

ETHANOL–WATER SEPARATION BY PERVAPORATION*

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Summary

The separation of ethanol–water mixtures is of great importance for the production of ethanol from biomass. Both ultrafiltration and pervaporation processes can be used for the continuous processing of fermentation and separation. The removal of ethanol from the ultrafiltration permeate can be accomplished by pervaporation. Separation of ethanol–water mixtures by the pervaporation process has been investigated. Results are presented for membranes which are preferentially permeable for ethanol and for others which are preferentially water permeable. Details on the preparation of several membrane types (homogeneous, asymmetric and composite) are given. A schematic process diagram is given in which the fermentation of sugars to ethanol is membrane-controlled

Introduction

The application of pervaporation in biotechnology

The application of membrane separation processes in biotechnology is rapidly growing. Conventional separation techniques such as distillation, adsorption, liquid–liquid extraction and crystallization are often inefficient and uneconomic. Contemporary membrane technology can save in process costs because energy consumption is low, raw materials and nutrients can be recovered and reused, fermentation processes can be carried out continuously and disposal problems can be reduced or eliminated.

Membrane processes can be applied to one of the oldest and most famous fermentation processes: the production of ethanol from the fermentation of biomass. In the past decade this process has become of renewed interest because of the impending petroleum shortage. One of the main advantages of this fermentation process is that fuels are produced from renewable resources.

Ethanol fermentation can be accomplished batchwise or continuously. A substantial reduction in costs can be realized by a continuous operation [1]

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According to Gregor [2,3] more cost saving can be achieved by the use of various membrane processes, such as ultrafiltration, reverse osmosis and electrodialysis in combination with distillation.

In principle, a combination of ultrafiltration and pervaporation makes it possible to remove and concentrate ethanol during a continuous fermentation process. It was demonstrated by Lee [3] that an ethanol—water mixture can be removed and that the rejection of suspended solids is complete when beer from the fermentor is ultrafiltrated.

Figure 1 gives a schematic presentation of a membrane-controlled continuous fermentation of sugars to ethanol. Before the sugars enter the fermentor reverse osmosis can be applied to concentrate the feed. In the fermentor glucose is converted to ethanol. The ethanol productivity is limited by ethanol inhibition and a low cell-mass concentration. Ultrafiltration can be used as a cell recycle system, where the rejected cells are returned to the fermentor and the ethanol is removed. Thus, the rate of ethanol production remains high. The ultrafiltration permeate contains components such as salts, glucose, ethanol and other low molecular weight substances. The ethanol concentration in the ultrafiltration permeate will be about 5 to 10% by weight. Ethanol can be purified to 99% or more by different separation techniques such as distillation, adsorption or extraction. At this moment, the most

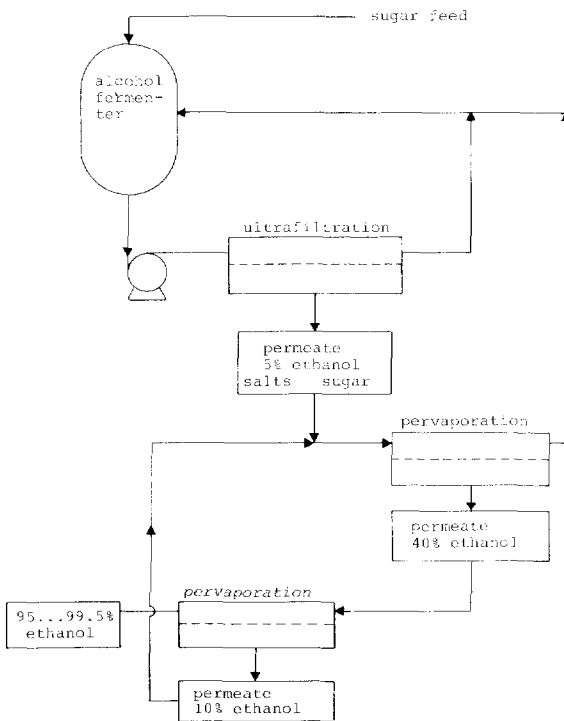


Fig. 1. Schematic presentation of membrane-controlled continuous fermentation process for the production of pure ethanol.

important process is distillation. The disadvantage of this process is that energy consumption is rather high, especially when the azeotropic composition is reached. Membrane processes are in general less energy consuming and a membrane process which can be used to separate ethanol—water of any composition is pervaporation.

In order to keep the energy consumption of this process as low as possible, for low ethanol concentrations in the feed pervaporation should be performed with ethanol-permeable membranes, and for high ethanol concentrations in the feed water should be preferentially removed. Therefore, Fig. 1 shows a two-stage pervaporation process with ethanol-selective membranes in the first stage and water-selective membranes in the second stage. It represents a conceptual diagram showing a possible application of different membrane processes in biotechnology. The value of 40% for the permeate concentration in the first stage is more or less arbitrary. From a commercial point of view, the purification of ethanol from 5% to 99% by pervaporation alone is not attractive, at least not at this moment.

Pervaporation in ethanol—water separation

Pervaporation involves selective sorption of a liquid mixture into the membrane, diffusion through the membrane, and desorption into a vapour phase on the permeate side. Until recently, pervaporation was not commercially available despite the prospect of interesting potential applications such as the separation of isomeric and azeotropic mixtures and the separation of aqueous organic mixtures. During the European Workshop on Pervaporation in Nancy a commercial pervaporation unit, in combination with distillation for the purification of biomass ethanol was presented [4]. A general disadvantage of the pervaporation process is the relatively high energy consumption in comparison to pressure-driven membrane processes such as reverse osmosis and ultrafiltration where no phase transition occurs. The pervaporation process consumes an amount of energy which is at least equal to the heat of vaporization of the complete pure product that has to be separated. Another disadvantage, the low permeation rate, can be compensated by membrane configurations with a large area to volume ratio such as hollow fiber systems.

Objectives of this research work

In this paper we will describe the separation of ethanol—water mixtures by pervaporation. In the past this has been carried out primarily using dense homogeneous membranes. Table 1 gives a summary of the selectivities and permeation rates found in the literature; from this table, it can be seen that the best results so far have been obtained with cellulose acetate and cellophane membranes.

In a search for new membranes, the type of membrane structure to be used has to be considered, because the membrane structure determines the

TABLE 1

Separation of ethanol-water mixtures by pervaporation

Feed (% by weight)		$\alpha_{A/B}^a$	Perm. rate (cm/hr)	Temp. (°C)	Type of membrane	Ref.
Water (A)	Ethanol (B)					
45	55	8.5	0.20	80	CA	[5]
4	96	2.9	0.24	25	PTFE-PVP	[6]
4	96	6.6	0.08	60	PTFE-PVP	[7]
4	96	6.2	0.01	20	cellulose	[7]
4	96	5.9	0.02	20	CA	[7]
50	50	9.0	0.13	30	cellophane	[8]
50	50	0.9	0.10	25	cellophane	[9]
50	50	2.0	0.46	45	cellophane	[9]
50	50	5.0	0.19	25	PTFE-PS	[10]
99.99	0.01	0.6 ^b	<0.01	25	PE	[11]
99.99	0.01	<0.0006 ^b	<0.01	25	PETF	[11]
99.99	0.01	0.4 ^b	0.05	25	PVA	[11]
99.99	0.01	7	<0.01	25	PDMS	[11]
4	96	11	0.05	60	CA	[12]
9.9	90.1	8	0.3	60	cellophane	[12]
50	50	4.6 ^b	<0.01	25	PDMS	[13]

^a $\alpha_{A/B}$: Concentration A/B (weight %) in the permeate divided by the concentration A/B in the feed.

^b $\alpha_{B/A}$.

separation mechanism. Pervaporation occurs according to a solution-diffusion mechanism [14-17], transport taking place only by diffusion and not by convective flow. This implies that very dense homogeneous membranes without permanent pores are necessary. There are several types of membranes possible with such a dense structure:

- homogeneous membranes;
- asymmetric membranes;
- composite membranes.

With symmetric homogeneous membranes the whole membrane thickness contributes to the resistance to mass transfer, while for asymmetric and composite membranes the major part of the resistance is situated in the thin dense toplayer. We have developed all three types of membranes for ethanol-water separation by pervaporation.

Experimental

Materials

Cellulose derivatives were obtained from Eastman Chemicals except for cellulose tripropionate which was obtained from Aldrich. Polysulfone (P 3500) was obtained from Union Carbide, polyvinylidene fluoride (Solef

2008) from Solvay, polydimethylsiloxane (RTV 670) and polydimethylphenyleneoxide from General Electric, polyacrylonitrile from DuPont and polyamide (Akulon M2) from Akzo. The solvents used were of analytical grade.

Membrane preparation

Homogeneous membranes

Polymer solutions were prepared by dissolving the polymer in a suitable solvent. The membranes were prepared by casting the polymer solution on a glass plate and allowing the solvent to evaporate in a nitrogen atmosphere. The membranes obtained were completely transparent.

Asymmetric membranes

Asymmetric membranes with a dense top layer and a porous sublayer were prepared by phase inversion. The polymer was dissolved in a solvent to form a solution containing 10 to 30% by weight of polymer. The polymer solution was cast on a glass plate and, after immersion in a nonsolvent bath, the membrane was obtained.

Composite membranes

Composite membranes were prepared by means of dip-coating. A suitable air-dried support layer was immersed in a dilute polymer solution and, after evaporation of the solvent, a composite membrane was obtained with a thin homogeneous polymer top layer on the support layer. As support layers, polyvinylidene fluoride (PVDF) and Nylon-6 membranes have been used.

PVDF membranes were prepared by casting a polymer solution containing 25% PVDF, 60% dimethylacetamide and 5% dioxane by weight on a glass plate; after immersion in a water bath at 20°C, the membrane was obtained.

Nylon-6 membranes were prepared by casting a polymer solution containing 9% Nylon-6, 18% calcium chloride and 73% methanol by weight on a glass plate; after an evaporation time of 60 seconds the film was immersed in a water bath at 0°C.

Pervaporation

The pervaporation experiments were carried out as described previously [18]. Vacuum at the downstream side was maintained at a pressure of 13.3 Pa (0.1 mmHg) by a Crompton Parkinson vacuum pump. The pressure was measured by an Edwards pirani. Permeation experiments were carried out for eight hours. After about three hours steady state conditions were reached. A product sample was taken at least every hour. In most experiments a 50–50% by weight ethanol–water mixture was used as feed at a temperature of 20°C. The asymmetric and composite membranes were installed with the top layer facing the feed.

Product analysis

Analysis of binary ethanol—water solutions was performed on a Varian model 3700 gas chromatograph fitted with a Chromosorb 60/80 column and equipped with a thermal conductivity detector. Low ethanol concentrations (0–5%) were determined with a flame ionization detector. D-glucose was determined as D-glucose phenylosazone by spectrophotometry at 390 nm. Sodium chloride was measured by conductometry.

Results and discussion

Homogeneous membranes

Homogeneous membranes have been prepared using different polymers. These are given in the first column of Table 2; membrane thickness is given in the second column.

TABLE 2

Pervaporation results using homogeneous membranes; feed: ethanol—water 50--50% by weight; temperature: 20°C

Polymer	Thickness (μm)	$\alpha_{\text{H}_2\text{O}}$	Weight % H_2O in permeate	Permeation rate (cm/hr) $\times 10^2$
CA 383 ^a	10	2.0	66.9	11.3
CA 398	20	4.2	80.7	6.8
CTA ^b	10	2.7	73.1	8.9
CTP ^c	20	2.6	72.0	5.5
CAB 171 ^d	30	4.0	80.0	4.2
CAB 272	20	4.1	80.5	3.3
CAB 381	30	3.2	76.3	2.3
PAN ^e	25	70	98.6	0.15
PVDF ^f	20	1.0	50	4.5
PSf ^g	20	332	99.7	0.04
PDMS ^h	10	0.3	21	1.7

^aCA: cellulose acetate.

^bCTA: cellulose triacetate.

^cCTP: cellulose tripropionate.

^dCAB: cellulose acetate butyrate.

^ePAN: polyacrylonitrile.

^fPVDF: polyvinylidene fluoride.

^gPSf: polysulfone.

^hPDMS: polydimethylsiloxane.

In pervaporation literature selectivity is usually expressed by a selectivity factor, α ($\alpha = (y_A/y_B)/(x_A/x_B)$, where y_A and y_B are concentrations of components A and B in the permeate and x_A and x_B are concentrations of components A and B in the feed). Because α may depend on the feed concentration, both selectivity factor and concentration in the permeate are given in Table 2 (third and fourth column). In the last column the permeation rates are given.

From Table 2 it can be concluded that in all cases, except that of polydimethylsiloxane (PDMS), water permeates preferentially through the

membrane. Polysulfone (PSf) and polyacrylonitrile (PAN) show the best selectivities, but the permeation rates, especially for PSf, are very low. The cellulose derivatives give moderate selectivities and rather high permeation rates.

From reverse osmosis experiments it is known that annealing strongly affects the performance of cellulose ester membranes. Homogeneous cellulose acetate (CA 398), cellulose triacetate (CTA) and cellulose acetate butyrate (CAB 171) membranes were annealed in water at 95°C for 10 minutes. The pervaporation results for these membranes are given in Table 3, which shows that annealing hardly affects CA 398 membranes but that the selectivity of CTA and CAB 171 membranes increases drastically in comparison with the unannealed membranes. All the above-mentioned experiments were carried out with a 50–50% by weight mixture of ethanol–water.

TABLE 3

Pervaporation results of some homogeneous membranes with and without heat treatment; feed: ethanol–water 50–50% by weight; temperature: 20°C; heat treatment: 10 min at 95°C

Polymer	Without heat treatment			With heat treatment		
	$\alpha_{\text{H}_2\text{O}}$	Weight % H ₂ O in permeate	Perm. rate (cm/hr) $\times 10^2$	$\alpha_{\text{H}_2\text{O}}$	Weight % H ₂ O in permeate	Perm. rate (cm/hr) $\times 10^2$
CA 398	4.2	80.7	6.8	3.9	79.5	6.5
CTA	2.6	72.0	5.5	36.0	97.3	2.3
CAB 171	4.0	79.8	4.2	9.6	90.6	2.9

Because selectivity may depend on liquid feed composition, the permeability and selectivity of different compositions of ethanol–water were investigated with homogeneous CA 398 (unannealed), PAN and CTA (annealed) membranes. The results are given in Figs. 2 and 3. PSf has not been considered further because of its extremely low permeation rate. In Fig. 2, the vapour–liquid equilibrium of ethanol–water at 20°C and 1 bar [19] is also given (dashed curve); from this figure can be seen that very high selectivities are achieved with simple (bulk) polymers. This result is very interesting from a commercial point of view.

Another objective of this research work was to find membranes which are preferentially permeable to ethanol in order to remove ethanol from the ultrafiltration permeate in the first step (see Fig. 1). From the results given in Table 2, it is important to note that if either a hydrophobic glassy polymer (PSf) or a more hydrophilic glassy polymer (CA) is used, water permeates preferentially in both cases. This means that for hydrophobic glassy polymers such as polysulfone (PSf) and polydimethylphenyleneoxide (PPO), which exhibit no significant water sorption, water permeates preferentially because of the presence of ethanol. With pure water, no permeability has been

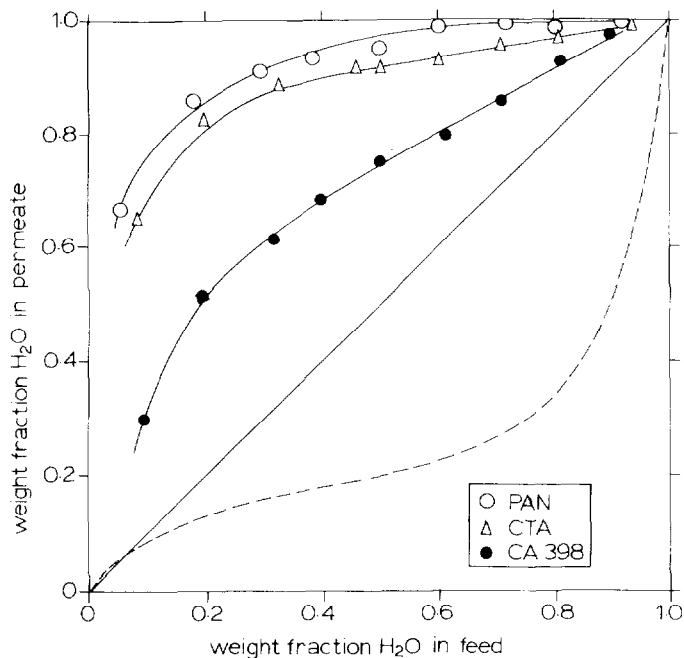


Fig. 2. Water concentration in the permeate as function of water concentration in the feed for different homogeneous membranes. The dashed line is the vapour-liquid equilibrium of ethanol-water at 20°C.

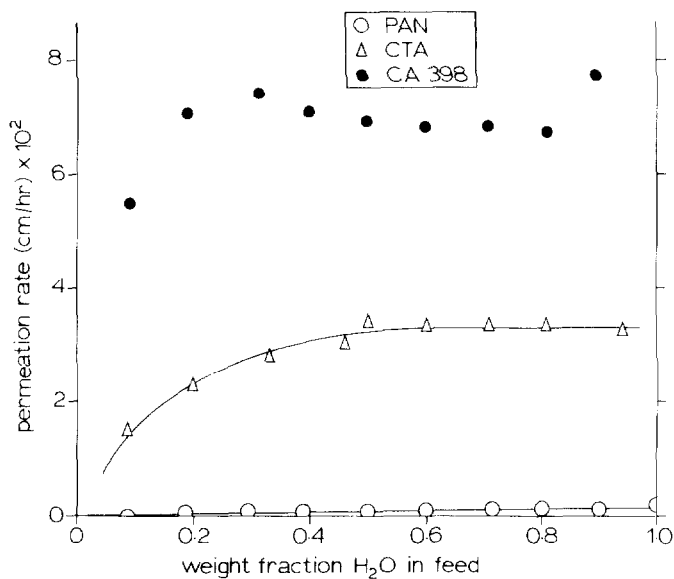


Fig. 3. Permeation rate as function of the concentration of water in the feed for different membranes.

observed at all with PSf membranes. We conclude from these examples that it would not be possible to predict selectivity for ethanol—water mixtures from pure component permeability measurements. In a forthcoming article [17] we will discuss these phenomena in more detail.

Another interesting point to be learned from Table 2 is that when using a hydrophobic rubber instead of a hydrophobic glassy polymer, ethanol permeates preferentially. Comparing this result with the investigations of Eustache [11] on the removal by pervaporation of a large number of traces of organic contaminants from water using polyethylene (PE), polyethylene-terephthalate (PETF), polyvinyl alcohol (PVA) and polydimethylsiloxane (PDMS), the rubber membranes (PE and PDMS) show a preferential permeability to all organic solutes while the glassy polymers (PVA and PETF) show a selectivity to water. From their extended investigations the only exception found was for the system polyethylene—water—ethanol. For glassy polymers diffusion through the membrane is rate determining. In the case of rubbers, where the chains between the crosslink points are much more flexible and segmental motions are less restricted than in glassy polymers, diffusion is much faster and therefore sorption on the feed/membrane interface will become important. Investigations by Hwang [29] on the permeation of oxygen through a silicone rubber membrane did show that, besides the membrane itself, interfacial resistance also contributes to the total resistance.

Because ethanol permeates preferentially through polydimethylsiloxane (PDMS) membranes, it is possible to apply pervaporation to remove ethanol from the ultrafiltration permeate. The ethanol content of the ultrafiltration permeate is low (5–10% by weight). The permeate also contains other low molecular weight substances such as salts, non-converted glucose and other organic components. To check the membrane selectivity for the various components present, we performed an experiment using a PDMS membrane and a 5% by weight solution of ethanol in water with D-glucose and sodium chloride added to the feed. Since the exact composition of the ultrafiltration permeate is difficult to establish (see Ref. [3]), we used the mixture of D-glucose, sodium chloride, ethanol and water to get an indication of the feasibility of the pervaporation process. The results are given in Table 4, from which it can be seen that the rejection of D-glucose and sodium chloride is

TABLE 4

Pervaporation results with a PDMS membrane and as feed a mixture of ethanol, D-glucose, sodium chloride and water; membrane thickness: 30 μm ; temperature: 30°C; permeation rate: 0.019 cm/hr

	Feed (ppm)	Permeate (ppm)
Ethanol	50,000	190,000
D-glucose	10,000	< 200
NaCl	5,000	< 200

complete. However, the selectivity is rather low for ethanol—water mixtures, lower than the vapour—liquid equilibrium.

The experiments performed with homogeneous membranes indicate that for all membranes tested except the PDMS rubber membranes, water permeates preferentially. Very high selectivities to water can be achieved with simple homogeneous membranes but the selectivity to ethanol in case of PDMS membranes is rather poor.

Composite membranes

The results obtained with homogeneous PAN and PSf membranes are very promising as regards their selectivity, but they show low permeability. Because the permeation rate through a homogeneous membrane is roughly inversely proportional to membrane thickness, a reduction of the thickness will improve the permeability. One can achieve this by preparing asymmetric or composite membranes. These membranes consist of a thin dense top layer and a porous sublayer with a much smaller resistance to mass transfer. In the case of composite membranes, top layer and sublayer originate from different polymeric materials. Each of the two layers can be optimized independently for maximum performance. Different methods can be used to apply the ultrathin top layer upon the support: dip-coating [20], interfacial polymerization [21] and plasma polymerization [22]. The most simple method is dip-coating. Hence, if it were possible to put a very thin homogeneous PAN or PSf layer, by dip-coating, upon a suitable support, we would expect an increase in permeability while the selectivity would remain the same or lessen only slightly. The choice of the support depends on the solvent used for preparing the polymer top layer; this solvent should not attack the microporous structure of the support.

PSf is soluble in chlorinated hydrocarbons like methylene chloride, trichloroethylene and tetrachloroethylene. Polyvinylidene fluoride (PVDF), however, is able to resist these solvents. A PVDF membrane has been used as support for a composite membrane with a PSf top layer. This PVDF membrane itself has no selectivity towards an ethanol—water mixture and the permeation rate is high (see Table 5).

PAN is soluble in amides like dimethylformamide (DMF), dimethylacetamide (DMAc) and *N*-methylpyrrolidone (NMP). Although there are few polymers which are resistant to these solvents, aliphatic polyamides can be used as support materials for a PAN top layer. We have used for this purpose a Nylon-6 membrane, which, uncoated, also shows no selectivity for ethanol—water mixtures, but still has a very high permeation rate.

The coating procedure has been described in the experimental section. The following factors have been varied:

- (1) Polymer concentration in the coating solution; 0.5—8% by weight of polymer.
- (2) Coating time; generally about 2 minutes, variation from 1 to 60 minutes.
- (3) Prewetting of the support.

- (4) Kind of solvent used in the coating solution; dichloromethane (b.p. 40°C) and tetrachloroethylen (b.p. 146°C) have been used as solvents for PSf. In the case of PAN, only dimethylformamide has been used as solvent.
- (5) Drying of the support; careful drying was carried out at elevated temperatures (90°C) and reduced pressure (0.6 kPa).
- (6) Coating in a nitrogen atmosphere.

The best results obtained are given in Table 5. These membranes are obtained by dip-coating a supporting PVDF membrane in a 6% PSf/CH₂Cl₂ solution and a Nylon-6 supporting membrane in a 8% PAN/DMF solution. The permeation rates of the composite PSf and PAN membranes are one order of magnitude higher than those of the homogeneous membranes; we had anticipated a larger increase. The reason for this low permeability is the resistance which the support layer also exerts on mass transfer, and the rather thick toplayers (6 μm) which were obtained by using the high (6–8%) polymer concentration during dip-coating. When lower polymer concentrations were used, the permeability did increase but the selectivity decreased drastically. According to Cadotte [21], the possible reason for this phenomenon is that dilute low-viscous polymer solutions tend to migrate upon drying to produce defective toplayers.

TABLE 5

Pervaporation results of composite membranes obtained by dip-coating; feed: ethanol—water 50–50% by weight; temperature: 20°C

Polymer (toplayer/sublayer)	α_{H_2O}	Weight % H ₂ O in permeate	Permeation rate (cm/hr) × 10 ²
PSf/PVDF	19.0	95.0	0.5
PAN/Nylon-6	9.0	90.0	2.0
PVDF support	1.0	50.0	20
Nylon-6 support	1.0	50.0	— ^a

^a Permeability too high.

One can conclude from these results that, in principle, it is possible to prepare composite membranes for ethanol—water separation by means of dip-coating. However, up to now we have not been able to prepare very thin (less than 1 μm) dense toplayers upon a support by this method without loss of selectivity. Even the best composite membranes did show a loss of selectivity with respect to homogeneous membranes.

Asymmetric membranes

Another type of membrane with a very dense toplayer and a porous sublayer is formed by the asymmetric membranes. Most asymmetric membranes are prepared by phase inversion. Morphology and performance of these membranes largely depend on the choice of the ternary system polymer/solvent/

nonsolvent. Two different demixing processes determine the formation of asymmetric membranes [23–27]:

- (1) (Micro)crystallization or gelation for the formation of the top layer.
- (2) Liquid–liquid phase separation followed by gelation of the concentrated polymer phase for the formation of the porous sublayer.

As already mentioned, during pervaporation transport takes place by diffusion. This requires asymmetric membranes with a very dense top layer. Different factors can favour the formation of a dense top layer [25, 27]:

- A high initial concentration of the polymer solution.
- A lower tendency of the nonsolvent to induce liquid–liquid phase separation. This means a low tendency of mixing of solvent and nonsolvent.
- A low temperature of the coagulation bath.
- An evaporation step before entering the coagulation bath.

Most of the commercially available asymmetric membranes are applied in hyperfiltration processes. The membranes generally used in the pervaporation process are of the homogeneous type. Only Aptel [7] reported on the separation of water–dioxane mixtures with asymmetric polytetrafluoroethylene membranes. In general, it can be said that asymmetric hyperfiltration membranes are not suitable for pervaporation because the top layer is not dense enough.

Experiments performed with a Loeb–Manjikian type of CA reverse osmosis membrane [30] obtained from a polymer solution consisting of 25% cellulose acetate (E 398-3), 30% formamide and 45% acetone, did not show any selectivity towards ethanol–water mixtures. Bøddeker [31] showed that reverse osmosis membranes (polybenzimidazolone (PBIL) and RC-100), which exhibit very high salt rejection ($R > 99\%$) and can be used for single-pass seawater desalination, have hardly any selectivity to ethanol–water mixtures in pervaporation processes.

With the procedure given above to obtain a denser top layer, we developed asymmetric pervaporation membranes for ethanol–water separation using different polymers. The results are given in Table 6.

The asymmetric CA membranes prepared from acetone-containing solutions show a better performance than the homogeneous ones: the permeability is slightly less but the selectivity is much better. The reverse is the case with PSf where the asymmetric membranes have a much higher permeability but a lower selectivity.

Polydimethylphenyleneoxide (PPO) membranes were obtained with a high selectivity but with a low permeability. CA, PSf and PPO membranes were also prepared from a more dilute polymer solution and the results are also given in Table 6. These latter membranes exhibit a much lower selectivity. It seems clear from these results that polymer concentration is a very important factor for obtaining dense-skinned asymmetric membranes suitable for pervaporation. Another important factor in obtaining dense top layers is the solvent–nonsolvent interaction. If the solvent–nonsolvent interaction is low (i.e., a high value of the excess free energy of mixing), the binodal de-

TABLE 6

Pervaporation results of asymmetric membranes obtained by phase inversion, feed: ethanol-water 50-50% by weight; temperature: 20°C

Polymer	Solvent	Nonsolvent	Polym. Conc. (%)	$\alpha_{\text{H}_2\text{O}}$	Weight % H ₂ O in permeate	Perm. rate (cm/hr) $\times 10^2$
CA	Acetone	Water	25	12.3	92.5	2.7
CA	Acetone	Water	18	5.9	85.5	4.2
CA	DMSO	Water	25	1.0	50.0	32.5
CA	DMSO	Water	18	—	—	^b
PSf	DMAc	Water	35	3.0	75.0	1.4
PSf	DMAc	Water	15	—	—	^b
PPO	TCE ^a	Methanol	20	9.3	90.3	0.2
PPO	TCE	Methanol	10	1.0	50.0	19.2

^aTCE: trichloroethylene.

^bPermeability too high.

mixing gap for liquid-liquid phase separation in the phase diagram is shifted to higher water concentrations. This is the case for CA as polymer, acetone as solvent and water as nonsolvent. Acetone-water solutions have a very high excess free energy of mixing whereas DMSO-water solutions show a negative excess free energy of mixing which means a high mutual affinity [28]. The binodals of these systems are given in Fig. 4. For solutions of CA in DMSO, where the location of the liquid-liquid phase separation demixing gap is near the polymer-solvent axis, addition of a small amount of water is sufficient to induce liquid-liquid phase separation. As a result, membranes are obtained with a less dense toplayer [27]. Also, membranes which were prepared from both dilute and concentrated solutions of CA in DMSO did not show any selectivity towards ethanol-water mixtures because the toplayer was not dense enough.

For solutions of CA in acetone, a relatively large amount of nonsolvent is necessary before liquid-liquid phase separation occurs. Consequently, a denser toplayer is the result.

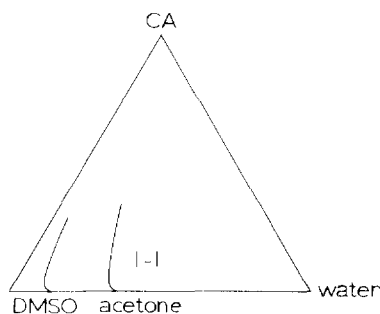


Fig. 4. Schematic presentation of the liquid-liquid separation demixing gap for CA/solvent/water systems with acetone and DMSO as solvent. (From Ref. [28].)

It is obvious that in preparing asymmetric membranes for pervaporation purposes two factors are very important: the polymer concentration in the casting solution should be high and the solvent–nonsolvent interaction should be low. Besides the above-mentioned thermodynamic aspects, kinetic factors such as nonsolvent flow into the nascent membrane and solvent flow into the coagulation bath, together with the gelation/crystallization kinetics, also play an important role in membrane formation.

Conclusions

With pervaporation in combination with ultrafiltration, it is possible to remove ethanol preferentially and continuously from a fermentation reactor. The ethanol–water mixture obtained after ultrafiltration can be purified by a two-stage pervaporation process with homogeneous, composite or asymmetric membranes.

The problem with the composite membranes prepared by dip-coating is the inadequate homogeneity and/or thickness of the selective top layer. We did not succeed in preparing very thin top layers (less than 1 μm) by this technique without loss of selectivity.

Both homogeneous and asymmetric membranes prepared from various polymers showed very high selectivities to ethanol–water mixtures. Annealing of the homogeneous cellulose ester membranes had a positive effect on the selectivity.

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