

Experimental Dehydration of the Water-Ethanol Mixture by Pervaporation through Membranes Based on Polyvinyl Alcohol: What Conditions for Better Performance?

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Abstract: The separation processes are of paramount importance in the industrial field. The techniques used to obtain separation membranes depend on the type of membrane and the applications envisaged.

Aim: The objective of the study is to focus on the master membrane allowing better pervaporation of the water-ethanol mixture by varying various parameters such as the polymer content, the polyacrylic acid (PAA) content and the operating variables such as the drying temperature and the stay in the oven.

Materials: We fabricated membranes to separate water-ethanol mixtures by the pervaporation process. First, films based on polyvinyl alcohol and acid polyacrylics were prepared using the appropriate solvent (water) with different PAA contents. We then characterized these films using the technique of infrared spectroscopy and the measurement of swelling of these membranes in water / ethanol mixtures. Pervaporation tests were carried out to measure the selectivity and flow of these films with respect to the mixture.

Results: All the membranes exhibit a higher permeation flux than that of pure PVA, especially when the PAA content is high. The selectivity to water of these crosslinked membranes, represented by the water content in the permeate is appreciable.

Conclusion: The addition of PAA to PVA makes possible the improvement of swelling, the flow is improved as well as the water selectivity and the permeability of the membrane which makes the PVA-PAA alloy a simple and effective method to ensure dehydration of the Water-Ethanol mixture.

Keywords: Pervaporation, Membrane, Separation process, Polyvinyl alcohol, Dehydration, Polyacrylic acid.

INTRODUCTION

Pervaporation, an emerging membrane process for separating liquid mixtures, is mainly applied for treating organic-organic mixtures, azeotropic mixtures, anhydrous organic mixtures, dehydrating of organic solvents, thermally sensitive compounds, and eliminating trace organic compounds from contaminated water [1-3]. There are essentially two types of membranes: Hydrophilic or Hydrophobic. Hydrophilic membranes have a strong affinity for water, which cross them much more easily than organic materials, which are preferably retained. Their active layer can be, for example, polyvinyl alcohol, cellulose or polyamide [4]. An efficient pervaporation membrane requires a high permeation flux and reasonable selectivity [5]. PVA is a synthetic polymer widely used for the development of pervaporation membranes due

to its solubility in water, high hydrophilicity [6]. The strong interaction due to the water PVA hydrogen bonds is one of the reasons, which accounts for its excellent selectivity to water during dehydration of organic solvents by pervaporation. However, problems of resistance and stability arise when it is used in an aqueous solution because it has a very strong hydration capacity, in particular at high temperature [7, 8].

The performance of the PVA membrane could be improved by forming alloys. However, their low resistance and their instability in aqueous solutions greatly limit their applications in pervaporation. It therefore seems appropriate to establish chemical bonds between the two macromolecular compounds of an alloy in order to stabilize the membranes obtained. Crosslinkers common to both compounds or a polymer having reactive groups (e.g carboxylic, hydroxyl or amine etc.) which can react with hydroxyl groups of PVA to form chemical bonds between them can be performed [9].

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The use of alloys proves to be one of the simple and effective means for obtaining high-performance films. Polymer alloying is a suitable technique for studying the influence of modification of the membrane nature on the characteristics of pervaporation. Rhim *et al.* [10] prepared membranes made of PVA-PAA crosslinked together by heating at 150 °C. IR analysis proved the formation of ester bonds. Using DSC, they found that these two polymers are perfectly compatible. K. Benzekri *et al.* [11] and C. Chen *et al.* [12] have also shown by infrared spectroscopy and by DSC that the specific interactions by hydrogen bonds are responsible for the miscibility of the two polymers.

The aim of this study was to prepare membrane with improved pervaporation performance to separate water-ethanol mixtures. First, films based on polyvinyl alcohol and polyacrylic acid were prepared using the appropriate solvent (water) with different PAA contents. We then characterized these films using the infrared spectroscopy technique and the measurement of swelling of these membranes in water / ethanol mixtures. On the other hand, pervaporation tests were performed to measure the selectivity and flow of these films with respect to the mixture.

MATERIALS AND METHODS

1. Aim

The performance of a pervaporating membrane depends on the physicochemical properties of the polymer, on the structure of the membrane and on the operating conditions. The objective of the study is to focus on the master membrane allowing a better pervaporation of the water-ethanol mixture and this by varying various parameters such as the polymer content, the polyacrylic acid (PAA) content and the operating variables such as the drying temperature and the stay in the oven.

2. Preparation of Collodion

PVA used without additional purification was supplied by Sigma-Aldrich. Its molecular weight was 160,000 Daltons and its level of purity was 98%. The polymer (PVA) is dissolved in a hot solvent (usually water) by gentle stirring for several hours at a temperature of 110 °C. The appearance of the membrane and its properties depend a lot on the conditions for preparing the collodion and its polymer value. After several tests, we chose to work with collodions containing 8%, 10% and 12% by mass of polymer. To obtain an 8% w / w PVA solution, we

weighed 8 g of PVA, then made up to 100 g with distilled water, then heated to 90° C and stirred the solution for 2-4 hours. In the case of PVA-PAA alloy, the counter-polymer (PAA) is dissolved in the solution of the polymer (PVA) at 110 °C in the proportion of 10%, 20% and 30% with moderate stirring for 2 hours.

3. Preparation of Membranes

The membranes studied in this work were all prepared by means of a collodion. We mix the required quantities of the polymer solution using magnetic stirring until homogenization. The clear solutions thus obtained are then poured onto a glass plate, then spread using a stainless steel knife, the adjustable spacing of which makes it possible to adjust the thickness of the membrane. Finally, we evaporate the solvent, at 60° C., in an oven for two hours before drying the film formed in a vacuum oven maintained at this same temperature for four hours. Finally, the membranes are peeled from their support and stored in a desiccator until use. The physical properties of membranes (Resistance, crystallinity, etc.) largely depend on the manufacturing conditions of the latter. Thus the temperature of the oven and the residence time are chosen in order to obtain films resistant to the treated mixture and easily removable from the support. All the membranes tested are prepared at around 110° C. This temperature was chosen to have films that resist the aggressiveness of this mixture (The thickness of the membranes was 20 mm).

4. Physico-Chemical Characterization of Membranes

4.1. Infrared Spectrometry

The solvent-polymer interactions are studied by samples placed beforehand in a water-alcohol mixture at 30° C for 24 hours. These, after recovery, are quickly wiped off with filter paper and immediately installed on the crystal. After each measurement, the crystal must be well dried to remove traces of residual solvents. Throughout this study, we take the peak at 1425 cm⁻¹, assigned to the strain vibration of the CH₂ group, as an internal reference [13].

We used infrared (IR) spectroscopy to estimate the crystal structure of these membranes. The spectra are obtained using a GENESIS SERIES Fourier Transform spectrophotometer (ATR: Attenuated Total Reflection) with a resolution of 8cm⁻¹ and an accumulation of 50 measurement cycles. All the samples are observed by ATR (attenuated transmitted reflection) on a ZnSe

(Zinc Selenide) crystal, because their thickness does not allow the use of transmission (saturation of all bands) [14].

4.2. Swelling Phenomenon

A sample of approximately 1 gram, carefully dried in a vacuum oven at 60° C for 8 hours, is weighed using a precision balance (nearest hundredth of a milligram). Then it is immersed in 50 ml of a test solution (water-alcohol) of known concentration, the latter is then placed in an oven at the desired temperature until sorption equilibrium. After reaching the latter, the sample is removed from the liquid medium, its surface is quickly wiped with a filter paper and it is weighed. The swelling G of the sample is calculated by the following equation:

$$G_m = \frac{m - m_0}{m_0} \times 100$$

m_0 : mass of the dry membrane

m : mass of the swollen membrane

4.3. Pervaporation

The behavior of a pervaporation membrane used to separate a binary liquid solution (compound A and B) is characterized by two parameters recommended by Néel [15] and obtained experimentally: the flow of permeate J (expressed in $\text{kg h}^{-1} \text{ m}^{-2}$) and selectivity.

The membrane is placed in a stainless steel tank whose upstream compartment is connected to the tank of the mixture to be treated and whose downstream compartment is maintained at constant low pressure by

a vacuum pump. The experimental device is maintained in a vacuum state by a vacuum pump (vane pump). The vapor recovered during the experiment is condensed in one of the two traps installed in parallel and immersed in liquid nitrogen. The circulation of the load is ensured by a mechanical pump. To bring the unit back to atmospheric pressure and prevent moisture from entering the trap, a desiccant is placed in the tank. (Figure 1)

RESULTS AND DISCUSSION

The dehydration of a water-alcohol mixture by pervaporation has hitherto been a privileged field of application. Pervaporation has indeed been implemented since 1984 in many chemical or agro-food production units to dehydrate alcohols. However, the use of pervaporation remains limited because of the low permeability of the membranes used. The membranes used for the dehydration of an organic solution must be resistant and stable in the solutions to be treated, this at the required temperatures. They must also be selective to water and very permeable, since better selectivity makes it possible to reduce energy consumption and a higher permeability makes it possible to ensure a greater production for a given membrane surface.

After several preliminary studies, we manufactured around twenty membranes based on polyvinyl alcohol (PVA) and polyacrylic acid (PAA) in water, which differ in their behavior from a morphological (transparency, thickness) and physical (resistance, flexibility) point of view by adjusting the polymer content, the drying temperature and the residence time in the oven. The results are shown in the table below: (Table 1)

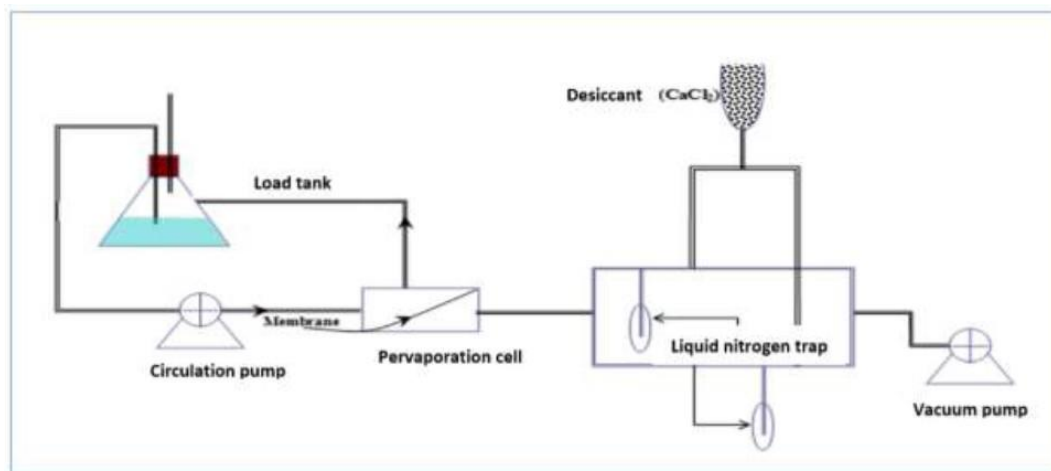


Figure 1: Experimental setup of the pervaporation cell [8].

Table 1: The Composition and Manufacturing Conditions of the Membranes Prepared in the Laboratory. (Solvent: water, Polymer Content / Solvent = 10%)

Polymer	Polymer Content %	Drying Temperature (°C)	Stay in the Oven (min)	Observation of Membranes
PVA	-	80	120	Thin, sticky
PVA	-	80	80	Fragile, thin, sticky
PVA	-	110	40	Fragile, thin, sticky
PVA	-	100	40	Fragile, thin, sticky
PVA	-	80	60	Soluble, fine, sticky
PVA/PAA	90/10	80	80	Transparent, easy to peel off, shiny
PVA/PAA	80/20	80	80	Transparent, easy to peel off, Resistant
PVA/PAA	70/30	80	40	Brittle, transparent, easy to peel off the support

We opted for the choice of the percentage of PAA according to a content up to 30% because the PVA polymer represents the base matrix, while the PAA counter-polymer is not film-forming which means that the higher the concentration of PAA increases, the more the membrane becomes brittle. We varied the concentration of PAA in order to estimate the effect of the COOH group on the transfer of water and ethanol through the membrane and therefore to deduce the flow J and the selectivity. The membranes manufactured have presented different appearances depending on the content and the concentration of the PAA: the membranes become more and more resistant and easy to peel from the support when the content of PAA increases. However, the high concentration of the PAA results in more or less brittle membranes probably related to the non-film-forming nature of the PAA.

1. Characterization of Membranes

1.1. Swelling

A series of membranes of different weights are left in contact with 100 ml of the prepared solution for 24 hours. The measurements were taken after having dried the membranes rapidly between two sheets of absorbent paper and systematically weighed.

We find that the swelling rate is greater for membranes based on PVA / PAA alloy than for membranes based on PVA alone. On the other hand, we notice a marked improvement in swelling by increasing the percentage of PAA introduced into the mixture (Figure 2). The increase in the swelling of these membranes can be explained by the introduction of acrylic groups into the polymer matrix which causes a disorganization of the crystalline structure of the film

and therefore allows a great penetration of water and ethanol molecules.

1.2. Infrared Spectrometry

Analysis of these spectra allows us to detect the following areas: - Between 3500 and 4000 cm^{-1} , bands corresponding to OH bonds. Infrared spectroscopy shows that water molecules react strongly with hydroxyl groups of PVA: thus the OH stretch band of water shifts to low frequencies when the water content does not exceed the saturation threshold in non-crystallizable water. Beyond this threshold, the corresponding band is located around 3400 cm^{-1} , as in pure water which is highly aggregated. - Between 1600 and 2600 cm^{-1} , bands corresponding to the CH and CH_2 bonds. - At 1500 cm^{-1} , a peak appears corresponding to the CO double bond present during the addition of PAA. In this study we will take the peak at 1141 cm^{-1} which corresponds to a symmetrical elongation vibration of the CC bond which is directly related to the crystallinity of the films and we will take the peak located at 1423 cm^{-1} , assigned to the vibration deformation of the CH_2 group, as an internal reference [16, 17]. Different studies show that as the swelling by water increases, we notice variations in band intensity or frequency in the three spectral zones studied: [18-21].

1) The band at 1141 cm^{-1} corresponding to the crystallinity of PVA decreases, that is to say that the crystallinity decreases with the swelling of the membrane. 2) The OH elongation vibration band of water is located at 3275 cm^{-1} when hydration is low (a rate of 45% RH corresponding to less than 15% water in the membrane), then moves towards higher frequencies (around 3370 cm^{-1}) when the membrane

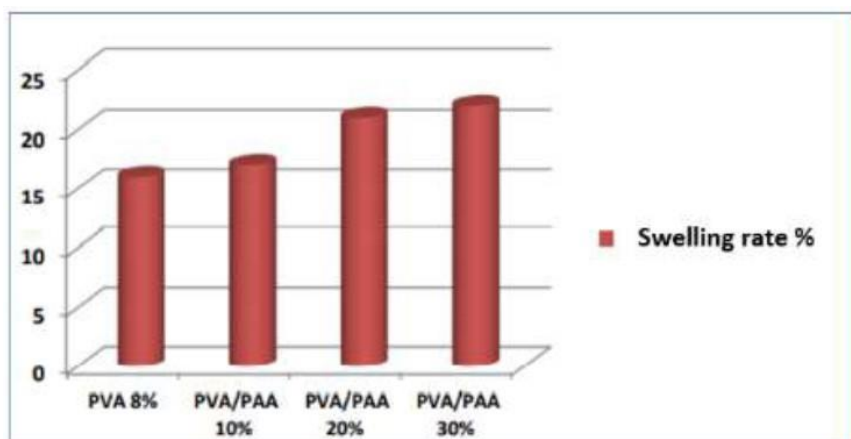


Figure 2: Swelling of dense membranes for 10% water-ethanol mixtures.

contains a greater quantity of water (in an atmosphere containing more than 90% RH). 3) The OH deformation vibration band of water, located at 1652 cm^{-1} under low hydration, shifts to 1642 cm^{-1} as hydration increases.

The appearance of the $\text{C}=\text{O}$ band at 1500 cm^{-1} is proof of the existence of an auto-oxidation reaction of the functions of this polymer in the presence of high air.

From the spectra obtained (Figure 3), we see that the 1141 cm^{-1} peak proportional to the crystallinity of the membrane decreases with the addition of PAA. In fact, the membranes based on 20% and 30% PVA / PAA do not exhibit crystallinity (disappearance of the peak at 1141 cm^{-1}). Therefore, an improvement in the flux is expected by addition of the PAA.

Hydrophilic polymers are the materials of choice for the dehydration of organic solvents by pervaporation. The high selectivity to water of these materials results essentially from strong interactions of the hydrogen bond type between the water molecules and the active groups of the polymer. The existence of these interactions has been demonstrated in infrared spectroscopy by observing the shifts of the vibration frequencies of the characteristic bands of the active groups of a polymer swollen by water or by a water-alcohol mixture. We have thus shown that the OH vibration band of PVA or that of COO of the ionic carboxylic polymer move towards low frequencies, while the deformation band of water, located at 1642 cm^{-1} , moves towards high frequencies [22, 23].

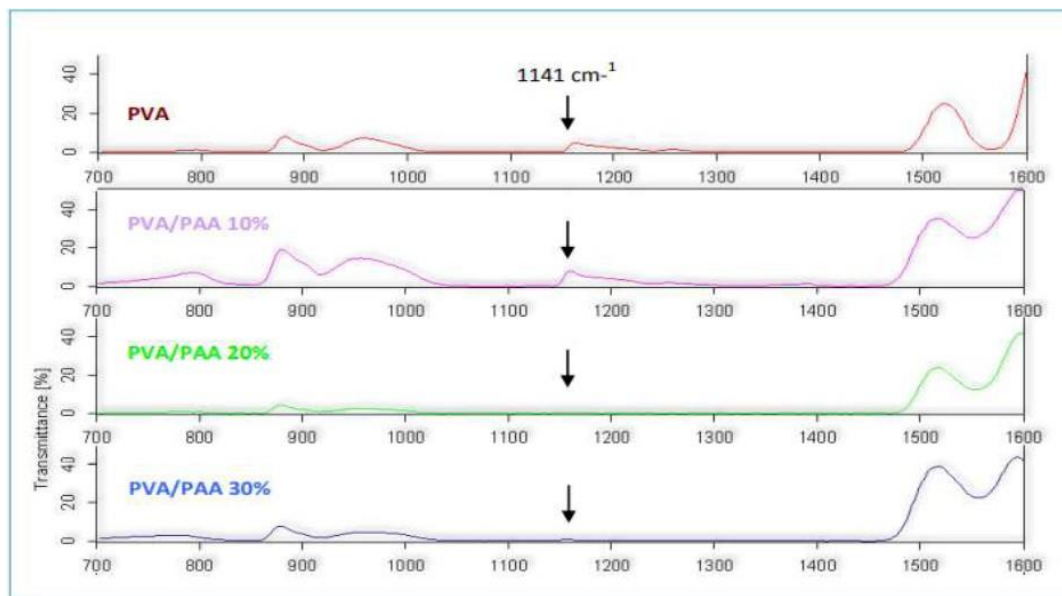


Figure 3: Infrared spectra of OH deformation bands of water absorbed at various PAA contents in PVA membranes (in the 700 cm^{-1} - 1800 cm^{-1} zone).

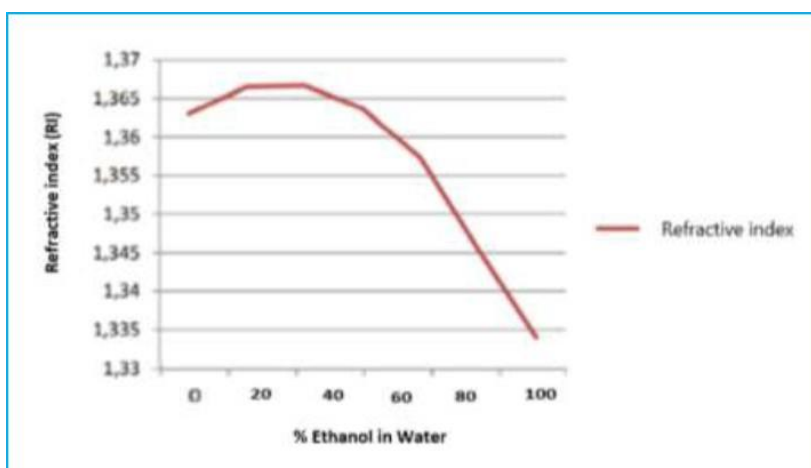


Figure 4: Refractive index as a function of the concentration of the water-ethanol mixture.

2. Pervaporation

All the membranes manufactured in the laboratory were used in pervaporation to evaluate the flux and the selectivity towards the 10% water/ethanol mixture, depending on the PAA content in the alloy.

One of the most interesting cases among the separation problems likely to be solved by pervaporation is the dehydration of ethanol from the binary water-ethanol azeotrope mixture at 4.4% water by weight. Indeed, this concentration corresponds to that of an azeotropic mixture that distillation cannot treat [11]. Since ethanol forms an azeotrope with water at atmospheric pressure containing 89.47% mol of ethanol and 10.53% mol of water, we were interested in studying the behavior of films based on ethanol. polyvinyl alcohol and the alloy of polyvinyl alcohol with polyacrylic acid with respect to the Water – Ethanol mixture at 10%.

2.1. Measurement of the Concentration of the Mixture and of the Pervaporate

The concentration of the mixture to be pervaporated is prepared by volumetric measurement. We used a

Zeiss immersion refractometer whose principle is based on the limit corresponding to the incidence of refraction of a liquid relative to air at the same temperature. The measurement is made in monochromatic light using a sodium lamp. The index of each sample allows the determination of the corresponding concentration. First, we calibrated the refractometer. To do this, we have drawn the figures representing the refractive index as a function of the concentration of the different mixtures that we prepared by weighing from pure ethanol. For a solution of unknown concentration, we measured the refractive index and deduced its concentration using the calibration curve below. (Figure 4)

2.2. Measurement of Selectivity and Flux J

The behavior of PVA films in the pervaporation of a water-ethanol mixture experiences an appreciable improvement in performance after addition of PAA. This improvement is due to a simultaneous increase in flux and selectivity (Table 2).

α is expressed by the ratio $(C_w)_p / (C_w)_f$ with $(C_w)_p$, the water concentration in the pervaporate and $(C_w)_f$, the water concentration in the feed.

Table 2: Performance of the Membranes in Pervaporation with Respect to the 10% Water/Ethanol Mixture

Membranes	α	J	$J (\text{l}''\text{1})$	$J (\text{l}''\text{1})^4$
PVA	2.5	0.11	0.165	0.556
PVA/PAA (10%)	2.7	0.18	0.306	1.503
PVA/PAA (20%)	3.6	0.34	0.884	15.537
PVA/PAA (30%)	3.8	0.48	1.344	29.503

Since selectivity and flux of a membrane generally change in opposite directions, we will use two indicators to assess the pervaporation performance of a membrane. The first index I_1 comes from the quantitative analysis of solvents purified by continuous pervaporation [19].

$$I_1 = J (S/P)$$

The index I_1 corresponds to the production capacity of purified solvent at the considered concentration of the liquid mixture. It combines a quality factor (S/P) and a quantity factor J to express the productivity of a unit pervaporator.

$$I_2 = J (S/P)^n \quad n = 4$$

The I_2 index is used when operating costs exceed the energy and performance of the capital investment (installation, membranes, etc.). In the case of water-ethanol mixtures, the value of n is taken equal to 4.

The improvement of the pervaporation flux with the PAA content of the membrane may be due to the strong swelling of the latter resulting in an increase in the transmembrane flux in relation to the disorganization of the crystalline structure of the film created by the introduction of the PAA allowing thus a great penetration of water and ethanol molecules in the film. On the other hand, the selectivity to water and the permeability of the PVA membrane alloyed with the PAA are, for their part, favored thanks to the hydrophilic nature of the membrane.

However, in other studies, membranes show better selectivities when the PAA contents in the alloy are lower [24, 25]. On the other hand, they are more permeable, which allows us to see the use of these membranes for various applications. The selectivity of the membrane decreases rapidly with the PAA content; this phenomenon is probably due to the stronger affinity of PAA with ethanol [26]. Urtiaga A. M. *et al.* note that the diffusion coefficient does not vary much with the PAA content in the alloy. On the other hand, the selectivity (S/P) decreases rapidly with this same content, which would correspond to the variation in selectivity observed in pervaporation [27]. In our study, by referring to the performance indices, the performance of a membrane based on PVA-PAA alloy (30%) is improved by increasing the production capacity $J (S/P)$ and on the other hand the yield $J (S/P)^4$. This improvement is mainly related to the

increased flux and selectivity which can be correlated with the increased swelling of the membrane.

All the membranes have a higher permeation flux than that of pure PVA, especially when the PAA content is high. The selectivity to water of these crosslinked membranes, represented by the water content in the permeate, is appreciable. The increase in permeability of the crosslinked PVA-PAA alloy could be explained by the fact that the PAA would play a role of inhibitor of crystallization of PVA [28].

The function of PAA is twofold: it is indeed the crosslinking agent, but also a macromolecular additive. Its crosslinking character gives the PVA a strong resistance to the aqueous solutions to be treated and limits the swelling of the membrane, which leads to an improvement in the selectivity to water. In addition, its role as an additive makes it possible to improve the permeation flow of the alloy. It is therefore possible to obtain a good permeability / selectivity compromise using macromolecular crosslinking agents [29, 30].

By varying the PAA content in the membranes, their properties can easily be modified: better selectivity at low PAA content and better permeability at high content.

CONCLUSION

The characteristics of PVA membranes and PVA-PAA alloys are influenced by the preparation conditions and by the PAA content of the membranes. The addition of PAA to PVA makes possible the improvement of swelling, the flow is improved as well as the selectivity to water and the permeability of the membrane which makes the PVA-PAA alloy a simple method and effective in ensuring the dehydration of the Water-Ethanol mixture.

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AUTHORS' CONTRIBUTIONS

The participation of each author corresponds to the criteria of authorship and contributor ship emphasized in the Recommendations for the Conduct, Reporting, Editing, and Publication of Scholarly work in Medical Journals of the International Committee of Medical Journal Editors. Indeed, all the authors have actively

participated in the redaction, the revision of the manuscript, and provided approval for this final revised version.

CONFLICT OF INTERESTS

The authors declare no conflict of interests in relation to this work.

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