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IMPEDANCE OF POLYPROPYLENE MEMBRANES HYDROPHELIZED WITH ETHYL ALCOHOL

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ABSTRACT

Impedance of hydrophobic polypropylene membranes, hydrophilized with aqueous ethyl alcohol solutions (EtOH) of varying concentrations, has been measured. It has been found that both the resistance and the Warburg coefficient decrease drastically in the EtOH concentration range of 0–31% (wt). For higher EtOH concentrations they remain essentially constant. Reciprocal behavior has been observed for the capacitance of the membranes studied which first increases and then stabilizes at concentrations higher than 31% (wt). It has been proved that hydrophilized membranes PP characterize a greater ion penetration with nonhydrolyzed membranes. Therefore, they are more effective as for as filtration processes are concerned.

INTRODUCTION

Wettability, in addition to porosity and pore distribution, plays an important role in the process of mass transport through a membrane. In the case of porous

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membranes, wettability is determined by three factors: the pore size, the surface tension of the liquid and the surface energy of the membrane material. The Laplace's equation [1] implies that the pressure to be applied to force the liquid into the membrane pores is lower if the material is more wettable. It is essential to the filtration processes where the mass transport is caused by pressure difference on both sides of the membrane.

The problem of wettability is particularly important for the filtration processes in which hydrophobic membranes are used. It is characteristic for such processes that the filtration efficiency decreases rapidly during a relatively short initial stage. The phenomenon called the fouling is observed if proteins are being separated; it consists in formation of a gel layer at the membrane surface and in the sorption in the pores. Therefore, hydrophobic membranes to be used in the filtration processes are hydrophilized.

One of the simplest modification methods is to treat the membranes with hydrophilizing agents such as alcohols, surfactants, polyelectrolyte complexes, or a coating with hydrophilic compounds [2,3]. However, it is difficult to sustain the initial hydrophilicity. The micropores of the alcohol wetted membranes sustain hydrophilicity during immersion in water; but once the membrane is dried, the hydrophilicity is instantly lost. In the case of surfactant impregnated membranes, the hydrophilicity decreases with time as the surfactant tends to leak out from the pores [4]. Although these techniques are extremely simple, they do not impart permanent hydrophilicity to the membranes because the tensides or surfactants adsorb only physically and do not bind chemically to the surface of the membrane. The methods of permanent hydrophilization of PP membranes are presented in paper [5].

In the case of PP membranes used in filtration processes [1,6] where the membrane is in the constant contact with aqueous solution a simple method of hydrophilization with ethyl alcohol gives satisfactory results. Franken [7] determined from the wetting angle measurements that the optimum ethanol concentration of hydrophilization of polypropylene is 30-40%.

Polypropylene membranes are high chemical resistance, broad pH range, the ease of hydrophilization and a remarkable electrostatic charge.

It was the purpose of this work to investigate the changes in hydrophilicity of polypropylene membrane in a large range of ethanol concentrations and determination of the optimal duration of the hydrophilization process. It has been attained by the measurements of penetration of ions through the studied membranes for various concentrations of ethanol used for hydrophilization of the membrane.

The impedance method was applied to this aim because of its accuracy, rapidly and efficiency if the study of membranes is computer-controlled [8]. The parameters determined by this method, particularly the changes in electric resistivity of the membranes, can yield information on their wettability and ion penetration.

EXPERIMENTAL

Membrane hydrophilization

Commercially available standard ACCUREL 2E-PP membranes (pore size 0.2-0.58 μ m) produced by AKZO (Germany) have been used in all experiments. They were hydrophilized with aqueous EtOH solutions of varying concentrations from 96% (wt) to 10% (wt). The hydrophilization has been achieved by immersion of the membrane in a hot aqueous EtOH solution, typically for 1 hour. The optimum hydrophilization time has been determined experimentally e.g. the immersion times leading to reproducible, stable values of impedance have been selected.

Porosities of the membranes have been measured using a JSM-51 Jeol (Japan) electron microscope.

Impedance measurements

Impedance has been measured on a 273A PAR apparatus, in which a four electrode input has been applied in the pre-amplifier. The measurement setup is schematically depicted in Figure. 1. Detailed description of the measuring cell can be found elsewhere [9]. 0.1M KCl solution has been used as the electrolyte.

In our previous paper [9] we have used chronovoltammetry to study the porosity of epoxy resin based membranes. The applied model enabled us to determine the resistances and capacitances of the membranes. However it did not take into account the diffusive transport of ions. Diffusive properties can be analyzed by adding so called Warburg impedance to the equivalent circuit [10].

For the studies of the changes of ion diffusivity in the membrane we have used impedance spectroscopy. In particular, for the description of the properties of membranes we have applied the Randles model in which two processes of charge transfer are considered [11,12].

The membranes were polarized with an alternating current of 5 mV amplitude in the frequency range of 5 Hz to 10 kHz.

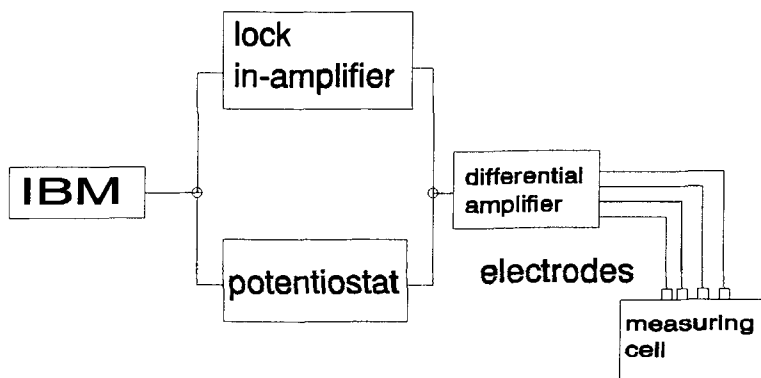


Figure 1. Impedance measurement scheme.

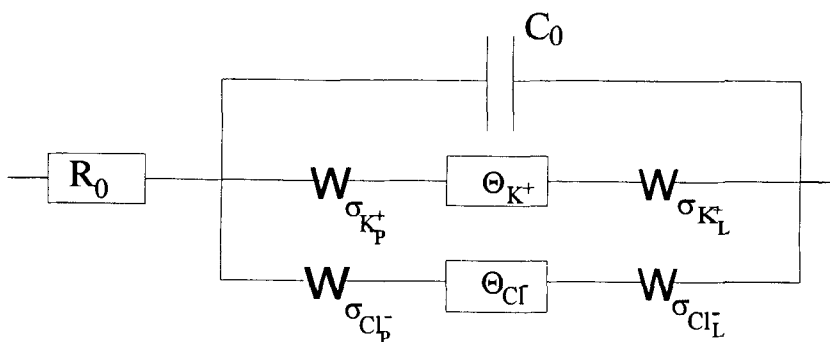


Figure 2. Equivalent circuit describing the membrane impedance (model 1) where:
 R_0 - electrolyte resistance,
 C_0 - membrane capacitance,
 $\sigma_{K^+}^p$, $\sigma_{Cl^-}^p$, $\sigma_{K^+}^L$, $\sigma_{Cl^-}^L$ - Warburg coefficients of K^+ and Cl^- ions at right and left side of the membrane, respectively,
 Θ_{K^+} , Θ_{Cl^-} - the resistance of the membrane against K^+ and Cl^- ions.

In Figure 2 the equivalent circuit, consisting of two branches corresponding to the transport of two types of ions across the membrane, is presented. The K^+ and Cl^- ions are present in the case of the electrolyte used in this work - 0.1M KCl.

The concentrations of the electrolyte on the right and left side of the membrane are equal and the diffusion and mobility coefficients of K^+ and Cl^- are close. Therefore, it can be written that $\Theta_{K^+} \approx \Theta_{Cl^-} = 2\Theta$ and $\sigma_{K^+}^p \approx \sigma_{K^+}^L$

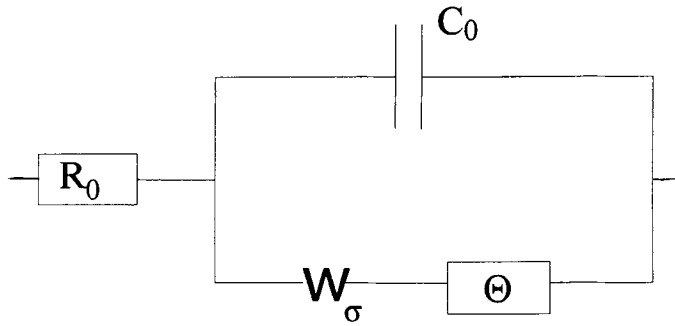


Figure 3. Equivalent circuit describing the membrane impedance (model 2).

$\approx \Theta_{Cl^- (p)} \approx \Theta_{Cl^- (l)} \approx \sigma$, the equivalent circuit can be significantly simplified as shown in Figure 3.

According to the accepted model, the process of membrane hydrophilization is characterized by the changes in Θ , σ , and C_0 which represent the charge transfer (the membrane resistance), the diffusion, and the capacitance, respectively. The procedure of determination of these parameters is presented below.

Calculation Methodology

The real and the imaginary component of impedance (Z' and Z'' , respectively) of $Z = Z' - jZ''$ are measured by the instrument in series arrangement.

Typical impedance curves obtained for a representative hydrophilic membrane are collected in Figure 4.

Using the symbols adopted in Figure 3, the system can be described by the equation:

$$\frac{1}{(Z' - R_0) - jZ''} = \frac{1}{\Theta + Z_w} - j\omega C_0 \tag{1}$$

where:

- $\omega = 2\pi f$,

- the Warburg impedance which represents the diffusion in the electrode zone can be described using Equation: [13]:

$$Z_w = \sigma\omega^{-1/2} - j\sigma\omega^{-1/2}$$

- the Warburg coefficient depends on the electrolyte concentration and diffusion coefficient according to Equation. (2)

After few transformations, the real and imaginary parts of the impedance can be expressed as follows:

$$Z' = R_o + C_o^{-2}\omega^{-2} \frac{\Theta + \sigma\omega^{-1/2}}{\Theta^2 + 2\Theta\sigma\omega^{-1/2} + 2\sigma^2\omega^{-1} + 2C_o^{-1}\sigma\omega^{-3/2} + C_o^{-2}\omega^{-2}} \quad (2)$$

$$Z'' = C_o^{-1}\omega^{-1} \cdot \frac{\Theta^2 + 2\Theta\sigma\omega^{-1/2} + 2\sigma^2\omega^{-1} + C_o^{-1}\omega^{-3/2}}{\Theta^2 + 2\Theta\sigma\omega^{-1/2} + 2\sigma^2\omega^{-1} + 2C_o^{-1}\sigma\omega^{-3/2} + C_o^{-2}\omega^{-2}} \quad (3)$$

The meaning of symbols is given in the Figure 2 legend.

The important parameters of the model: Θ , σ , and C_o cannot be directly determined from Equations (2) and (3) because it is a quotient of polynomials hardly usable in calculations.

The above equations can be expressed in a form of a power series for increasing and decreasing power coefficients of ω :

For the increasing coefficient we obtain:

$$Z' = \sigma\omega^{-1/2} + R_o + \Theta - 2C_o\sigma^2 + 2C_o\sigma(C_o\sigma^2 - \Theta)\omega^{1/2} + (8\Theta C_o^3\sigma^3 - 4\sigma^5 - 3\Theta^2 C_o^2)\omega^{3/2} + \dots \quad (4)$$

$$Z'' = \sigma\omega^{-1/2} + 2C_o\sigma(\Theta - C_o\sigma^2)\omega^{1/2} + C_o(\Theta^2 - 6\Theta C_o\sigma^2 + 4C_o^2\sigma^4)\omega + C_o^2\sigma(8\Theta C_o\sigma^2 - 3\Theta^2 - 4C_o^2\sigma^4)\omega^{3/2} + \dots \quad (5)$$

whereas for the decreasing ones:

$$Z' = R_o + \Theta^{-1}C_o^{-2}\omega^{-2} - \Theta^{-2}C_o^{-2}\sigma\omega^{-5/2} + 2\Theta^{-3}C_o^{-2}\sigma(C_o^{-1}\sigma^2 - C_o^{-1})\omega^{-7/2} + \Theta^{-3}C_o^{-2}(6\Theta^{-1}C_o^{-1}\sigma^2 - 4\Theta^{-2}\sigma - C_o^{-2})\omega^{-4} + \dots \quad (6)$$

$$Z'' = C_o^{-1}\omega^{-1} - \Theta^{-2}C_o^{-2}\sigma\omega^{-5/2} + \Theta^{-2}C_o^{-2}(2\Theta^{-1}\sigma^2 - C_o^{-1})\omega^3 + 2\Theta^{-3}C_o^{-2}\sigma(C_o^{-1} - \Theta^{-1}\sigma^2)\omega^{-7/2} + \dots \quad (7)$$

For high frequencies the term containing negative power coefficients can be neglected. Similarly for low frequencies terms with positive power coefficient can be omitted. As a result we obtain:

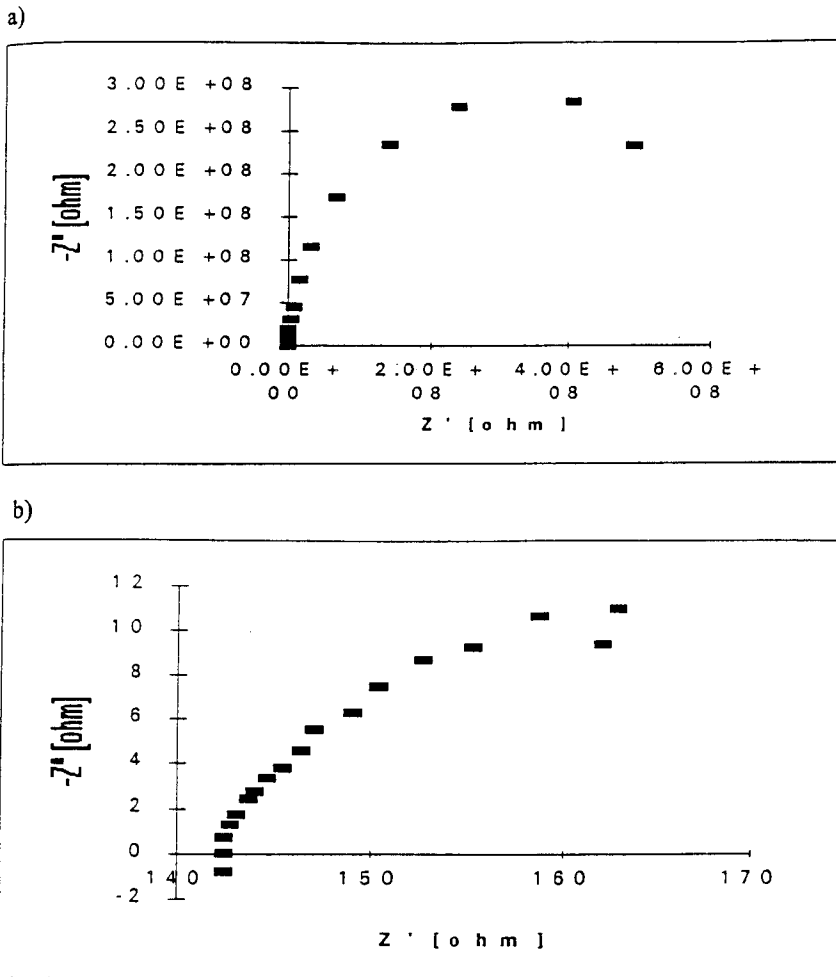


Figure 4. Real (Z') and imaginary (Z'') parts of impedance registered for:
 a) hydrophobic membrane
 b) same membrane hydrophilized with 39 % (wt) EtOH solution.

$$Z'\omega^{1/2} = R_o \omega^{1/2} \quad \text{when } \omega \rightarrow \infty \quad (8)$$

$$(Z'-Z''-R_o)\omega^2 = -C_o^{-1}\omega + \Theta^{-1} C^{-2} \quad \text{when } \omega \rightarrow \infty \quad (9)$$

$$Z'+Z''' = 2\sigma\omega^{-1/2} + R_o + \Theta - 2 C_o\sigma^2 \quad \text{when } \omega \rightarrow 0 \quad (10)$$

Equations (8-10) can be used for the extrapolation of the obtained curves in the high frequency limit (when $\omega \rightarrow \infty$) and in the low frequency limit (when

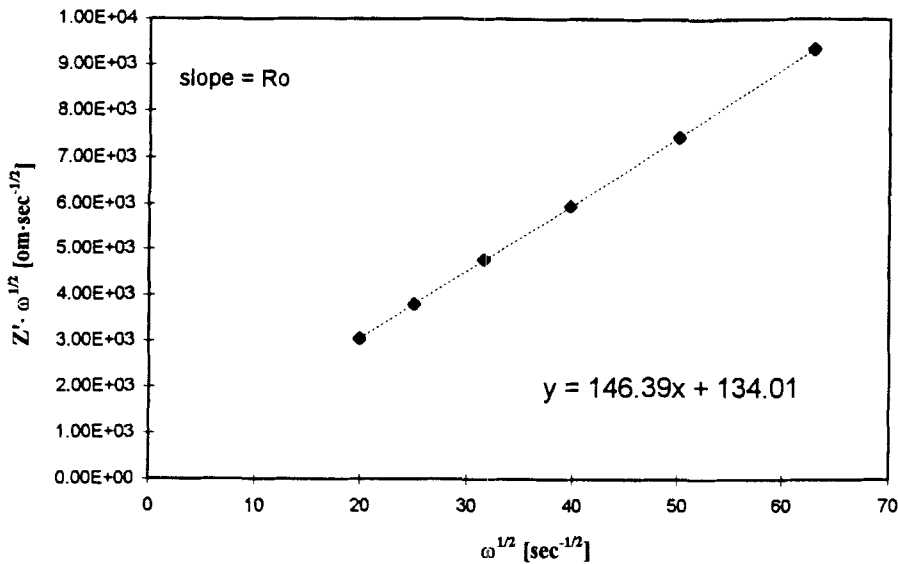


Figure 5. Determination of electrolyte resistance (R_0).

$\omega \rightarrow 0$). In these conditions they can be linearized. From the slope and the ordinate at 0 abscissa of the linearized curves the elements of the equivalent circuit can be derived which characterize electrochemically the studied membrane.

Determination of R_0

The straight line in the coordinate system $Z' \omega^{1/2} = f(\omega^{1/2})$ was obtained from Equation (8). The R_0 value was determined from its slope.

Determination of C_0

The straight line in the coordinate system $(Z - Z'' - R_0) \omega^2 = f(\omega)$ was obtained from Equation (9). The slope of this line yielded the $-C_0^{-1}$, whereas its intersection with the ordinate axis OY yields $(\Theta^{-1} \cdot C_0^{-2})$. The C_0 value was substituted and Θ was calculated.

Determination of σ

The straight line in the coordinate system $Z' + Z'' = f(\omega^{-1/2})$ was obtained from Equation (10). Its slope yielded σ .

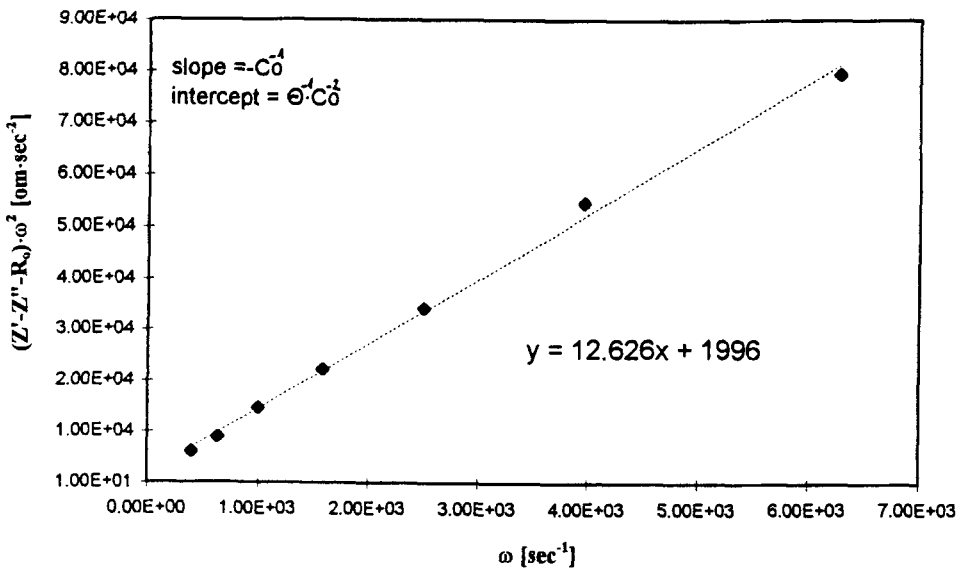


Figure 6. Determination of membrane capacitance (C_0).

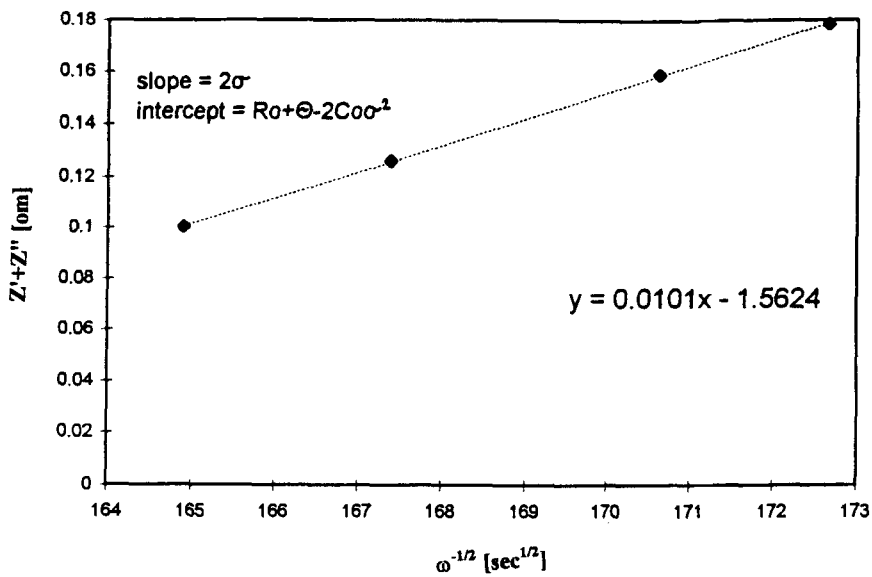


Figure 7. Determination of Warburg coefficient (σ).

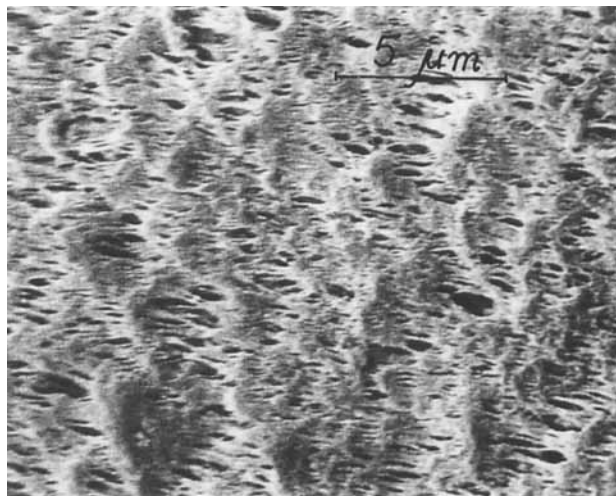


Figure 8. SEM of the surface of PP membrane (magnification 3000x).

RESULTS AND DISCUSSION

A fragment of the porous surface of the studied membrane is shown in Figure 8.

The area of the membrane surface occupied by the pores was evaluated from the SEM (Figure 8) taking into account that the cosine of the angle of membrane inclination to the detection plate of the electron microscope was 0.2. The porosity found in this way is about 50%. The evaluation was done for several studied membranes and the obtained value is characteristic for the entire sample.

The values of Θ , σ and C_0 are presented in Figures 9 -11.

It is seen in Figures 9 and 10 that the membrane resistance (Figure 9) and the Warburg coefficient (Figure 10) drastically decrease in the 0-31% (wt) range of EtOH and then become constant in the 31-96% (wt). These facts suggest that the adsorption of the alcohol molecules on the surface occurs in the 0-31% (wt) of EtOH and the constant values in the 31-96% (wt) of EtOH indicates that no further adsorption of alcohol takes place. Therefore, the membranes can be considered to be completely hydrophilized in that concentration range.

The solution readily penetrates into the pores of the hydrophilized membranes whereas the hydrophobic membranes remain unfilled. The hydrophobic membranes of large pore diameters can be expected to be partly filled. This is the

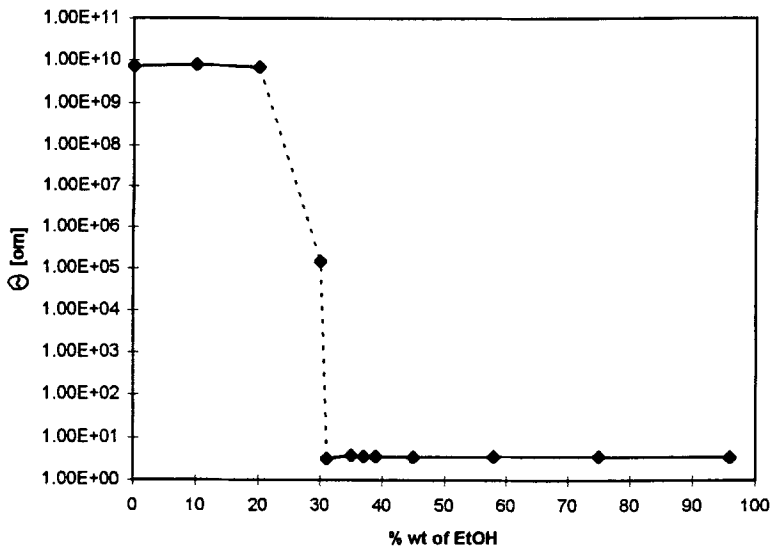


Figure 9. The dependence of resistance of the membrane on EtOH concentration.

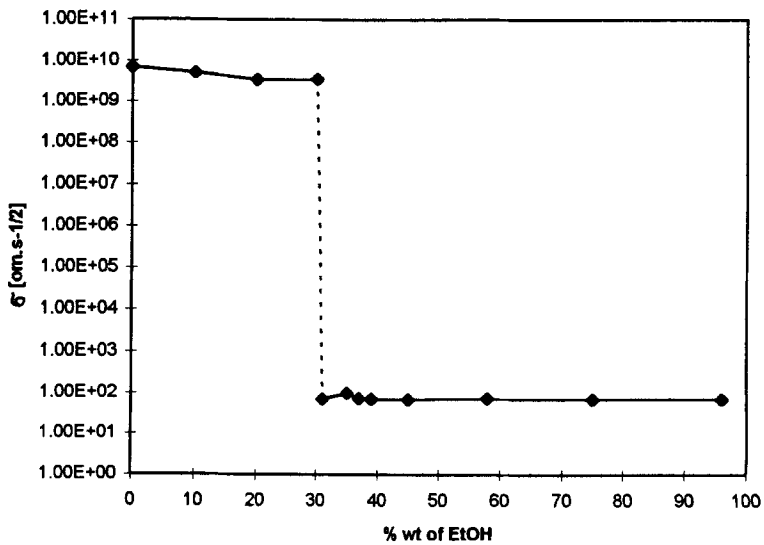


Figure 10. The dependence of Warburg coefficient on EtOH concentration.

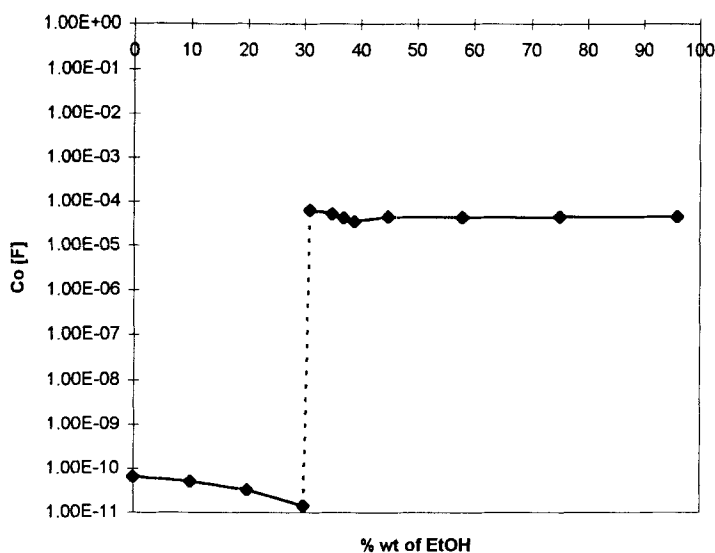


Figure 11. The dependence of capacitance on EtOH concentration.

reason for relatively small resistance values (Θ) of the hydrophilic membranes and of relatively high resistance values of hydrophobic ones.

The capacitance of the membranes (Figure 11) increases in the 0-31% (wt) EtOH concentration range. The further increase in the EtOH concentration (31-96%) does not effect the membrane capacitance. The insignificant increase in the membrane capacitance in the 0-31% (wt) range of EtOH with the simultaneous decrease in the resistance (Figure 9) suggests that some pores are only partly hydrophilized. The decrease in the resistance can be supposed to be caused by the ion transport through the completely hydrophilized pores, whereas the partly hydrophilized ones provoke the capacitance increase only when filled with the electrolyte.

The stabilization of Θ , σ and C_0 in the 31-96% (wt) EtOH concentration range suggests that the membranes are completely hydrophilized in that concentration range and that the ion transport is stable.

The experimental numerical values are compared with those calculated theoretically.

The mean resistance value of the membranes hydrophilized with EtOH in the 31-96% (wt) EtOH concentration range calculated from the experimental results is 3.6Ω (Figure 9), whereas the resistance calculated using the second Ohm law for

the layer of the thickness equal to that of the membrane (100 μm) and the 31.17 10^{-6} m^2 area (taking into account that 50% of the area is occupied by the pores filled with 0.1M KCl of specific conductance equal to $\kappa = 1.11667 \Omega^{-1}\text{m}^{-1}$) is equal to 5.74 Ω .

In light of the accuracy of the measurements and of the surface area evaluation, as well as the fact that the pores are not ideally cylindrical, the conformity of the experimental and calculated resistance values (Θ) is satisfactory.

The mean Warburg coefficient value calculated as that of the resistance for the experiments with the membranes hydrophilized with ethyl alcohol in the 31-96% (wt) EtOH concentration range amounts to 70 $\Omega\text{s}^{-1/2}$, whereas the Warburg coefficient value calculated from Equation (11) is 1.37 $\Omega\text{s}^{-1/2}$.

$$\sigma = \frac{R.T.D^{-1/2}}{F \cdot n^2 \cdot \sqrt{2} \cdot c \cdot S} \quad (11)$$

where:

- D - the diffusion coefficient of the K^+ and Cl^- ions
- c - the electrolyte concentration (0.1M);
- S - the membrane area - 31.17 10^{-6} m^2

However, Equation.(11) applies to the diffusion to a flat uniform surface [13] while the membrane is porous. Thus, the system for which the equation has been deduced differs from the studied one. This is probably the reason for the discrepancy in the obtained values.

The relative electric permittivities of the hydrophobic and hydrophilic membranes were calculated from the experimental capacitancies using Equation (12):

$$\epsilon = \frac{C \cdot l}{\epsilon_0 \cdot S} \quad (12)$$

where:

- C - capacitancies were about 10^{-11}F for the hydrophobic membranes and about 10^{-5}F for the hydrophilic ones (Figure 11);
- l - the membrane thickness - 10^{-4} m ;
- S - the area - 31.17 10^{-6} m^2 .

The relative electric permittivity is 3.8 for the hydrophobic membranes and $3.8 \cdot 10^6$ for the hydrophilic ones. The difference is due to different membrane capacitancies. It is difficult to explain such an increase in capacitance. It may be speculation that the hydrophilizing molecule being attached (adsorbed) with its

end to the pore surface can execute movements with the other end. It makes it possible to store the potential electric energy, hereby increasing the capacitance. Similar permittivity values were obtained by the authors of the paper [14] from the studies of ion-exchanging membranes as the temperature function. According to them, the increase in the electric permiffivity is due to increased mobility of the ion-exchanging groups of the membranes, in their case attributed to the temperature increase.

The analysis of the measured parameters, particularly of the changes in the resistance of the studied membranes as function of EtOH concentration enables us to state that the hydrophilization process of polypropylene membranes is completed at about 31% (wt). A further increase in the hydrophilic agent concentration does not effect the membrane hydrophilization.

In this work, the optimum EtOH concentration range for the hydrophilization has been established as 30-40%(wt). It seems that the exact concentration for a given membrane depends on the propylene structure and, in particular, its crystallinity and processing method .

A decrease in resistance of the hydrophilic membranes with respect to the hydrophobic ones indicates that hydrophilic membranes are considerably more permeable. Due to the wettability obtained in this manner, the solution more readily penetrates into the membrane pores allowing for lower pressures to be applied in the filtration process. Thus, fouling is prevented and the separation effectiveness is improved.

CONCLUSION

On the basis of the results of impedance spectroscopy measurements, carried out for polypropylene membranes hydrophilized with EtOH, it can be concluded that the hydrophilization is a one-step process occurring at EtOH concentration of 31% (wt). Transport properties of polypropylene membranes stabilize above 31% (wt) of EtOH.

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