SEPARATION OF ETHANOL-WATER MIXTURES BY PERVAPORATION THROUGH POLY (ACRYLAMIDE-co-BISACRYLAMIDE) GEL MEMBRANES

MARIA S. VICENTE*, ELIO E. GONZO AND JUAN C. GOTTIFREDI

Instituto de Investigaciones para la Industria Química, INIQUI, Universidad Nacional de Salta, CONICET, Buenos Aires 177, 4400 Salta, Argentina

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Abstract

Separation of water-ethanol mixtures by pervaporation through poly (acrylamide-co-bisacrylamide) gel membranes has been studied. Pervaporation rates and selectivities were measured at different ethanol feed concentrations, at temperatures in the 20°C to 50°C range. The influence of crosslinking agent (bisacrylamide) concentration on permeation and selectivity was also analyzed.

Results indicate that this gel membrane is suitable to obtain high water selectivity and appreciable pervaporation rate. The maximum ethanol content of the mixture, below which the membrane is permeable, was also established. Ethanol concentration in the permeate stream was always lower than 7%, owing to the small affinity between membrane and ethanol.

Pervaporation rates decrease linearly while selectivities increase exponentially when bisacrylamide/ acrylamide ratio (R) increases. The pervaporation activation energy increases, and at low R values, is smaller than those obtained with elastomeric membranes.

1. Introduction

The purification of organic compounds is usually carried out by distillation orcrystalization techniques which can be considered as heat energy consuming operations. Thus, separation by membranes is becoming one of the most promising alternative operations to save energy costs (Melita, 1982; Mulder et al., 1983; Kimura, 1985). It can also be used to separate mixtures whose components have nearly the same physico-chemical properties or are structural isomers with almost the same molecular behavior within the solution system (Volpe and Collino, 1984; Cabasso, 1983; Yoshikawa et al., 1984).

Pervaporation is one recently introduced membrane operation allowing to separate a component of a liquid mixture by partial vaporization of the species through a non-porous selective membrane.

Transport phenomena in pervaporation are usually more complex than in other membrane operations because of the multiple and simultaneous interaction between mixture constituents and membrane polymers which produce modifications on the system such as membrane swelling. The separation mechanism can be conceptually described by the following steps: 1) Selective sorption, eventually producing swelling; 2) Selective diffusion of sorbed species accross the membrane; 3) Desorption from the downstream side of the membrane to the vapor phase which can be usually regarded as a non-selective phenomenon (Wenzlaff et al., 1985). These must be treated as coupled mechanisms depending on the interaction strenghs of the particular system to be analyzed (Wenzlaff et al., 1985).

Recently, membrane separation processes have been also suggested to separate water-ethanol mixtures. Actually, ethanol produced by fermentation is obtained as a 5—10% aqueous solution. Separation by destillation to obtain 95% ethanol involves over 60% of production cost (Itoh et al., 1985). Several

* To whom correspondence should be addressed

efforts have been made to develop the adequate membrane for this separation.

Selectivity of a polymeric membrane results to be a direct function of the component solubility in the membrane. Thus, the most successful membranes are those prepared by incorporating functional groups into the polymer structure, which may cause a strong interaction with one of the solute. These differences in the interaction strenghs may lead to a selective separation. Some examples are membranes obtained by radiation-induced grafting of vinyl monomers into PTFE films (Tealdo et al., 1981; 1982) or the ion exchange membrane (Cabasso and Lin, 1985; Cabasso et al., 1985).

There are other types of membranes such as the asymmetric and composite ones, which have been developed to increase the pervaporation rate, based on the fact that the main resistance to diffusion is located in a very thin and dense toplayer (Mulder et al., 1983; Neel et al., 1985; Schissel and Orth, 1984).

Nevertheless, industrial applications of pervaporation techniques are just beginning as described in a few reports related with ethanol and isopropanol dehydratation. (Tusel and Brüschke, 1985).

The present contribution contains an analysis of the behavior of (acrylamide-co-bisacrylamide) gel membranes to permeate water from water-ethanol mixtures. Membranes permselectivity and pervaporation rates were measured and correlated as a function of ethanol composition in the feed. The maximum ethanol content of the mixture, below which the membrane is permeable, and the influence of crosslinking agent (bisacrylamide) composition on flux and selectivity values are also reported.

2. Experimental

Materials: Acrylamide (AA), NN-methylene bis acrylamide (bis AA), tetramethylethylene diamine (TEMED) and trihydroxy-methylamine (TRIS) extra pure grade were used without further purification. All other reagents and solvents were analytical grade.

Polymerization and Membrane Preparation: Three different solutions were prepared as is shown in Table 1. Solution A is a buffer solution (pH 8.9) also containing TEMED. Solution B contains the monomers (AA and bis AA) dissolved in water. To analyze the influence of the crosslinking agent (bis AA), the following values, 3×10^{-3}, 5×10^{-3} and 7×10^{-3} of bis AA/AA mass ratio (R), were investigated. Solution C provides the catalyst, which acts simultaneously with TEMED as initiator of the polymerization reaction. The polymer was prepared by mixing solutions A, B and C in a volume ratio of 1/12/1, respectively, and allowing the polymerization to occur in the absence of oxygen.

The initiator of the free radical polymerization arises from the reaction between ammonium persulfate and TEMED, in which the last molecule is left with an unpaired valence electron.

To give an adequate mechanical resistance the membrane was prepared carrying out the polymerization on a filter paper (Wathman 541).

Pervaporation experiments: The apparatus used for measuring the pervaporation rate through the membrane is shown in Fig. 1(a). A cross-section showing the details of the pervaporation stainless steel cell is given in Fig. 1(b). The feed solution is introduced into the upper compartment from a large capacity container and is recirculated by means of

Table 1

R	Solution A*	Solution B*	Solution C*
0.003	HCL 1N : 48 ml	Acrylamide : 45 g. bis Acrylamide : 0.47 g	
0.005	TRIS : 36 g	Acrylamide : 45 g. bis Acrylamide : 0.225 g	Ammonium Persulphate 0.14 g.
0.007	TEMED : 0.46 ml	Acrylamide : 45 g bis Acrylamide : 0.315 g	

* All the solutions were made up to 100 ml with distilled water.
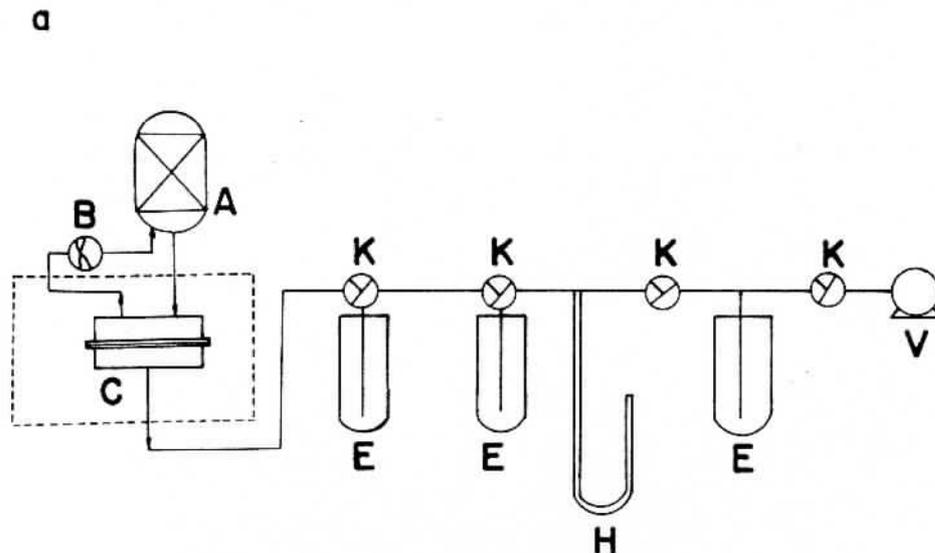
a

Fig. 1a.— Schematic diagram of the pervaporation apparatus: A) feed solution container, B) recirculation pump, C) pervaporation cell, E) condenser traps, K) three ways cocks, H) manometer, V) vacuum pump.
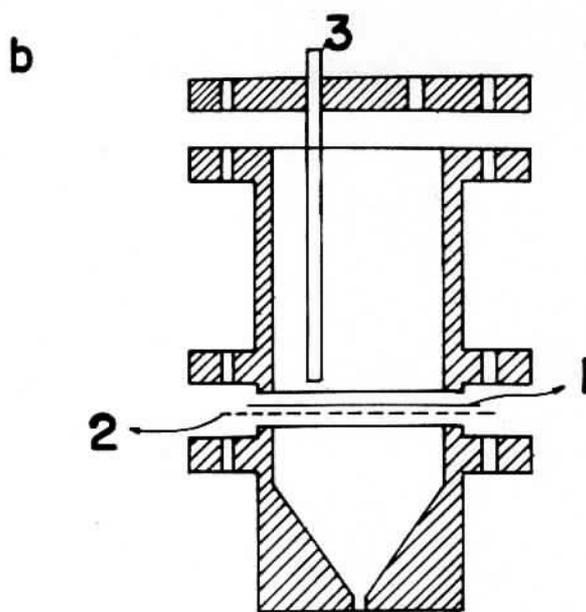
b

Fig. 1b.-- Pervaporation cell: 1) membrane, 2) stainless steel mesh, 3) to the recirculation pump.

a small pump to maintain constant the composition of the solution in contact with the membrane. The membrane was supported on a stainless steel mesh and the area in contact with the liquid was about 33.2 cm². The lower compartment was evacuated and the pressure maintained below 1 mm Hg. The permeate was collected in a liquid nitrogen trap. The permeate flux was determined by gravimetry and its composition by measuring the density using a PAAR DMA 46 Densimeter. All of these measurements were repeated until a steady state was reached.

The permeation rate was calculated as:

$$J = \frac{q}{t \times A} \ ,$$

where q is the amount permeate in Kg, t the time in hours and A the membrane area in contact with the feed solution.

The separation factor, α, is defined as:

$$\alpha = \frac{WA/WB}{YA/YB} \ .$$

where WA/WB and YA/YB denote the weight fraction ratio of permeate and feed solution, respectively (A=water, B=ethanol).

Pervaporation experiments were carried out at constant temperature in the 20°C to 50°C range, and with ethanol feed composition values of 9, 28, 45 and 59% by weight.

The effect of ratio R on J and α was determined using a unique feed composition (45%). The results are summarized in Tables 2 and 3.

Each experimental point shown in the figures or given in tables is the mean value of four independent runs.

Table 2

Temp (K)	9% ethanol		28% ethanol		45% ethanol		59% ethanol	
	J	α	J	α	J	α	J	α
293	0.51	6.8	0.22	9.5	0.122	10.9	0.08	24
296	—	—	0.25	13.1	0.148	15.1		
301	0.69	6.4	0.30	9	—	—		
308	0.85	6.0	0.40	8.2	0.225	9.37	0.104	30
318	1.25	5.7	0.60	7.1	0.302	8.60	0.14	37
323	—	—	—	—	0.34	7.65	0.22	31
							—	—

Table 3

Temp (K)	R=0.003		R=0.005		R=0.007	
	J	α	J	α	J	α
303	0.23	7.20	0.18	9.60	0.127	28.6
308	0.26	5.10	0.225	9.37	0.190	18.0
313	0.30	3.05	0.285	8.60	0.280	16.0
328	0.40	1.40	0.53	7.00	1.05	—

3. Results and discussion

Membrane Description

The synthesized membrane is a gel of cross-linked polyacrylamide molecules, immersed in a liquid medium. The gel consistency is determined by a balance of forces that act to expand or shrink the polymer network. Three of such forces have been identified (Tanaka et al., 1980): the rubber elasticity, the polymer —polymer affinity and the hydrogen ion pressure. The third is associated with the ionization of the polymer network and has influence only if the gel has been previously hydrolyzed in basic solution.

The rubber elasticity derives from the resistance that the individual polymer strands offer to either stretching or compression. The strength of the rubber elasticity depends on.how actively the polymer segments are moving and this is proportional to the absolute temperature. So, the temperature influences the magnitude of the force, but the direction of it is determinated by whether the strands are stretched or compressed compared with the equilibrium length.

The polymer-polymer affinity can be traced to an interaction between the polymer strands and the solvent. As the gel is not soluble in ethanol, its immersion in a mixture of water and ethanol makes it to coagulate. This trend increases as the concentration of ethanol increases.

Separation of water-ethanol mixture using bis AA/ AA 5x10⁻³ membranes

Figure 2 indicates the effect of feed composition on pervaporation rate and selectivity at 308 K. The flux decreases with increasing ethanol weight fraction in the feed, as was expected from the membrane description. Since as ethanol concentration increases polymer affinity becomes stronger, the gel contracts lowering the flux. The pervaporation rate becomes negligible at a weight fraction of ethanol about 70%. On the other hand, it is shown that a values increase from 6 to 37 as the ethanol fraction in the feed increases, in agreement with the membrane behavior suggested in the previous section.

Figure 3 shows the relation between alcohol weight fractions in the feed and in the permeate streams measured in pervaporation runs at 308 K. It can be clearly concluded that the ethanol weight fraction in the permeate stream is always substantially smaller that its corresponding value in the feed stream. The same behavior was observed in all the range of temperatures investigated. It must be stressed that the small affinity between the membrane and alcohol is responsible for the very low ethanol concentration in the permeate stream.

The influence of bis AA introduction and Temperature on Permselectivity

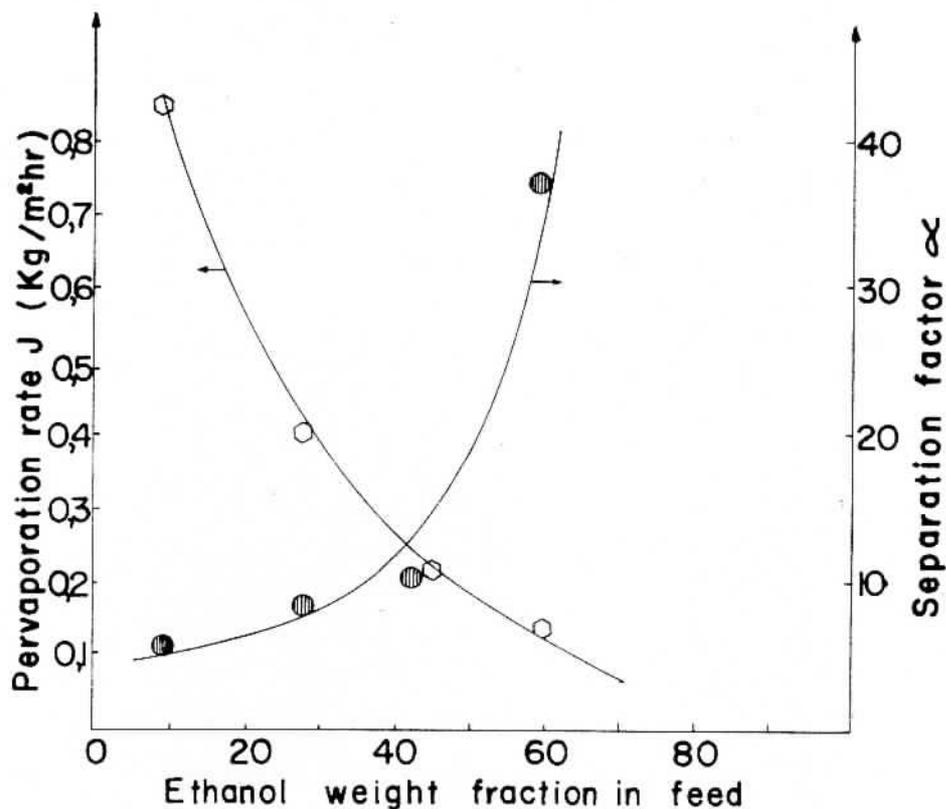To study the influence of cross linking all the pervaporation experiments were carried out

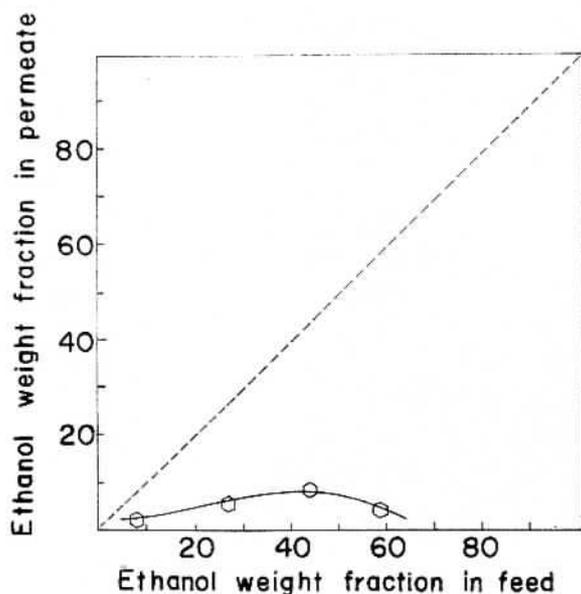Fig. 2.— Effect of feed composition on flux and selectivity (R=0.005, T = 308 K)

Fig. 3.—Relation between ethanol weight fraction in feed and in permeate (R = 0.005, T = 308 K)

with 45% ethanol aqueous solutions as feed stream.

Figure 4 shows pervaporation rates and permselectivities as a function of bis AA/AA ratio. It is interesting to note that the permeation rate decreases linearly with R within the range investigated although the influence of cross linking is smaller as temperature increases. However, selectivity increases exponentially with R. The effect of temperature on α is significant since it decreases around 50% in this small temperature range.

To observe the effect of introducing the cross linking agent (bis AA) on diffusion, the pervaporation activation energy and the activation energy for each component were determined.

As shown in Table 4, values of total and water pervaporation activation energies increase as R increases, while for ethanol there is a minimum.

When the degree of cross-linking is small (R=0.003) the polymer structure can be well represented by a number of linear strands and due to the rubber elasticity these chains will be extended up to their equilibrium length (which depends on tempera-
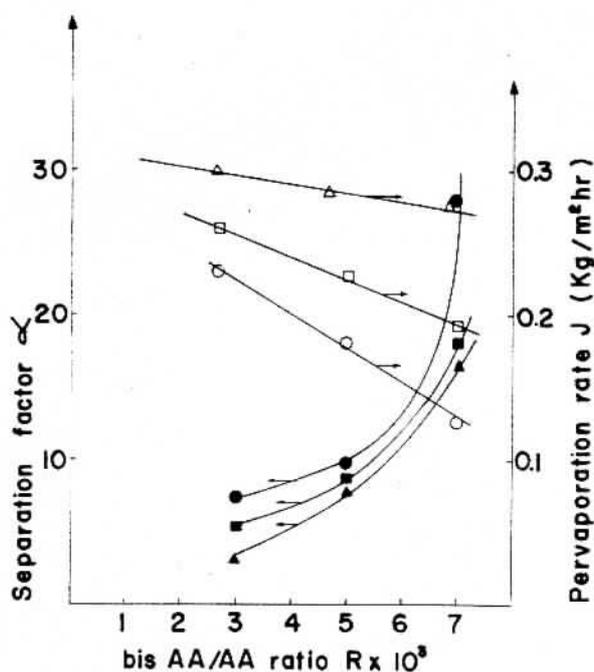
Fig. 4.—pervaporation rates and selectivities as a function of R. Filled symbols: selectivity, open symbols: pervaporation rate. O: 303 K, □: 313 K, Δ: 318 K.

Table 4

R	Activation Energy (kcal/mol)		
	Total	Water	Ethanol
0.003	4.4	1.5	14.7
0.005	6.5	6.3	9.4
0.007	14.3	13.6	26.0

ture). Moreover, under these conditions, the polymer-polymer affinity, being a short range force, has negligible influence on the rubber elasticity.

Therefore, the polymer can reduce its total energy by surrounding itself with water molecules rather than with alcohol molecules or other polymer chains. This physico-chemical picture can explain the large water flux observed which in turn increases the total flux.

As the bis AA/AA ratio increases, the permeate pathway becomes smaller. Furthermore, the polymer-polymer affinity becomes stronger and the solvent molecules begin to be excluded. These effects produce a diminution of diffusivity through the membrane lowering the flux and increasing selectivity to water.

4. Conclusions

It can be concluded that bis AA/AA gel membranes are suitable to achieve high water selectivity and appreciable pervaporation rates for separating the ethanol-water liquid system. Results indicate that these variables are much higher than those reported in previous contributions (Wenzlaff et al., 1985; Nagy et al., 1983). Under the experimental conditions investigated in this work, pervaporation rates and selectivity values as higher as 1.2 Kg/m^2hr (9% ethanol, 318 K, $\alpha=5.7$) and 37 (50% ethanol, 308 K, J=0.14 Kg/m^2hr) respectively can be reached. Moreover, it should be stressed that ethanol concentration in the permeate stream was always extremely small in comparison with the corresponding feeding values and was never higher than 7%. These membranes could be used with ethanol concentrations below 70% by weight since at this point the permeate flux vanishes.

It should be pointed out that the simple preparation membrane technique can be used on different support materials according to process requirements.

The general behavior of the obtained kinetic and selectivity results were explained with a very simple and realistic model.

Since pervaporation rates vary linearly while selectivity varies exponentially with R, optimization procedures can be used to design and find the more convenient experimental conditions for economic water-ethanol separation operation using these kind of membranes.

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