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THE EFFECT OF HYDROPHILIZATION OF POLYPROPYLENE MEMBRANES WITH ALCOHOLS ON THEIR TRANSPORT PROPERTIES

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ABSTRACT

The effect of alcohol alkyl chain length on hydrophobic character of polypropylene (PP) membranes has been studied. The polypropylene membranes hydrophilized with methyl, ethyl, n-propyl and n-butyl alcohol were used in the studies. The studies were carried out by the impedance method and the changes in transport properties of the studied membranes at various hydrophilizing agent concen-trations were estimated. The polypropylene membranes were found to be firmly hydrophilized with methyl, ethyl and n-propyl alcohol at about 31% by weight and with n-butyl alcohol at about 40% (wt) and that the effect is absent at lower concentrations. It was shown that the results of polypropylene membrane hydrophilization were better if the alcohols with shorter alkyl chains were used, i.e. methyl, ethyl, and n-propyl alcohol. The use of a long-chain alcohol, e.g. n-butyl alcohol reduced the "effectness" of hydrophilization because the penetration of such an alcohol into the polypropylene membrane pores was hampered.

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INTRODUCTION

Hydrophobic microporous polypropylene membranes were mainly applied to the filtering and membrane distillation processes [1-3]. Their hydrophobic character is highly advantageous in the membrane distillation but it is disadvantageous in the filtration processes as it can possibly provoke fouling [3-5]. For this reason, the polypropylene membranes to be used in the filtering processes are subjected to hydrophilization. Hydrophilization of hydrophobic membranes can be carried out by various methods which have been reviewed in the paper [6]. Among these methods, the most efficient were the plasma treatment [7-10], the plasma- induced graft polymerization [11, 12], the high-energy radiation treatment (γ radiation) [13], the electron-beam irradiation [14-17], the induced graft polymerization, as well as the chemical modification [18]. However, those methods are complicated, expensive, and time consuming. Therefore, simpler hydrophilization methods are preferred because of economic reasons. A simple and rapid method to prepare a hydrophilic membrane surface is to immerse the membrane in ethyl alcohol solution of proper concentration [1, 19]. This method was also used in preliminary hydrophilization of the membranes to be thereafter subjected to the chemical modification [6] or to the plasma treatment [3].

In the previous work [19], the effect of ethyl alcohol concentration on hydrophilization of polypropylene membranes was studied . The hydrophilization was found to be a one-stage process and to occur at 31% (wt). It seemed reasonable to extend the studies to other short-chain alkyl alcohols. The effect of the alcohol alkyl chain length on hydrophilization of polypropylene membranes has been studied in this work. The impedance method was applied because of its accuracy and effic-iency in electrochemical studies of such membranes [20].

EXPERIMENTAL

Materials

Porous PP membranes (ACCUREL 2E-PP) were obtained from AKZO (Germany). Their physical properties are as follows [21]:

Thickness (μm) - 100±3%; pore size (μm) - 0.2-0.58;

Bubble point (N_2 against IPA) 1.05 bar;

Transmembrane flow at 25^{o}C; nitrogen - 1.5 l/cm^2 min bar

IPA - 4 ml/cm^2 min bar

Methanol, ethanol, n-propanol, n-butanol were purchased from POCh Gliwice (Poland) and used without further purification.

Membrane Hydrophilization

The hydrophilization of the membranes with all the studied alcohols was carried out by the procedure described in the paper [19].

Impedance Measurements

The model 273A apparatus from the PARC company was used in the measurements; its block diagram was presented in the paper [19]. The membrane was polarized with alternating current of 5 mV amplitude. The measurements were done within the 5Hz-10 kHz frequency range. 0.1 M KCl was used as the electrolyte.

The Randles' model was applied to describe the permeability of ions through the membranes hydrophilized with alcohols; its assumptions and diagrams were presented in the paper [19]. The process of membrane hydophilization is characterized by the changes in Θ, σ, and C_0 representing the charge transport (the membrane resistance), the diffusion and the capacitance, respectively. Their determination method has been presented in the paper [19].

RESULTS AND DISCUSSION

The dependence of the model elements: the resistance (Θ), the capacitance (C_0) and the Warburg coefficient (σ) of polypropylene membranes are presented in Figures 1-3 as functions of alcohol concentration for methanol, ethanol, n-propanol and n-butanol. The mean values of the experimental parameters are collected in Table 1.

As seen in Figure 1, the resistance of the membranes hydrophilized with all the studied alcohols decreases with the alcohol concentration in the low-concentration range, and then becomes constant. However, the decrease rate depends on the used alcohol. In the case of methanol and ethanol of 0-30% (wt) concentrations, the resistance decrease is slow. There is a drastic drop in the 30-32% (wt) concentration range, and the resistance becomes constant in the 32-100% (wt) range. The case is different for the membranes hydrophilized with n-propanol and n-butanol: as can be observed in the drastic resistance drop occurring at about 2% (wt) for n-butanol and 10% (wt) for n-propanol. A complete stabilization of the resistance is observed at 30% (wt) for n-propanol and at 40% (wt) for n-butanol. However, it should be stressed that the resistance value after the stabilization (Table 1) is the highest for the membranes hydrophilized with n-butanol (6.34Ω).

The capacitance of the membranes (Figure 2) changes reversely to the resistance. Generally, the membrane capacitance increases with increasing alcohol

TABLE 1. Mean Values of the Calculated Parameters: C_0, σ and Θ After Their Stabilization

Alcohol	C*	Θ [Ω]	C_0 [F]	σ[$\Omega \cdot s^{-1/2}$]
Methanol	32% (wt)	2.25	4.49×10^{-5}	72.28
Ethanol	31% (wt)	3.60	4.70×10^{-5}	72.13
n-Propanol	30% (wt)	3.54	6.24×10^{-5}	57.58
n-Butanol	40%(wt)	6.34	1.70×10^{-4}	43.73

C* - the alcohol concentration at which the hydrophilization takes place

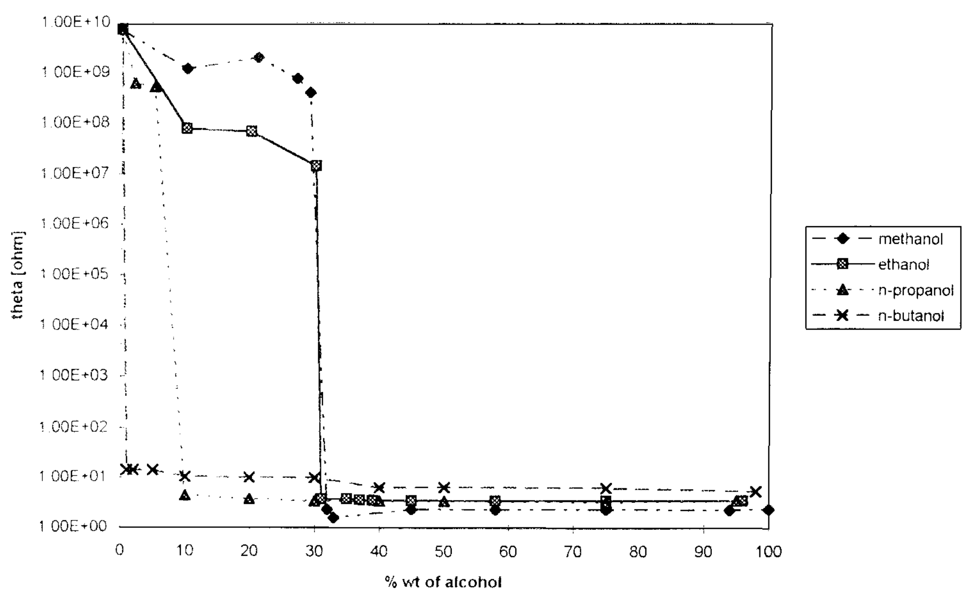

Figure 1. Dependence of the membrane resistance (Θ) on alcohol concentration.

concentration and then it becomes constant. In the case of methanol and ethanol, the capacitance changes insignificantly in the 0-30% (wt) concentration range and it becomes stable above about 32% (wt), whereas the capacitance begins to increase at the concentration as low as 10% (wt) in for n-propanol and 2%(wt) for n-butanol

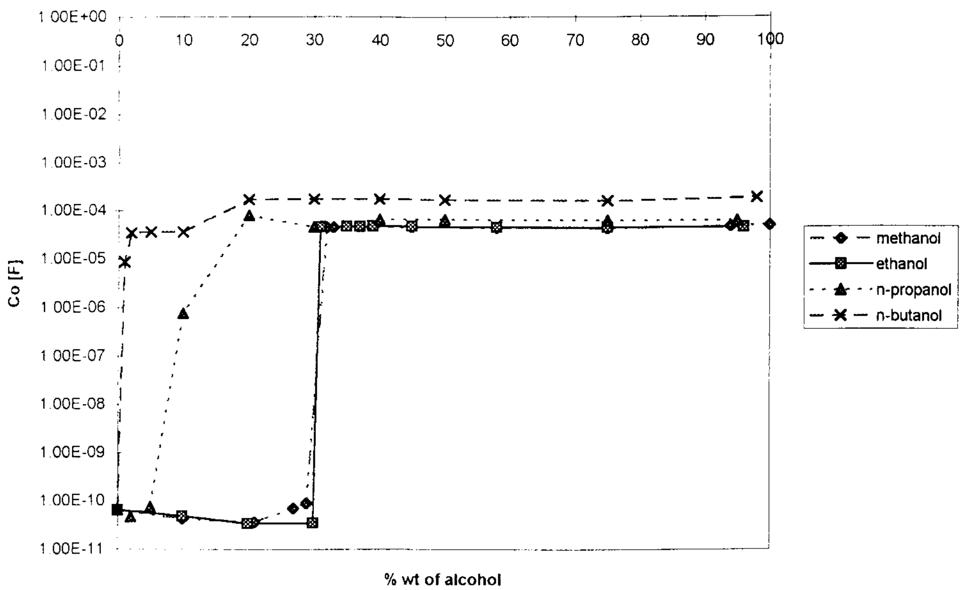

Figure 2. Dependence of the PP membrane capacitance on alcohol concentration.

and it becomes stable at 30 and 40% (wt), respectively. The capacitance values are the highest for the membranes hydrophilized with n-butanol (Table 1).

The Warburg coefficient (Figure 3) decreases with increasing alcohol concentrations similarly to the membrane resistance and it becomes constant at about 32% (wt) in the case of methanol, ethanol and n-propanol. In the case of n-butanol, the Warburg coefficient value decreases in the 0-2% (wt) range and is little affected by a further concentration increase.

By analyzing the results of membrane resistance (Θ), capacitance (C_0) and Warburg coefficients (σ), it can be found that the hydrophilization of a polypropylene membrane is completed at 30-32% (wt), if methanol, ethanol and n-propanol are used and that a further increase in alcohol concentration does not change the hydrophilic character of the membrane. It is indicated by constancy of the parameters characterizing the membrane.

The hydrophilization of the membranes with n-butanol proceeds differently. In this case, the hydrophilization process starts at much lower alcohol concentration, i.e. at about 2% (wt) as it is indicated by the remarkable decrease in the resistance and in the Warburg coefficient (Figures 1 and 3) and by capacity increase (Figure 2).

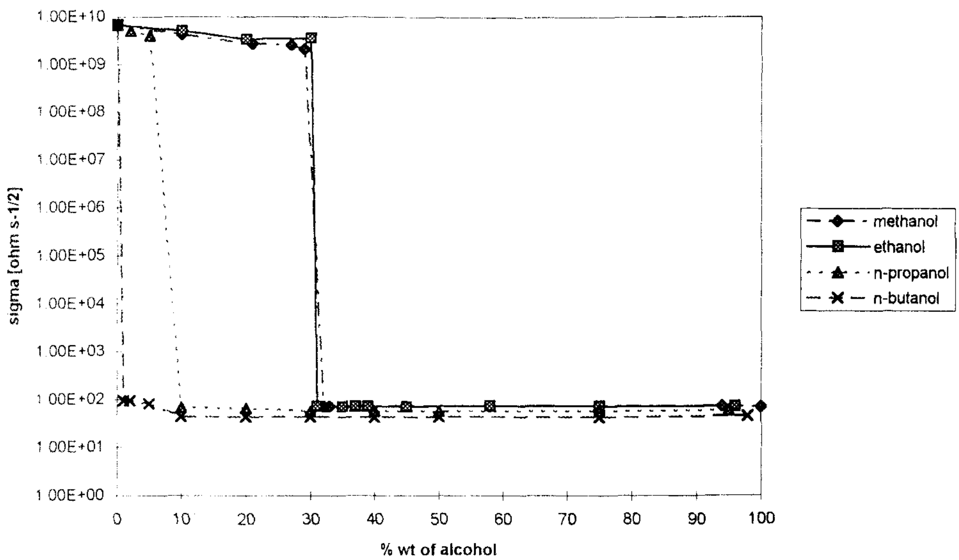

Figure 3. Dependence of the Warburg coefficient (σ) on alcohol concentration.

However, the hydrophilization of the membrane is completed at n-butanol concentration as high as about 40% (wt). In addition, the membranes hydrophilized with this alcohol are characterized by the highest capacitance value and by the lowest Warburg coefficient (Table 1).

It results from the comparison of the resistance, the capacitance, and the Warburg coefficient of the membranes hydrophilized with alcohols (Table 1) that permeability is the highest (the lowest resistance) if methanol is used for hydrophilization, the permeability is similar in the case of ethanol and it is the lowest (the highest resistance) in the case of n-butanol.

The mechanism of hydrophilization maybe explained by the content of the hydrophilizing group and solubility parameters.

Thus, it can be stated that the effectivity of hydrophilization decreases with the increase of the length of alcohol alkyl chain. The above can be explained by the following scheme shown in the Figure 4.

The shorter the alkyl chain, the more hydrophylizing groups can be placed on the surface.

In the case where a short-chain alcohol (i.e. methanol, ethanol or n-propanol) is used to hydrophilize a polypropylene membrane the chains can assume the perpendicular orientation to the membrane surface. In the case of n-butanol, the

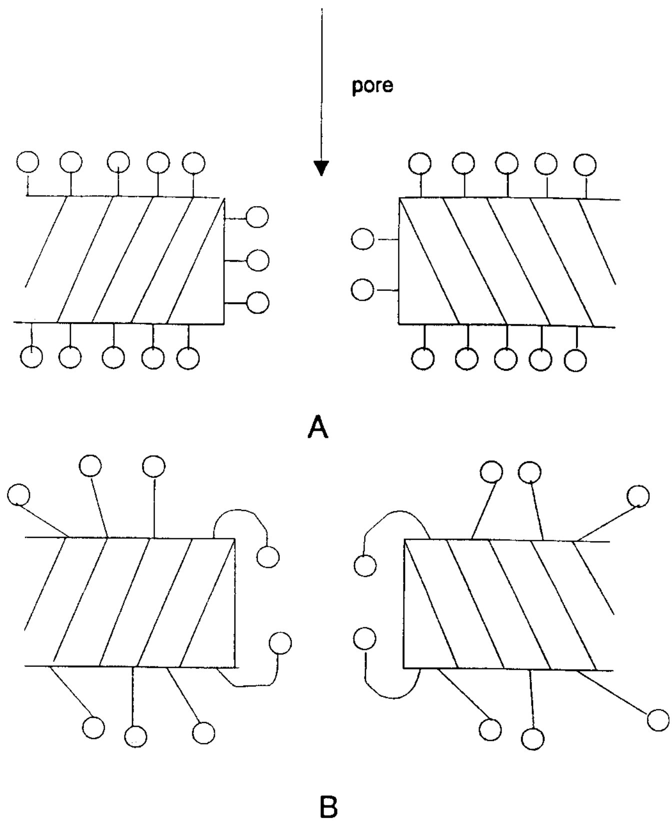

Figure 4. Scheme of hydrophilization of o PP membrane with alcohols.
A - a shorter alkyl chain
B - a longer alkyl chain

alkyl chain, which is longer, its molecules can be situated both perpendicularly and parallel to the membrane surface and to the pore walls. The perpendicularly oriented n-butanol molecules execute movements which are a form of energy storage; there-fore increased capacitance of such membranes.

The solubility parameter order of alcohols studied is: Methanol (14.5) > Ethanol (12.7) > n-propanol (11.9) > n-butanol (11.4) [22].

CONCLUSION

Summarizing, we can state that better hydrophlization membranes results are obtained using shorter alkyl chain alcohols which has higher hydrophilicity.

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