

# PERVAPORATIVE INVESTIGATION OF ETHYL ALCOHOL DEHYDRATION

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## **Abstract**

*Pervaporative separation properties of crosslinked chitosan and alginate membrane on ethanol-water mixture at room temperature was studied. The influence of crosslinking agents on the separation properties were discussed. Selected crosslinking agents were affected differently on used polymer matrices. The better separation properties were obtained for membranes crosslinked by phosphoric (V) acid. The highest pervaporation separation index (309.6 kg/m<sup>2</sup>·h) and separation factor (52.6) were obtained for phosphoric (V) acid crosslinked alginate membranes, however, the greatest total flux (12.4 kg/m<sup>2</sup>·h) obtained for phosphoric acid crosslinked chitosan membranes.*

**Keywords** – *chitosan, alginate, pervaporation, crosslinking, dehydration*

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## **1. Introduction**

Pervaporation is a technique aimed at the separation of liquid mixtures, involves a membrane that is in contact with the feed solution on the one side, while vapour permeate is removed from the other side. Pervaporation allows breaks the technological barriers in chemical industry enabling the separation of organic mixtures, which are difficult to be separated by other methods like extraction or distillation. In recent times, pervaporation is mainly used for the dehydration of alcohols, especially for ethanol [1-8,10-14]. Dehydration process requires the application of hydrophilic membranes, for example, on the basis of chitosan [2,4,5,10,13,14] and alginate [3,6-8,11,12].

The aim of this work was the comparison of the effect of crosslinking with the transport behaviour of chitosan and alginate membranes in the pervaporative dehydration of ethanol.

## **2. Experimental part**

### **2.1 Preparation of membrane**

Membranes were prepared by solution casting and solvent evaporation technique according with [4-8]. The prepared 3 wt.% chitosan solution in 1 vol.% acetic acid was casted into a 16 cm diameter Petri dish and left until solvent evaporation at 40 °C. Next, chitosan membranes were immersed in a crosslinking solution, and subsequently washed with distilled water, immersed in 2 wt.% sodium hydroxide solution. After membranes were taken off were washed again with distilled water until neutral pH and dried in room temperature.

Alginate membranes were prepared by similar technique. The prepared 1.5 wt.% sodium alginate solution was casted into a Petri dish and left until solvent evaporation at 36 °C. Next, alginate membranes were immersed in a crosslinking agent solution for certain time, then washed with water to clean off an excess of the crosslinking agent. Ethanol was used to support its removal from a Petri dish. Next, membranes were dried in room temperature.

Details about crosslinking time and crosslinking agent for prepared membranes are given in Table 1.

### **2.2 Pervaporative separation**

Pervaporation experiments were performed at room temperature. Prepared membrane was placed in a membrane chamber. Measurements were performed for membranes in contact with solution containing 93 wt.% of ethanol. Mixture (1 dm<sup>3</sup>) was poured into the feed tank and pumped, using a circulation pump, to the membrane chamber where feed was separated. Next, retentate was recirculated to the feed tank, however permeate vapours were condensed in a liquid nitrogen cooled trap. Permeate was collected for duration of 7.5 h and weighed after defrosting on analytical balance to determine the value of total flux. The reduced pressure on the permeate side was 190 – 300 Pa was produced

**Table 1.** Experimental parameters of the crosslinked chitosan and alginate membranes preparation.

|                 | Crosslinking agent   | Time [min] |
|-----------------|--|------------|
| <i>Chitosan</i> |  |            |
| CHPA            | 13.61 wt.% phosphoric (V) acid in 88 vol.% isopropanol solution                    | 30         |
| CHGA            | 1.25 wt.% glutaraldehyde solution  | 5          |
| <i>Alginate</i> |  |            |
| ALPA            | 3.5 vol.% phosphoric (V) acid in 90 vol.% isopropanol solution                     | 120        |
| ALGA            | 0.71 wt.% glutaraldehyde, 1.15 wt.% hydrochloric acid in 75 vol.% acetone solution | 1440       |

by a vacuum pump and controlled with a vacuum gauge. Before measurements, each membrane was conditioned for 0.5 h in a membrane chamber being in contact with circulating feed solution. After applying of reduced pressure and its stabilization, usually within 2 min., flux measurement was started.

The collected samples of permeate as well as retentate and feed were analyzed by gas chromatography technique. Measurements were performed on a Perkin Elmer Clarus 500 GC equipped with an Elite-WAX ETR column (30 m), and FID detector.

### 2.3 Theoretical part

For the estimation of the membrane efficiency, several parameters are evaluated. First of all, flux is determined by the amount of permeate collected over a given period of time. The permeation flux  $J$  of component  $i$  is calculated using the following equation [9]:

$$J_i = \frac{m_i}{A \cdot t} \left[ \frac{kg}{m^2 \cdot h} \right] \quad (1)$$

*where:*  $m_i$  – weight of component  $i$  in permeate [kg],  $A$  – effective membrane area [ $m^2$ ],  $t$  – permeation time [h].

For homogeneous membrane, flux could be normalized to the equal thickness of  $1\mu m$  and calculated as the normalized flux of component  $i$  [9]:

$$J_{Ni} = J_i \cdot d \left[ \frac{\mu m \cdot kg}{m^2 \cdot h} \right] \quad (2)$$

*where:*  $d$  – membrane thickness [ $\mu m$ ].

Knowing the normalized flux and partial vapour pressure of component  $i$  in feed it is possible to estimate the permeability coefficient of component  $i$  [9]:

$$P_i = \frac{J_{Ni}}{p_{if}} \left[ \frac{\mu\text{m} \cdot \text{kg}}{\text{m}^2 \cdot \text{h} \cdot \text{Pa}} \right] \quad (3)$$

where:  $p_{if}$  – partial vapour pressure of component  $i$  in feed [Pa].

For describing the separation properties of the membrane, two parameters are used: separation factor ( $\alpha_{AB}$ ) and selectivity coefficient ( $Sc_{AB}$ ). Separation factor determines the separation of mixture through the changes of component concentration in the feed and permeate and is calculated by [4,9]:

$$\alpha_{AB} = \frac{y_A / y_B}{x_A / x_B} \quad (4)$$

where:  $x_A, x_B$  – weight fraction of component in the feed [wt.%],  $y_A, y_B$  – weight fraction of components in permeate [wt.%].

Selectivity coefficient indicates the component which is preferentially transported through the membrane and is equal to the ratio of permeability of separated components [9]:

$$Sc_{AB} = \frac{P_A}{P_B} \quad (5)$$

In order to compare the separation efficiency of different investigated membranes, a pervaporation separation index, PSI expressed by following equation [9,10] is used:

$$PSI = J(\alpha_{AB} - 1) \left[ \frac{\text{kg}}{\text{m}^2 \cdot \text{h}} \right] \quad (6)$$

where:  $J$  – total permeate flux [ $\text{kg}/\text{m}^2 \cdot \text{h}$ ],  $\alpha_{AB}$  – separation factor.

## 2.4 Degree of swelling

The membrane swelling test was determined by weight method. Membrane samples were weighting before and after their immersions in distilled water or ethanol for about 24 h. Mass changes of analysed membranes were measured using analytical balance and degree of swelling was calculated using following equation:

$$DS = \frac{W_S - W_D}{W_D} \cdot 100 [\%] \quad (7)$$

where:  $W_S$  is the weight of the swollen membrane and  $W_D$  is the weight of the dried membrane samples.

### 3. Results and Discussion

For investigation of the influence of polymer matrix and crosslinking agents on the ethanol dehydration by pervaporation process, four different membranes were prepared. Chitosan and alginate crosslinked with phosphoric (V) acid or glutaraldehyde were used as a material for membrane preparation. Subsequently, properties of membranes were determined to 93 wt.% ethanol mixture in order the crosslinking agent for the efficient of transport parameters. The calculated parameters for chitosan and alginate crosslinked membranes were collected in Table 2.

Although the thickness of alginate membranes is 2-3 times lower than chitosan ones, for phosphoric (V) acid crosslinked membranes obtained total flux was greater than for similar alginate membrane.

**Table 2.** Transport characteristic of chitosan and alginate membranes crosslinked with different crosslinking agents evaluated for 93 wt.% ethanol mixture.

|  | Chitosan membranes |                  | Alginate membranes |                  |
|--|--------------------|------------------|--------------------|------------------|
|  | CHPA               | CHGA             | ALPA               | ALGA             |
| Thickness, $d$ [ $\mu\text{m}$ ]   | $50.8 \pm 4.9$     | $56.5 \pm 5.4$   | $22.1 \pm 1.8$     | $26.2 \pm 1.5$   |
| Total flux, $J_{total}$ [ $\text{kg}/\text{m}^2 \cdot \text{h}$ ]                                | $12.4 \pm 1.2$     | $3.0 \pm 0.3$    | $6.0 \pm 0.4$      | $6.7 \pm 0.6$    |
| Total normalized flux, $J_{N total}$ [ $\mu\text{m} \cdot \text{kg}/\text{m}^2 \cdot \text{h}$ ] | $629.4 \pm 61.5$   | $171.8 \pm 16.9$ | $133.1 \pm 9.3$    | $182.3 \pm 16.4$ |
| Separation factor, $\alpha_{AB}$   | $11.5 \pm 1.0$     | $7.0 \pm 0.6$    | $52.6 \pm 5.0$     | $17.6 \pm 1.7$   |
| Selectivity coefficient, $S_{CAB}$   | $0.6 \pm 0.1$      | $0.5 \pm 0.1$    | $3.2 \pm 0.3$      | $5.3 \pm 4.8$    |
| Pervaporation separation index, $PSI$ [ $\text{kg}/\text{m}^2 \cdot \text{h}$ ]                  | $129.8 \pm 12.7$   | $18.4 \pm 1.7$   | $309.6 \pm 30.4$   | $111.2 \pm 10.9$ |

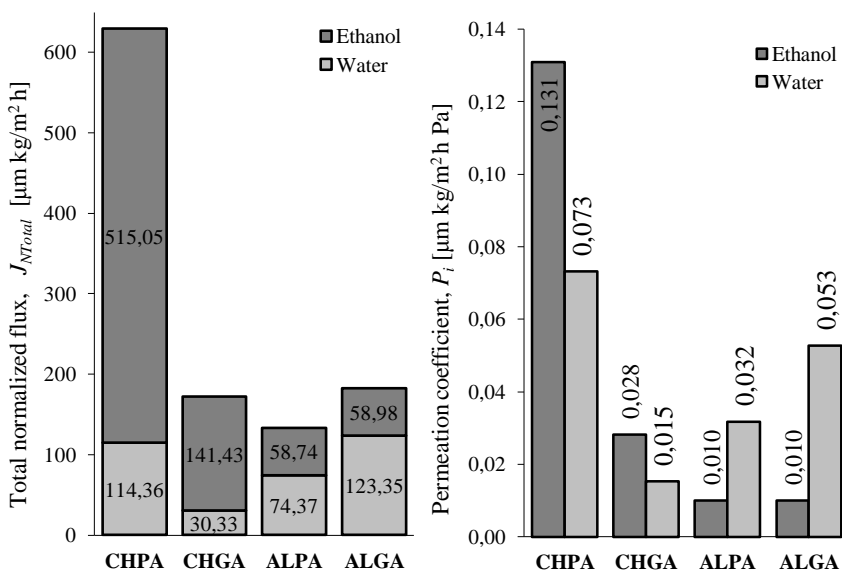
Contents of water and ethanol normalized flux in total normalized flux for all obtained membranes is shown in Fig 1. Ethanol normalized fluxes obtained for both, phosphoric (V) acid and glutaraldehyde crosslinked chitosan membranes are approximately 4.5 times higher than water normalized fluxes, whereas normalized fluxes of water for phosphoric (V) acid and glutaraldehyde crosslinking alginate membranes are higher than ethanol normalized fluxes by 27% and 112%, respectively.

Separation factor is two times higher for glutaraldehyde and five times higher for phosphoric (V) acid crosslinked alginate membranes than for analogical chitosan membranes, however, both chitosan and alginate membranes obtained greater value of separation factors for phosphoric (V) acid crosslinking agent.

Alginate membranes exhibit a significantly greater selectivity coefficient. Selectivity of glutaraldehyde crosslinked membrane is about 7 times and

phosphoric (V) acid crosslinked one is about 10 times higher than the selectivity coefficient of corresponding chitosan membranes. Low value of selectivity coefficients for both types of chitosan membranes is caused by the permeability coefficients which for water are two times smaller than for ethanol (Fig. 1).

For both alginate membranes, the relationship between permeation coefficients and normalized fluxes of water and ethanol can be observed. In case of glutaraldehyde crosslinked alginate membrane increases the water permeability coefficient is higher by 65% resulting in a similar rise of its normalized flux, while, at the same time, permeation coefficient of ethanol and its normalized flux were unchanged. In the case of alginate membranes affects crosslinking agent the ratio of the permeability coefficients of separated components but slightly the value obtained fluxes. Yeom and Lee prepared alginate and alginate/poly(vinyl alcohol) membranes crosslinked with 10 % glutaraldehyde solution [11,12]. They conducted pervaporative dehydration of 90 % ethanol solution at 50 °C. Obtained by Yeom total flux for glutaraldehyde crosslinked blends was 2.5 times lower and separation factor 6 times higher than for similar alginate membrane, while measured total flux was 0.1 kg/m<sup>2</sup>·h and separation factor 500. Yeom and Lee reported that increase in glutaraldehyde concentration in the crosslinking bath slightly decrease flux but pronounced increase the separation factor what is consistent with our results, that in case of alginate membranes crosslinking agents mainly affect the separation properties.



**Figure 1.** The total normalized fluxes and the contribution of normalized fluxes of each component (left), and the permeation coefficient of water and ethanol (right) for chitosan and alginate membranes with different cross-linking agents.

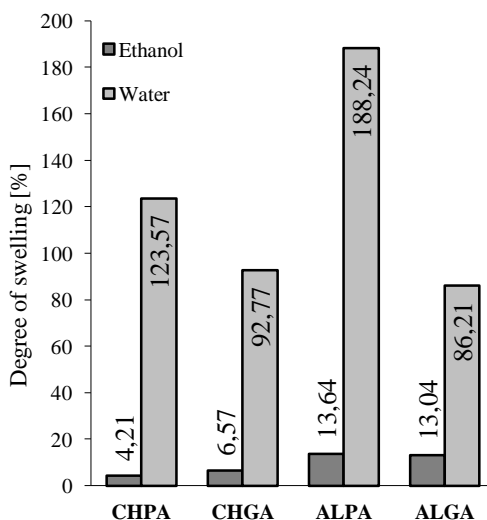
Observed ratios of water and ethanol permeation coefficients for both types of chitosan membranes are the same, however, the values of the permeation coefficients of phosphoric (V) acid crosslinked chitosan membranes have been higher than for glutaraldehyde crosslinked one more than 4.8 and 4.6 times for water and ethanol, respectively. Received ethanol normalized fluxes for both chitosan membranes was 4.5 – 4.7 times higher than for water, and their values also are higher for phosphoric (V) acid. At most, crosslinking agent could stronger influence on the separation properties, in the case of alginate membranes, whereas the flux is mainly changing for chitosan membranes.

On the other hand, Zhang et al. used glutaraldehyde crosslinked chitosan membranes to dehydration different mixtures, including 90% ethanol solution [13]. Their research conducted at 50 and 60 °C and showed, that in higher temperature, observed decline value of separation factor (105) and increase of total flux (0.25 kg/m<sup>2</sup>·h). Additional, scientists modified membrane surface by maleic anhydride what pronounced increase of separation factor while total flux changed slightly. It is possible that additional modifications to the membranes obtained by us will improve the separation factor without a significant decline of the flux which is very high.

The most commonly used criterion for comparing membranes is the value of their pervaporation separation index (PSI). Comparing only the PSI between all obtained membranes can be said that the best properties have phosphoric (V) acid crosslinked alginate membranes. Kalyani et al. studied pervaporative ethyl alcohol dehydration on blend alginate/poly(vinyl pyrrolidone) crosslinked in an analogous manner by phosphoric (V) acid. Although they obtained better separation factor (364), determined PSI index is approximately 9.5 times lower than obtained in presented work [8].

On the other hand, PSI index value depends on flux and separation factor but is not sensitive to the selectivity coefficient. Glutaraldehyde crosslinked alginate membrane had the highest value of separation factor and high selectivity coefficient and showed good separation properties whereas the total flux obtained for this membrane was two times lower than for phosphoric (V) acid crosslinked chitosan membranes. However, their PSI was only a little lower than for phosphoric (V) acid crosslinked chitosan membrane. Although Sunitha et al. in work [14] for similar membrane reported lower total flux (0.2 kg/m<sup>2</sup>·h) and much higher separation factor (125), however, their membrane had a significantly lower PSI index (24.8 kg/m<sup>2</sup>·h).

Ratio of swelling in water and ethanol for crosslinked chitosan membranes are two times higher than for analogical alginate membranes (Fig. 2). The highest difference between the degree of swelling in water and ethanol was observed for phosphoric (V) acid crosslinked chitosan membrane and the lowest for glutaraldehyde crosslinked alginate membrane.



**Figure 2.** Degree of swelling in water and ethanol for all prepared membranes.

Glutaraldehyde crosslinked membranes, independently of polymer matrix and differences in crosslinking process, not drastically influence the membrane's swelling behaviour in water what contrast to the phosphoric (V) acid crosslinked ones. Glutaraldehyde is more hydrophobic and strongly connects crosslinked polymer chains, not allowing to swell in water, opposite to phosphoric (V) acid crosslinker. Higher degree of swelling for phosphorylated membranes may be related with the presence of polar groups in spite of crosslinking [14] and the solvation of phosphate ions through water. Concentration of phosphoric (V) acid in crosslinking process was much lower for alginate than chitosan membranes. Therefore, solvation of phosphate ions is better and degree of swelling is greater. Unfortunately, adsorption of the large amount of water at higher feed concentration cause enhanced swelling and subsequently falls in membrane selectivity due to plasticization of the polymer matrix.

## 5. Conclusions

In this paper, homogenous chitosan and alginate membranes crosslinked by phosphoric (V) acid and glutaraldehyde were prepared and influence of the crosslinking modification on the efficiency of ethanol dehydration in the pervaporation process was studied.

The investigated crosslinking agents differently affected on the membrane separation properties. In the case of alginate membranes crosslinking agent can influence the separation properties, whereas in chitosan membranes it influences on the value of obtained fluxes. On the other hand, better results observed when phosphoric (V) acid was used as the crosslinking agent.



All obtained membranes have a much higher value of the total flux and significantly lower separation factor, however, the values of pervaporation separation index are very high and are higher than presented in literature.

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