the pervaporation cell assembly was approximately 20 sq. cm. The experimental procedure is described in detail elsewhere [20]. Permeate was collected for a duration of 6 - 8 hours. Tests were carried out at room temperature (30 ± 2°C) and repeated twice using fresh feed solution to check for reproducibility. The collected permeate was weighed after allowing it to attain room temperature in a Sartorius electronic balance (accuracy: 10^{-4} gms) to determine the flux and then analyzed by gas chromatography to evaluate the membrane selectivity.

Analytical procedure

The feed and permeate samples were analyzed using a Nucon Gas Chromatograph (Model 5765) installed with Thermal Conductivity Detector (TCD) and packed column of 10% DEGS on 80/100 Supelcoport of 1/8" ID and 2 m length. The oven temperature was maintained at 70°C (isothermal) while the injector and detector temperatures were maintained at 150°C. The sample injection size was 1 μl and pure hydrogen was used as the carrier gas at a pressure of 1Kg/cm^2. The GC response was calibrated for this particular column and conditions with known compositions of organic solvent-water mixtures and the calibration factors were fed into the software to obtain correct analysis for unknown samples.

Dynamic swelling

Dynamic and equilibrium swelling of the known weight circular pieces of crosslinked polymer films (3 cm dia.) were carried out at 30°C until equilibrium was attained in the presence of THF/water azeotropic mixtures and as well as individual components. Sorption was one of the control steps in PV separation in the solution-diffusion models. The films were taken out after different soaking periods and quickly weighed after carefully wiping out excess liquid to determine the amount absorbed at the particular time ‘t’. The films were then quickly placed back in the solvent. During this period, total time spent by the membrane out side the solvent medium was kept minimum (25-35 s) to minimize the experimental error due to solvent evaporation. This error was negligible when the time spent by the membrane outside the test bottles is compared to the time spent inside the solvent medium. The process was repeated until the films attained steady state as indicated by constant weight after a certain period of soaking time. Weight gain, Q_t of the soaked polymer membranes is expressed in mole percent units (i.e., number of moles of solvent sorbed by 100 g of the polymer), which is calculated as [21]

$$Q_t = \left(\frac{W_t - W_i}{W_i} \right) \frac{100}{M_s} \qquad \mathbf{(1)}$$

where W_t and W_i are, respectively weight gains at time, t and initial weight; M_s is molecular weight of the sorbed liquid. When equilibrium was reached Q_t was taken as Q_∞.

Since permeation of a solvent through a polymeric membrane occurs due to diffusion of molecules and hence, permeability coefficient, P can be calculated as

$$P = DS \qquad (\mathbf{2})$$

where D is diffusion coefficient and S is solubility or sorption coefficient. Sorption coefficient is simply equilibrium sorption, which was calculated as

$$S = \frac{M_\infty}{M_0} \qquad (\mathbf{3})$$

where M_∞ is equilibrium mass of the membrane and M_0 is its initial mass.
Diffusion coefficient was computed from sorption results using the equation [22]

$$D = \pi \left(\frac{h\theta}{4Q_\infty} \right)^2 \qquad (\mathbf{4})$$

where θ is slope of the linear portion of the sorption curve before attainment of 60 % equilibrium and h is initial film thickness. Estimated values of D, S, and P are given in Table 1.
Swelling coefficient α was calculated using the following equation [23]

$$\alpha = \left(\frac{M_\infty - M_0}{M_0} \right) \times {}^{1}\!/_{\rho_s} \qquad (\mathbf{5})$$

where M_∞ and M_0 are masses of the swollen membrane and initial mass of the membrane, and ρ_s is density of the solvent.
The percent sorption is obtained from

$$\%\ \text{Sorption} = \frac{Ms - Md}{Md} \text{x}100 \qquad (\mathbf{6})$$

where
Ms = mass of the swollen polymer in g
Md = mass of the dry polymer in g

Flux and selectivity equations

In pervaporation the flux J of a given species, say faster permeating component i of a binary liquid mixture comprising of i (water) and j (solvent) was given by:

$$J_i = \frac{W_i}{At} \qquad (\mathbf{7})$$

where W_i represents the mass of water in permeate (Kg), A is the membrane area (m^2) and t represents the evaluation time (hr). In the present study, though different membrane thicknesses were utilized, the flux has been normalized and reported for thickness of 10μm.
The membrane selectivity was the ratio of permeability coefficients of water and solvent and can be calculated from their respective concentrations in feed (X) and permeate (Y) as given below:

$$\alpha = \frac{Y_{H_2O} / Y_{THF}}{X_{H_2O} / X_{THF}} \qquad (\mathbf{8})$$

Often, enrichment factor, β calculated from Eq. (9) has been used to test the membrane performance [24, 25]

$$\beta = C_w{}^p / C_w{}^F \qquad \textbf{(9)}$$

Here, $C_w{}^p$ and $C_w{}^F$ are concentrations of water in permeate and feed sides. The PV separation results are compiled in Table 2.

Quite often, pervaporation separation index (PSI) is used to describe the overall performance of a membrane for a selected feed mixture. This can be calculated from the product of water flux, j, and selectivity, α.

$$PSI = J_i \times \alpha \qquad \textbf{(10)}$$

Results and discussion

The solubility behavior of the membranes synthesized in the present work is studied by dissolving in different solvents such as dimethyl formamide (DMF), isopropyl alcohol (IPA), diethyl ether (DEE), and chloroform along with distilled water. PVA is soluble in water and DMF, PEI is soluble in water, IPA and DEE but their blend is insoluble in all the solvents including water. However, their blend undergoes swelling to some extent in water. This nonsolubility of the blend may be due to the formation of a weak force of interaction, resulting on blending the two homopolymers. PVA/PEI blend membrane is highly hydrophilic in nature and it preferentially absorbs water owing to extensive intra- and intermolecular hydrogen bonding and dipole–dipole interactions between water and the functional groups of PVA/PEI membrane such as amine, acetal, and hydroxyl besides unreacted amine moieties. The membranes were extensively characterized by FTIR, XRD, TGA, and tensile testing respectively, to observe its intermolecular interactions, crystallinity, temperature resistance, and mechanical strength of membranes. Detailed characterization of all membranes of PVA/PEI is given elsewhere [26].

Sorption effects

Sorption is the other significant step other than diffusion in solution-diffusion models. This section is to determine the influences of sorption in pervaporation performance. The pervaporation transport mechanism can be well interpreted by the solution-diffusion model. The water sorption of PVA/PEI membranes for THF/water mixture is shown in Table 1, where water amount sorbed in the membrane decreases with PVA content in the membrane ratio i,e, 2:1 to 5:1 at azeotropic concentration of THF/water mixture. The hydrophilic groups in these membranes are responsible for the preferential water sorption. Results of *S*, *P* and *D* for THF, water and THF/water mixture (94.5/5.55 wt%) are presented in Table 1 at temperature (30°C). It is evident that the permeability coefficient value decreases with increase in PVA content in the blends. The presence of PVA hinders the movement of solvent molecules between the polymer chains due to more interactions with excessive amino groups of polyethyleneimine. So a lower value of *D* as PVA content increases. The S value also shows a same trend. Since the permeability coefficient is the net effect of D and S the P value decreases with increase in PVA content in the blends. The values show that PVA/PEI membranes allow only the molecules of water than THF and confirmed that present membranes are hydrophilic.

Table 1: Dynamic Swelling studies of PVA/PEI membranes in THF, Water and THF/Water azeotropic mixtures

PVA/PEI Membrane Ratio	Sorption Coefficient (S)	Diffusion Coefficient D x 10^7 (cm^2/s)	Permeability Coefficient P x 10^7 (cm^2/s)	Swelling coefficient (α)
		THF		
2:1	1.030	0.020	0.021	0.033
3:1	1.014	0.018	0.018	0.016
4:1	1.008	0.009	0.009	0.009
5:1	1.006	0.004	0.004	0.006
		Water		
2:1	5.788	100.458	581.46	4.788
3:1	4.903	90.817	445.26	3.902
4:1	3.798	72.383	274.92	2.798
5:1	3.304	58.024	191.75	2.304
		THF/Water (94.5/5.5)		
2:1	1.152	0.915	1.054	0.167
3:1	1.136	0.682	0.776	0.151
4:1	1.075	0.471	0.507	0.082
5:1	1.050	0.294	0.309	0.055

Effect of PVA ratio in the membranes on the pervaporation performance

Table 2 shows the effect of the membrane composition on pervaporation performance for the separation of THF/water mixtures at azetropic feed composition, at a temperature of 30°C, constant permeate pressure of 0.25mmHg and a membrane thickness of 50 µm. From this table, it is noticed that water flux decreased from 0.79 to 0.73 kg/m^2.h and selectivity increases from 107.9 to 181.5 with increasing PVA concentration. Increased swelling makes the polymer chains more flexible and allows unrestricted transport of both the feed components resulting in high flux. At lower PVA concentration, the membrane swells appreciably because of the presence a number of $-NH_2$ groups of the relatively more hydrophilic PEI. Higher concentration of PVA causes increased interaction between amino groups of PEI and hydroxyl groups of PVA. The alignment of polymer chains in the polymer network also plays a crucial role in the separation performance. This is essential because it is the consideration of the entire membrane property not the structure of one component polymer. The morphological structures of polymer network highly influence the free volume in the matrix and eventually affect the solubility and diffusivity of feed components through the membranes. The total flux from 5:1 membrane was lower but the selectivity was higher than those from the other membranes. This could be attributed to the free volume reduction in polymer network of 5:1 membrane. Thus increase of PVA content in a membrane allows lower mass transport of water across membrane. As can be seen from Table 2, water content in permeate increases when PVA composition in a membrane increased from 2:1 to 5:1. Even though the polymer matrix of 5:1 membranes is likely to be more compact than that of 2:1 membranes, both selectivity and water concentration in permeate from the 5:1 membrane were higher than those from the 2:1 membrane. This could be due to the reduction of intersegmental spacing with increasing PVA content in the membranes. However, the flux content in 5:1

membrane was lower than from other membranes. This could be because of the fact that polymer matrix of the 5:1 membrane is more condensed than that of the 2:1 membrane. It is possible that the polymer chains fill in free volume and this leads to higher density of polymer network in the 5:1 membrane. Increased interactions also reduces the degree of swelling which lowers the free volume of the polymer due to the close proximity of the chains thus enabling preferential permeation of water molecules which are smaller in size and therefore diffuses faster than THF molecules. The right proportion of PVA and PEI in a membrane will result in the best selectivity. Thus, in this case, the 5:1 PVA/PEI membrane is the best.

The separation performance of the membranes is evaluated in terms of pervaporation separation index (PSI), which gives the combined result of selectivity and flux. The variation of PSI with the concentration of PVA in the membrane is also shown in Table 2. From this Table, it is evident that 5:1 membrane yields higher value of PSI at the 5.55 wt.% concentration of water in the feed, and it decreases with decreasing PVA content. According to the PSI values, PVA/PEI (5:1) membrane performed a better separation at azeotropic feed THF concentration. With these results the optimum ratio of PVA/PEI blends for the dehydration of THF is 5:1.

Diffusion Coefficient

Transport of molecules in PV experiments has been explained by the solution–diffusion model, since molecular transport in PV depends upon sorption and diffusion of liquid molecules through the barrier membrane and hence, attempts have been made to compute the diffusion coefficients of liquids through PVA/PEI membranes [27]. Diffusion in PV experiments occurs as a result of concentration gradient and driving force across the membrane created as a result of pressure differential due to the application of high vacuum (lower pressure compared to feed side) on the permeate side. Diffusion coefficient, D_i of J_i solvent molecules were computed from the PV results using the equation [28,29].

$$J_i = (D_i \times C_i)/h \qquad \textbf{(11)}$$

where C_i is concentration of water or THF in the feed mixture after completion of the PV process, J_i is flux of the given species and h is membrane thickness. Computed values of D_i at 30°C are also included in Table 2. Notice that diffusion coefficients calculated from Eq. (4) i.e., before completion of 60 % equilibrium sorption are quite different than those computed from Eq. (11) due to different processes (see Tables 1 and 2). However, these cannot be compared on an absolute scale due to the fact that experimental set up and the systems chosen for the study are different. In order to ascertain the mechanism of liquid diffusion through PVA/PEI membranes, we have analyzed the mol % sorption data using the empirical equation [30]

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \qquad \textbf{(12)}$$

where Q_t and Q_∞ are mol % uptake values at time, t and at equilibrium, respectively; k and n are the system parameters that depend upon the structural characteristics of PVA/PEI. These values give valuable information about the nature of interactions between liquid components and PVA/PEI membranes. Values of k and n have been estimated by the method of regression analysis by fitting $\log\left(Q_t/Q_\infty\right)$ vs log t. The value of *n* indicates the type of diffusion mechanism. It was found that *n* value varied from 1 to 1.7, indicating relaxation-controlled transport i.e., Case II type transport. However n values were found 1.18 for 2:1, 1.15 for 3:1, 1.14 for 4:1 and 1.12 for 5:1 membranes respectively at azetropic concentration of THF/water indicates the diffusion follows relaxation controlled mechanism.

Table 2: Effect of blending ratio of PVA/PEI membrane on pervaporation parameters for THF/water (94.45/5.55) azeotrope mixture

PVA/PEI membrane composition ratio	Permeate concentration		Normalized Flux (J_i) ($Kg/m^2.h$)	Selectivity $\alpha = \frac{y(1-x)}{x(1-y)}$	Enrichment factor (β)	Diffusion coefficient D x 10^7 (cm^2/s)	PSI= $J_i \times \alpha$
	THF (1-y)	Water (y)					
2:1	13.62	86.38	1.384	107.9	15.56	0.856	149.4
3:1	12.39	87.61	1.367	120.3	15.78	0.832	164.5
4:1	10.68	89.32	1.321	142.4	16.09	0.788	188.1
5:1	8.57	91.43	1.286	181.5	16.47	0.748	233.5

Conclusions

PVA/PEI blend membranes appear to have promising potential for dehydration of aqueous solution of THF especially at the azeotropic composition of 6 wt% concentration of water. The blend membranes showed good ability for processing the aqueous azeotrope of 94 wt.% THF concentration, besides dehydrating the solvent to ≥99wt.% purity. With increasing PVA concentration in PVA/PEI blend membranes, permeate rate decreases, selectivity increases; this mainly includes the contribution of both decrease of the swelling degree, which reduces the free volume and also the effect of diffusion coefficient of water through a membrane. In this case pervaporation is proven as the most promising, alternative technology for the separation of aqueous-organic of THF/water at their azeotropic mixtures. In actual practice, PV could be effectively combined with distillation in a hybrid process, where THF could be distilled up to azeotropic composition from where on PV could be applied to achieve a final purity of ≥99% of tetrahydrofuran.

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