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Pervaporation Properties of Dense Polyamide-6 Membranes in Separation of Water–Ethanol Mixtures

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ABSTRACT

Several dense polyamide-6 membranes were prepared by casting 7 wt% and/or 10 wt% solutions of polymer in trifluoroethanol. The cast membranes were dried at different temperatures from 25 to 80°C. Sorption and pervaporation properties of PA-6 membranes in water–ethanol mixtures were obtained. The data obtained showed that water was preferentially sorbed into the membrane and transported through the membrane; however, the pervaporation selectivity factor α^{PV} was close to unity at higher concentrations. The selectivity parameters in pervaporation were improved for membranes obtained from 10 wt% polymer and dried at higher temperatures.

INTRODUCTION

Pervaporation is a membrane separation process used to separate liquid mixtures. In this technique the liquid feed mixture is in contact with one side of a membrane while the permeate in the vapor phase is continuously removed from the other side of membrane into a vacuum or the sweeping gas.

Pervaporation is already used in many practical applications like organics dehydration, water purification, organic–organic separation, and beverage processing (1, 2). Despite this large number of applications, current research studies in pervaporation are still focused on new polymeric membranes as well as on the optimization of the process on an industrial scale (3).

Many membranes made from different polymers using different preparation techniques have been tested for the separation of water/organic and/or organic/organic solutions by pervaporation (4), but there have been only a few reports on the applications of dense polyamide membranes (5–8).

The objective of this work was to investigate the preparation of polyamide-6 dense membranes and their pervaporation properties in the separation of water–ethanol mixtures.

THEORETICAL

The performance of a pervaporation membrane can be characterized in terms of the overall separation factor α^{PV} and the permeation flux (9, 10):

$$\alpha^{PV} = \frac{w'_{H_2O}/w'_{EtOH}}{c_{H_2O}/c_{EtOH}} \tag{1}$$

where w'_i = weight fraction of i in the permeate
c_i = weight fraction of i in the feed

Due to the coupling effects usually occurring during the transport of a binary mixture through the membrane, there is no linear relationship between the permeation flux and its concentration in the feed mixture (4, 11, 12). Huang et al. (13) and Drioli et al. (14) introduced the permeation ratio parameter Θ_i to express the deviation of the permeation of a component i when in a binary mixture from the permeation of a single component.

$$\Theta_i = J_i/X_iJ_{i,0} \tag{2}$$

where Θ_i = permeation ratio of component i
J_i = permeation flux of component i in a binary mixture
$J_{i,0}$ = permeation flux of pure component i
X_i = mole fraction of component i in the feed mixture

When $\Theta_i > 1$, the permeation of component i is enhanced by the presence of the other component; whereas for $\Theta_i < 1$, the permeation of component i is retarded by the other component.

As the swelling properties give a qualitative indication of the membrane affinity to a given liquid mixture, the sorption separation factor α^S and the sorption ratio Φ_i were also introduced to describe the behavior of a given membrane in contact with the liquid mixture (15):

$$\alpha^S = \frac{w_{H_2O}/w_{EtOH}}{c_{H_2O}/c_{EtOH}} \tag{3}$$

$$\Phi_i = S_i/X_iS_{i,0} \tag{4}$$

where w_i = weight fraction of i in the permeate
c_i = weight fraction of i in the feed
S_i = partial uptake of i component from the external solution onto a dry membrane, according to Eq. (6)
$S_{i,0}$ = swelling degree in the pure i solvent
X_i = mole fraction of component i in the feed mixture

The sorption ratios indicates the synergetic effects in the sorption of a liquid mixture into the membrane. The permeation ratio $\Phi_i > 1$ indicates that the sorption of i is increased by the presence of the other component, whereas $\Phi_i < 1$ points to the reduction of sorption.

EXPERIMENTAL

Membrane Preparation

Polyamide-6 dense membranes were prepared by using a casting method. In this method 7 and 10 wt% solutions of PA-6 in trifluoroethanol were cast onto a glass plate using a casting knife (16). The films obtained were then placed into a thermostated dryer for 24 hours at 25, 40, 60, and/or 80°C.

Polyamide-6 (MW = 30,000) was supplied by Stilon (Gorzów Wlkp., Poland). Trifluoroethanol of analytical grade was supplied by Fluka.

Swelling and pervaporation experiments were performed for PA-6 membranes prepared from a 10 wt% polymer solution cast at 40°C (PA-6 10/40) and with water–ethanol feed solutions within the whole concentration range. The performance parameters in pervaporation of water–ethanol were measured for the other prepared PA-6 membranes at a water feed concentration of 30 wt%.

Swelling Measurements

The sorption capacity of the PA-6 membranes was measured by immersing the membranes in water–ethanol solutions of a given concentration in a thermostated vessel at 25°C for 24 hours. After blotting off any excess solution, the swelled membranes were weighed and then dried in a vacuum oven at 100°C to constant weight.

The composition of sorbed liquid was determined using the system presented in Fig. 1. The swollen samples wiped off with a filter paper were placed into the sampler. The vacuum-evaporated vapors were collected into the trap cooled with liquid nitrogen and analyzed by using a Varian GC 3300 gas chromatograph.

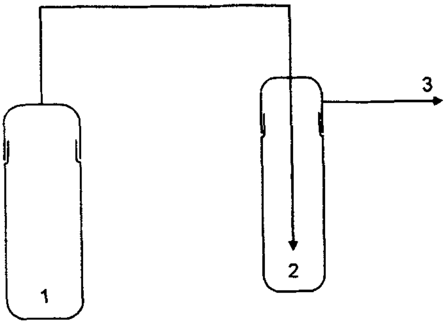

FIG. 1 Schema of the setup for the sorption measurements: (1) sampler, (2) cooled trap, (3) vacuum.

The total solution uptake S onto a dry membrane and the partial uptake of water and ethanol (S_{H_2O} and S_{EtOH}) were calculated according to the following relations:

$$S = (m - m_0)/m_0 \quad \text{(g of sorbed solution/g dry membrane)} \tag{5}$$

$$S_i = Sw_i \quad \text{(g of } i\text{/g dry membrane)} \tag{6}$$

where S = total sorption uptake (swelling degree)
S_i = partial sorption uptake of i (i = H_2O, EtOH)
m = weight of swollen membrane
m_0 = weight of dry membrane
w_i = weight fraction of i in the solution sorbed in a membrane

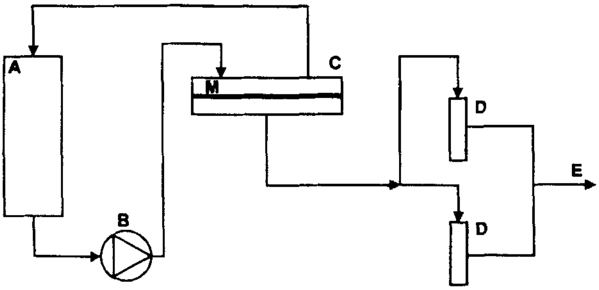

FIG. 2 Schema of pervaporation setup: (A) feed tank, (B) circulating pump, (C) pervaporation cell, (D) cooled traps, (E) vacuum, (M) membrane.

Pervaporation Experiments

Pervaporation experiments were performed using the standard setup configuration (Fig. 2). The membrane area was 19.62 cm^2. The membrane was supported by a sintered stainless-steel disc. The permeate was collected in a trap cooled by liquid nitrogen and analyzed by a Varian 3300 gas chromatograph. The permeation rate was determined by weighing the permeate. The system was operated at 25°C and at a pressure on the permeate side below 1 hPa.

RESULTS AND DISCUSSION

Swelling Experiments

Figure 3 presents the results of swelling experiments. The total swelling of the PA-6 (10/40) membrane reached a maximum with a feed solution of water weight fraction 0.5–0.6.

Sorption of water and ethanol increase monotonically, but not linearly, against the feed solution concentrations (Fig. 3). In contact with pure solvents, PA-6 (10/40) membrane sorbed 0.35 g (i.e., 1.94 × 10^{-2} mole) of H_2O and 0.30 g (i.e., 0.65 × 10^{-2} mole) of EtOH per gram of dry polymer. The sorption ratio (Fig. 4) indicates that sorption of water is enhanced by ethanol when the concentration of water in the feed solution

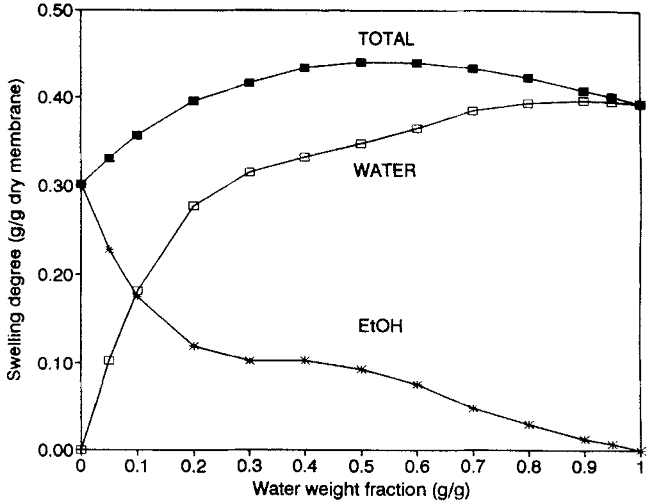

FIG. 3 Swelling of PA-6 (10/40) membrane in water–ethanol mixtures; (■) total solution uptake, (□) water uptake, (*) ethanol uptake.

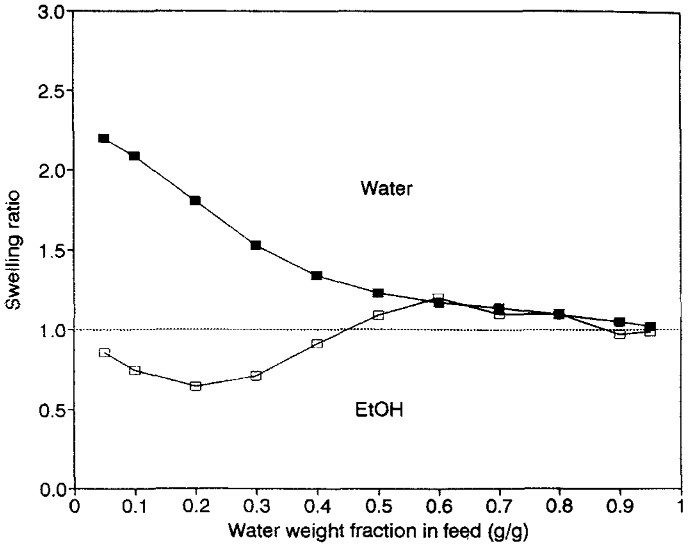

FIG. 4 Swelling ratio of ethanol (☐) and water (■) vs water weight fraction in the feed.

is below 0.5. On the other hand, the sorption of ethanol is slightly depressed at water feed concentrations below 0.4. The McCabe–Thiele separation diagram (Fig. 5) shows that water was sorbed preferentially in the whole concentration range.

Pervaporation Characteristics of PA-6 (10/40) Membrane

The total and the partial permeation fluxes of water–ethanol mixtures through a PA-6 (10/40) membrane are shown in Fig. 6. The total flux passes through a local maximum at a feed concentration range of water of 0.40–0.65, corresponding to the maximum in the sorption (Fig. 3).

The ethanol flux decreases monotonically with increasing water concentration in the feed. The concentration dependence of this flux at the lower water concentrations suggests that ethanol is transported by both a push–pull and a solution–diffusion mechanism (14, 17, 18). On the other hand, the flux of water reaches a maximum of about 0.5 $kg/m^2 \cdot h$ when the water weight fraction in the feed is 0.55–0.70 (Fig. 6).

The pervaporation ratios for water/ethanol fluxes (Eq. 2) are shown in Fig. 7. It is seen that the permeation of ethanol during pervaporation was practically unaffected by water molecules at water feed concentrations below 0.4 ($\Phi_{EtOH} \approx 1$). Positive couplings during the transport of ethanol

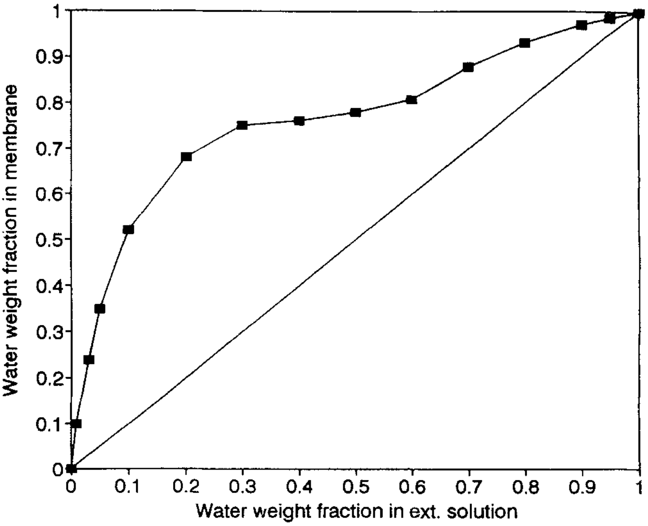

FIG. 5 McCabe–Thiele separation diagram for sorption experiment.

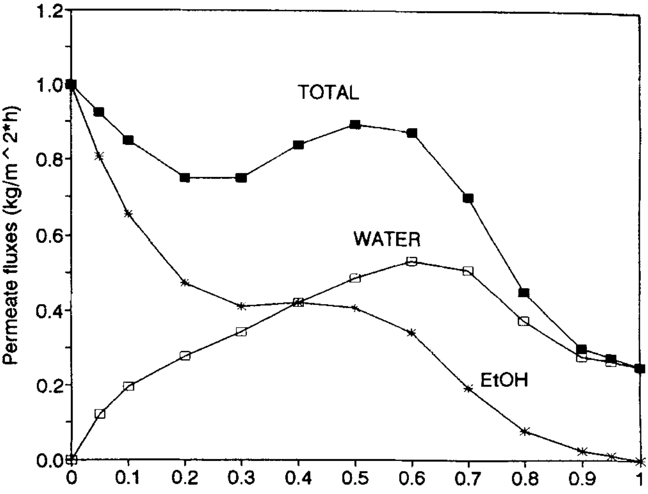

FIG. 6 Pervaporation fluxes through PA-6 (10/40) membrane; (■) total flux, (□) water flux, (*) ethanol flux.

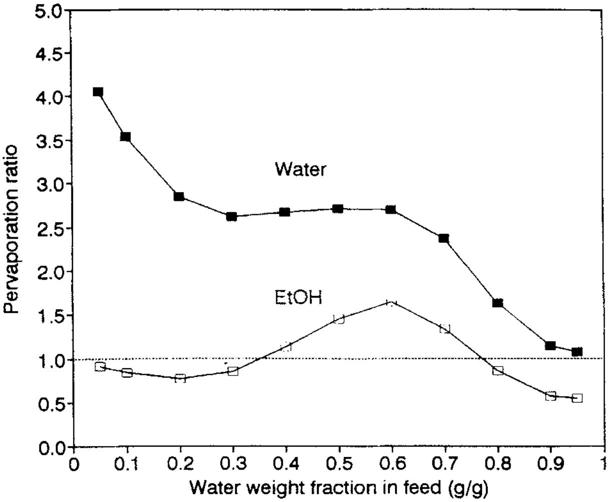

FIG. 7 Pervaporation ratio of ethanol flux (□) and water flux (■) vs water weight fraction in the feed.

molecules occur only in the feed concentration range corresponding to the maximum on the flux curve (Fig. 6). On the other hand, the flux of water is strongly influenced by ethanol over the whole concentration range. The strongest positive couplings occurred at water concentrations in the feed below 0.3 (Fig. 7).

Figure 8 presents the McCabe–Thiele separation diagram for the pervaporation of water–ethanol mixtures through a PA-6 (10/40) membrane.

The permeate is enriched in water at feed concentrations of water in the feed below 0.6. At higher feed concentrations the selectivity of a membrane decreases. The overall separation factor α^{PV} is close to unity for feed concentrations higher than 0.6 (Fig. 9). Comparing these results with the sorption results presented in Fig. 5, one can conclude that overall separation in pervaporation is governed not only by the sorption factor but also by the relative mobility of the permeating components (Fig. 9). The selectivity of the phase-transition step is another important factor which can influence the overall separation substantially (10, 12, 19).

Effect of Membrane Formation Conditions on Pervaporation Performance

The results of pervaporation experiments performed with polyamide-6 membranes prepared in different conditions are presented in Table 1. The

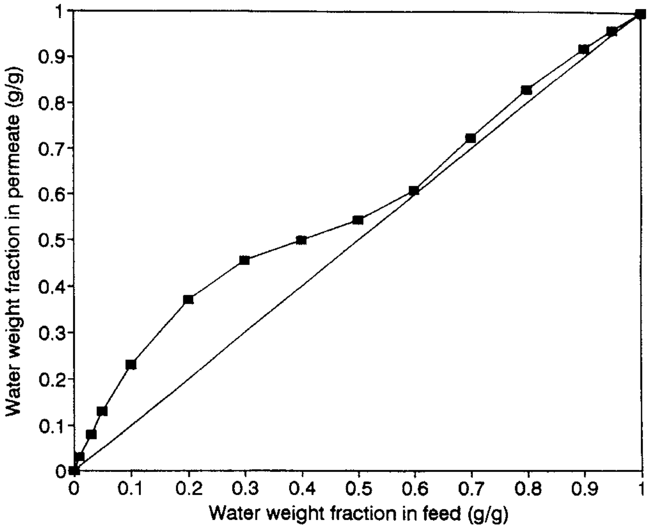

FIG. 8 McCabe–Thiele separation diagram for the pervaporation of water–ethanol mixtures using PA-6 (10/40) membrane.

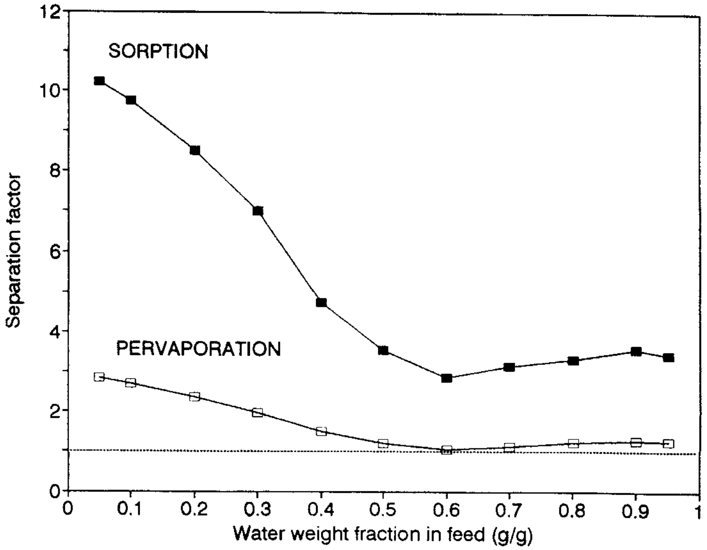

FIG. 9 Comparison of overall separation factor α^{PV} (□) and sorption separation factor α^{S} (■) for PA-6 (10/40) membrane and water–ethanol mixtures.

TABLE 1
Pervaporation Characteristics of PA-6 Membranes. Feed Concentration: 30 wt% Water in Water–Ethanol Mixture

Temperature of drying (°C)	Water weight fraction in permeate	Fluxes			$J^{\mathrm{mol}}_{\mathrm{H_2O}}/J^{\mathrm{mol}}_{\mathrm{EtOH}}$
		Total	Water	Ethanol	
		$(\mathrm{kg \cdot m^{-2} \cdot h^{-1}})$			
	PA-6 Membranes Cast from 7 wt% Polymer Solution				
40	0.411	1.470	0.604	0.866	1.78
60	9.454	1.350	0.613	0.737	2.12
80	9.472	1.150	0.543	0.607	2.29
	PA-6 Membranes Cast from 10 wt% Polymer Solution				
25	0.437	1.160	0.507	0.653	1.98
40	0.470	0.750	0.353	0.397	2.27
60	0.537	0.878	0.471	0.407	2.96
80	0.545	1.020	0.556	0.464	3.06

concentration of polymer in the casting solution and the temperature of drying were the variable parameters.

With an increase of the polymer concentration in the casting solution, the permeate flux decreases whereas the concentration of water in the permeate increases. Membranes dried at higher temperatures also improved the selectivity in the separation of water–ethanol mixtures although the permeate fluxes were generally lowered.

The last column of Table 1 presents the ratio of water/ethanol molar fluxes. These data show additionally the improvement of pervaporation performances for membranes cast from a solution of higher concentration and at elevated temperatures.

CONCLUSIONS

Polyamide-6 dense membranes prepared by the casting method from trifluoroethanol solution showed a hydrophilic character in contact with water–ethanol solutions. The best pervaporation performances occurred at feed concentrations below 30 wt% water. The enhancement of selectivity was found with membranes cast from more concentrated solutions and at higher temperatures.

Strong synergetic effects occur during pervaporation between water and ethanol fluxes in a concentration range below 0.6 water weight fraction in the feed.

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