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ELECTROLYTES DIFFUSION THROUGH MODIFIED PVA HYDROGEL MEMBRANE

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Abstract: *During or after synthesis through the freeze-thaw technique, poly(vinyl alcohol) [PVA] hydrogel membranes were subjected to different physical or chemical treatments in order to study the diffusion of NaCl and KCl in comparing to the PVA hydrogel membrane. The structure modifications have been made by inserting chitosan in the PVA solution before the freeze-thawing process or by treating the hydrogel membrane after synthesis with ethyl alcohol solution, boric acid, oxidizing mixture or by compounding PVA hydrogel with* Cu^{2+}*. The results show promising possibilities to tailor the membrane permittivity and transport properties.*

Key words: *PVA, hydrogel, permittivity coefficient, diffusion coefficient.*

1. Introduction

Diffusion of electrolytes in polymeric materials have been intensively studied [4], [9], [22], [25] in order to develop the knowledge of the transport mechanism of such specific solutes through membranes and is having various practical applications [6], [11], [23-24]. Among polymers, hydrogels have been successfully used for removal and separation of metal ions [2], [5], [10], [13].

PVA is known to form thermo- reversible (physical) hydrogels upon freeze-thaw cycles [7], hydrogels that have a good mechanical strength and a good elasticity. Moreover, because the mechanism of electrolyte transport may involve a variety of interactions between the system constituents the transport through PVA modified membranes still is an interesting study subject [3], [8], [15-18], [20-21].

There are a number of models describing how diffusion coefficients of solutes in hydrogels vary with water concentration, polymer volume fraction, structure modifiers etc.

In this paper, structure modifications (by using oxidizing agents such as a mixture of potassium permanganate and sulphuric acid, complexing agents such as boric acid and copper ions, solvents such as ethylic alcohol or bio-insertions like chitosan) of the PVA hydrogel membranes where made in order to study how these treatments are changing the diffusion process.

To follow the diffusion process, the conductimetric method was chosen, even if it is not a selective method, but because it is a rapid, without additional costs (no reagents needed) and it is easy to follow.

2. Experimental

2.1. Materials

- PVA 90-98% industrial grade (polymerization degree 900; hydrolysis degree 98 mol %; polydisperse), was supplied

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- Sodium chloride, potassium chloride (Merk, pro analysis) were used without further purification. Solutions of 0.1 M NaCl and KCl have been prepared with distilled water.
- Chitosan powder from Merk, pro analysis.
- Solutions of boric acid 0.1 M and 1 M; solution of potassium permanganate 0.1 N and sulfuric acid 20% and tetra ammonia copper (II) complex.
- PVA cryogelic membranes were synthesized according to the method presented somewhere else [15]. After synthesis the PVA membranes were conditioned in distilled water for two to three weeks.
- PVA modified membranes were obtained as it follows:

- PVA membrane doped with Cu^{2+} [PVA_{Cu2+}] - after removing from distilled water and whipping off with filter paper, the PVA membrane was immersed for 14 days, in a copper tetra-amino complex solution with pH > 8. After that the membrane has been placed in water in order to eliminate the salt surplus. Figure 1 shows the equation of chemical reaction that describes the process.

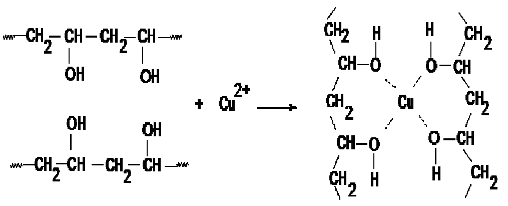


Fig. 1. *Chemical reaction between PVA and Cu^{2+}*

- PVA membrane treated with alcohol [PVA_{alc}] - after removing from distilled water and whipping off with filter paper, the PVA membrane was immersed for 3 hours in ethylic alcohol and then rehydrated in water. As in dried membrane case, the resulting membranes were more rigid then the initial one, and the water quantity sorbed at equilibrium was smaller.

- PVA membranes treated with boric acid membranes [$PVA_{ba0.1}$] [PVA_{ba1}] - after water conditioning, the PVA membranes were immersed for one hour in two different solutions of boric acid of 0.1 and 1 N. After immersion the membranes were washed and then immersed in distilled water to eliminate the acid surplus. The equation of chemical reaction is given in Figure 2:

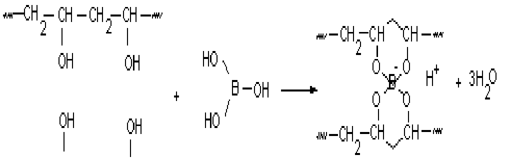


Fig. 2. *Chemical reaction between PVA and boric acid*

- PVA membrane treated with oxidizing mixture, $KMnO_4$ and H_2SO_4, [PVA_{ox}] - after water conditioning the PVA membrane was immersed for 20 minutes in an oxidizing mixture formed by 30 mL of $KMnO_4$ 0.1N and 37 mL of H_2SO_4 20%. After immersion the membranes were washed with distilled water to eliminate the oxidizing mixture surplus.

- PVA membranes with chitosan [PVA_{chit}] - the membranes were obtain by dispersing 1 g of chitosan powder into the PVA solution under continuous stirring and then following the synthesis presented elsewhere [15].

2.2. Diffusion Studies

Diffusion experiments were carried out in a diffusion cell (represented in Figure 3) with two compartments: (A): the donor compartment and (B): the receptor compartment.

Each compartment has a volume V of 250 mL and they are interconnected through an opening of 0.659 cm^2 area (A). The membrane, with a thickness l, previously balanced in water, was placed between the two compartments. Solutions in both cells were stirred by using a magnetic stirrer F20 FALC.

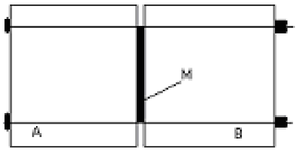


Fig. 3. *Diffusion cell*

A Radelkis Conductometer OK-114 was placed into the B compartment and every 5 minutes the solution conductivity was noted. Based on these measurements, the diffusion, D_θ, and the permittivity, P, coefficients were calculated [17] by the following Equations:

$$D_\theta = \frac{l^2}{6\theta}, \tag{1}$$

$$p = \frac{Vl}{Ac_i}\frac{dc}{dt}, \tag{2}$$

where θ is the time-lag, t is the time, V is the volume of one compartment of the diffusion cell, A is the area of the opening between the two compartments of the diffusion cell. dc/dt is the dye permeation rate and c_i is the initial concentration of the dye in solution in the compartment A of the diffusion cell.

3. Results and Discussions

Since the PVA hydrogelic membranes are porous [7], the separation is induced by the differences in particle size and the high selectivity will be obtained when the particle size (Table 1) is larger than the pore size of the membrane [14].

To highlight what is the effect of PVA modifying treatments on membrane selectivity, diffusion through membranes of PVA and modified PVA for two electrolytes was followed.

Table 1
Ionic and hydration radius for sodium and potassium ions [12]

Ion	r_i [Å]	r_H [Å]
Na^+	0.95	3.58
K^+	1.33	3.31

In Table 2 the permitivity and diffusion coefficients of NaCl and KCl obtained for the PVA treated and untreated membrane are presented (membranes thiknesses were between 0.8 and 1.2 mm).

From the experimental data from Table 2 it can be observed that the permittivity of PVA hydrogel membranes can be altered by the treatment with various oxidizing agents or complexing agents. In all cases, the permittivity coefficient of the PVA membrane is higher for KCl than for NaCl, with a percent comprised between 15.68% and 34.63%. This can be explained by taking into account the Hofmeister series [26], chaotropic species respectively, determining the salting-out processes and, as consequence, the breaking of the hydrogen bonds from water structure. The well-known chaotropic effect of K^+ ion determines the breaking of the hydrogen bonds both between the water molecules and between water and PVA molecules.

Also the smaller hydration radius of K^+ compared to Na^+ (Table 1) determines a higher permittivity coefficient for KCl ($P_{KCl} = 6.16 \cdot 10^{-6}$ cm^2 s^{-1}) than for NaCl ($P_{NaCl} = 4.54 \cdot 10^{-6}$ cm^2 s^{-1}). Thus, the K^+ ion can interact with the polymer determining a lower diffusion coefficient in all cases, except for the PVA_{ba1} and PVA_{ox}, than for Na^+ ion. This interaction leads to its retention in the PVA membrane up to a saturation level; then, due to the concentration gradient generated between the membrane and solution compartment B, K^+ and Cl^- ions permeate the membrane leading to a rapidly increase of the permeability coefficient in comparing to NaCl.

Table 2

Salt permitivity and diffusion coefficients through the PVA and PVA treated membrane

No	Membrane type	$P_{\mathrm{NaCl}}\cdot10^6$ [cm^2/s]	$D_{\mathrm{NaCl}}\cdot10^6$ [cm^2/s]	$P_{\mathrm{KCl}}\cdot10^6$ [cm^2/s]	$D_{\mathrm{KCl}}\cdot10^6$ [cm^2/s]	A^* [%]	B^{**} [%]	*A-B* [%]
1	PVA	4.54	4.60	6.16	3.91	-	-	-
2	$\mathrm{PVA_{Cu2+}}$	4.22	3.12	5.18	3.01	-6.98	-15.91	8.93
3	$\mathrm{PVA_{alc}}$	4.96	4.45	6.98	4.01	9.49	13.31	-6.33
4	$\mathrm{PVA_{ba0.1}}$	7.26	7.91	8.61	5.54	59.91	39.77	20.14
5	$\mathrm{PVA_{ba1}}$	4.74	3.62	5.81	3.76	4.36	-5.73	10.09
6	$\mathrm{PVA_{ox}}$	5.96	5.55	9.12	5.71	31.28	48.02	-16.74
7	$\mathrm{PVA_{chit}}$	3.33	3.69	4.76	4.51	-26.65	-22.76	-3.89

$$^{*}\ A=\frac{(P_{NaCl})_{modif.membr.}-(P_{NaCl})_{unmodif.membr.}}{(P_{NaCl})_{unmodif.membr.}}\times100, \tag{3}$$

$$^{**}\ B=\frac{(P_{KCl})_{modif.membr.}-(P_{KCl})_{unmodif.membr.}}{(P_{KCl})_{unmodif.membr.}}\times100. \tag{4}$$

Comparing the permittivity coefficient of NaCl and KCl to the untreated and treated PVA membrane, the following could be concluded:

- For the copper ions dopped membrane, $\mathrm{PVA_{Cu2+}}$, the permittivity coefficient is decreased by 6.98% for NaCl and by 15.91% for KCl. This behavior is due to the membrane densification under the cross-linking effect of the copper ion. Nevertheless the gels collapsed and the water is eliminated under the electrolytes influence. So the decrease in the pores dimension and in the water quantity inside of the gel, determine a more pronounced decrease of the diffusion rate and of the permittivity coefficient.
- The alcohol treatment increases the permittivity coefficient from 9 to 13%, by washing out the small PVA molecules not involved in the PVA crosslinking during the membrane obtaining.
- When the PVA membrane is treated with concentrate boric acid, a decrease of 5.73% in the permittivity coefficient is observed in the case of KCl and an increase of 4.36% for NaCl.
- On the other hand, treatment of the PVA hydrogel membranes with diluted boric acid or oxidizing mixture ($\mathrm{KMnO_4/H_2SO_4}$) increases the permittivity coefficient of the membrane by 59.91% and 31.28%, respectively for NaCl, and by 39.77% and 48.02%, respectively for KCl.
- Dispersion of chitosan into the hydrogelic matrix lead to a decrease of pores availability for salt diffusion and like in previous cases, membrane permittivity coefficient is reduced by 26.65% for NaCl, and 22.76% for KCl in comparing to the PVA unmodified membrane.

In Figure 4 graphical representations of the concentration of the salt diffused C_{salt} (mol/L) vs. time (*s*) are shown:

a) for PVA membrane treated with oxidizing mixture (□ - for NaCl diffusion; ■ - for KCl diffusion);

b) for PVA membrane treated with boric acid (for NaCl diffusion: □ boric acid 0.1 N and Δ boric acid 1 N; for KCl diffusion: ■ boric acid 0.1 N and ▲ boric acid 1 N);

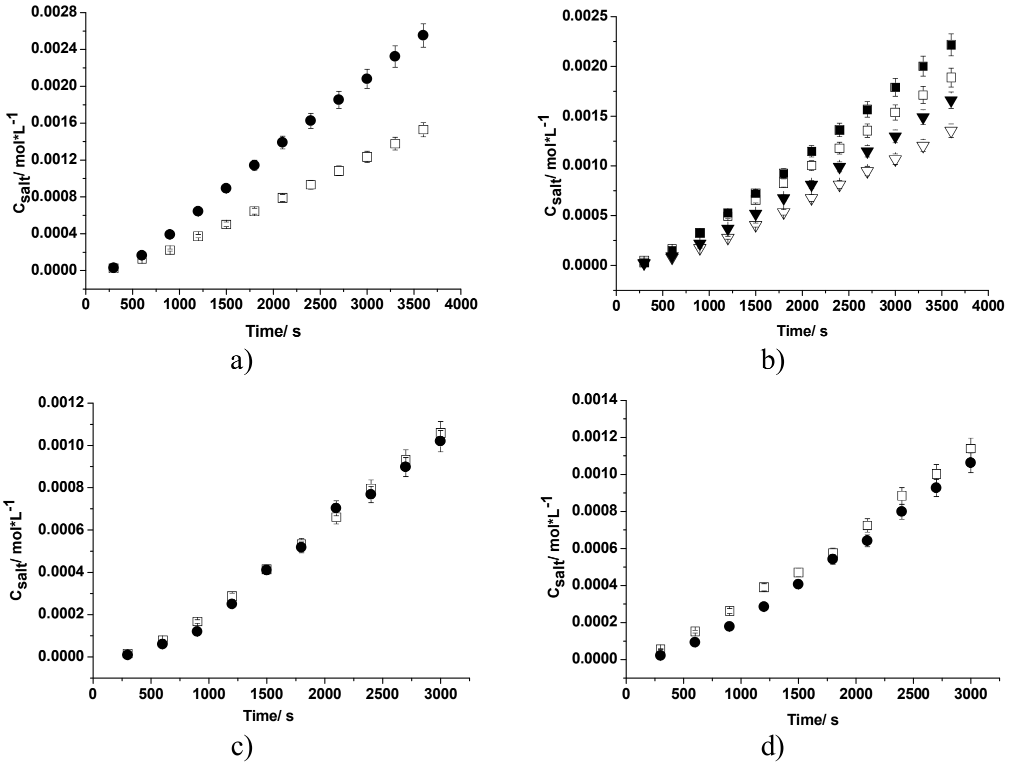
c) for PVA membrane compounded with copper (□ - for NaCl diffusion; ■ - for KCl diffusion);

d) for PVA membrane with chitosan (□ - for NaCl diffusion; ■ - for KCl diffusion).

The retaining efficiency of the metal ions by the PVA and modified PVA membrane after 50 minutes was determined and is represented in Figure 5.

The yield of retention was determined by conductometric measurements using the following Equation:

$$\eta = 100 - \frac{C_B}{C_A} \cdot 100, \tag{5}$$



a) b)

c) d)

Fig. 4. *Concentration of the salt diffused, C_{salt} (mol/L) vs. time (s)*

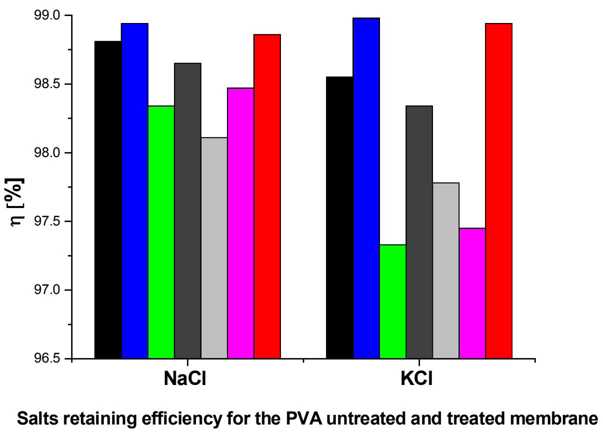


Fig. 5. *Salts retaining efficiency for:* ■ *PVA,* 🟦*$PVA_{Cu^{2+}}$,* 🟩*PVA_{alc},* ■*PVA_{ba1},* ■*$PVA_{ba0.1}$,* 🟪*PVA_{ox},* 🟥*PVA_{chit} membranes*

where: C_B is the concentration in the B compartment of the diffusion cell after 3000 seconds of electrolyte diffusion through the PVA modified membrane and C_A is the initial electrolyte concentration, 0.1 M for both salts, in compartment A of the diffusion cell.

As can observed in Figure 5, the treatment with boric acid, oxidizing mixture or ethyl alcohol, which are washing the small polymer chains, are decreasing the yield of the PVA in retaining the two salts but inserting into the hydrogelic membrane of copper or chitosan is increasing the retention of salts, being more effective especially for KCl.

4. Conclusions

A higher value of the coefficient of permeability may be due to increased pore size.

This increase can be achieved by crosslinking the macromolecular chains that are forming the walls of the pores, under the dilute boric acid action, resulting in a pore deformation, caused by the polymer chains elasticity, from the hydrogel matrix, which collapses.

Also, the increase in pore size after oxidizing treatment may be explained by the polymer chains breaking due to PVA OH secondary group's oxidation.

Chains break and polar group formation can cause changes in the membrane crystalline structure and increase interactions between the electrolyte and the membrane, causing the highest difference between the two ions permittivity.

On the other hand, dispersion of chitosan or copper complexation are closing the pores which leads to a decrease of the permittivity coefficient and to an increase of the salt retention.

When used as biomaterials, the copper complexed membranes or treated with boric acid can be thermally sterilized being non thermal reversible gels (they can be even boiled without modifying their structure and properties).

The obtained results are promising to tailor the permittivity of the PVA hydrogel membranes by different treatments after membrane synthesis or by introducing bio insertions in the PVA solution before the freeze-thawing process.

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