

# Sulfonation of Polyethylene Membranes

A. DIMOV\* and M. A. ISLAM

Department of General Chemical Technology, Higher Institute of Chemical Technology, 8010 Bourgas, Bulgaria

## SYNOPSIS

The polyethylene membranes are hydrophilized under the action of chlorosulfonic acid. Such a hydrophilized membrane shows much better water permeability in comparison with the unmodified one. The ion-exchange capacity of the sulfonated membrane is taken as a measure for the hydrophilicity. The influences of the concentration of the sulfonating agent, temperature, and reaction time, on the ion-exchange capacity and water permeability, are investigated. It is shown that the increase in the degree of sulfonation does not always lead to an increase in the water permeability of the membrane. A lower concentration of the sulfonating agent and a lower temperature are to be chosen, so that only the surface and the inner walls of the pores are sulfonated. Sulfonation in the bulk leads to the deterioration of mechanical properties of the membrane without having any contribution to the increase in the water permeability of the membrane.

## INTRODUCTION

In the recent years, uses of semipermeable polyolefine membranes continuously increase. Microfiltration membranes from polyethylene, polypropylene, and polytetrafluoroethylene are used to obtain superpure water for electronic, medical, and pharmaceutical industries. Many authors subject hydrophobic polyolefine membranes to chemical modification in order to expand the spectrum of their practical applications.<sup>1,2</sup> Hydrophilized polyolefine membranes are more stable in acidic and basic media in comparison with those from unmodified hydrophilic polymers. In aqueous solution, the latter swell and in some cases are plasticized. At higher pressures, physical and morphological changes take place as a result of which membrane porosity decreases. Matsuda et al.,<sup>3</sup> first successfully sulfonated porous polyolefine membranes providing them hydrophilic properties. It is well known that sulfonation usually is accompanied by a process of destruction. The purpose of the present investigation is to achieve the maximum hydrophilization of the polyethylene membranes (correspondingly maximum water permeability) at a possibly lower degree of sulfonation in order to keep their mechanical properties.

## EXPERIMENTAL

### Preparation of Polyethylene Membranes

A mixture of high density polyethylene (HDPE) with melt index 3.1 g/10 min, Vulcasil KS-404 (product of Degussa, FRG), Oil OK-1 (petroleum fraction 340–500°C, product of NEFTOCHIM, Bulgaria) in a ratio 1 : 1 : 2 was homogenized and granulated with an extruder. Sheets with a thickness of 0.4 mm were prepared from a compression-molded mixture. Oil was extracted with tetrachloroethylene. The sheets were dried and subjected to thermomechanical deformation in a thermal chamber especially prepared for that purpose, to form porous structure.

### Sulfonation of Polyethylene Membranes

A solution of chlorosulfonic acid in dichloroethane was used as a sulfonating agent. Polyethylene membranes prepared under identical conditions were immersed in a solution of chlorosulfonic acid with a concentration of 30–50 mass % for 50 min at room temperature. Then they were taken out blotted with a filter paper and placed between two glass plates in a thermal chamber at a temperature of 40–60°C for 5–25 min. The modified membranes were washed consecutively with water, a diluted solution of

\* To whom correspondence should be addressed.

NaOH, distilled water, a diluted solution of hydrochloric acid, and again distilled water.

### Flux Measurement

The flux through the membranes was determined with a laboratory cell at a pressure of 0.1 MPa. The flux  $F$  was calculated by the following formula:

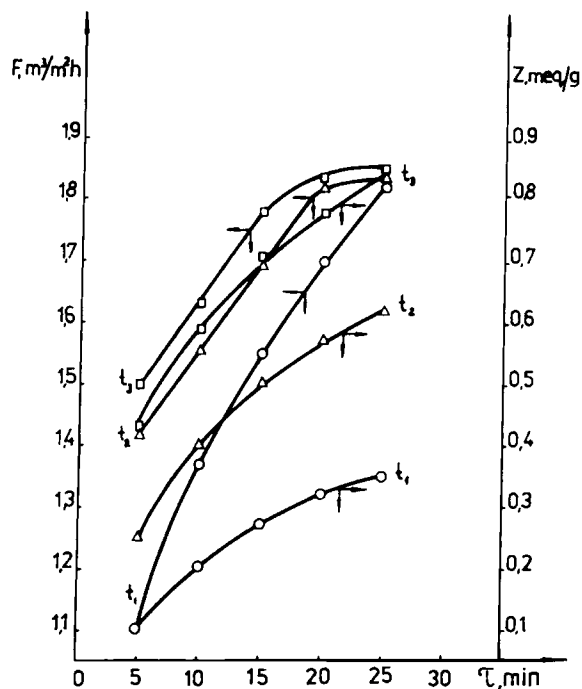
$$F = \frac{V}{S \cdot \tau} \quad (\text{m}^3 \text{ m}^{-2} \text{ h}^{-1})$$

where  $V$  is the volume fluid permeated through the membranes ( $\text{m}^3$ ),  $S$  the membrane area ( $\text{m}^2$ ), and the time required by the volume of the fluid to pass through the membranes ( $\text{h}$ ).

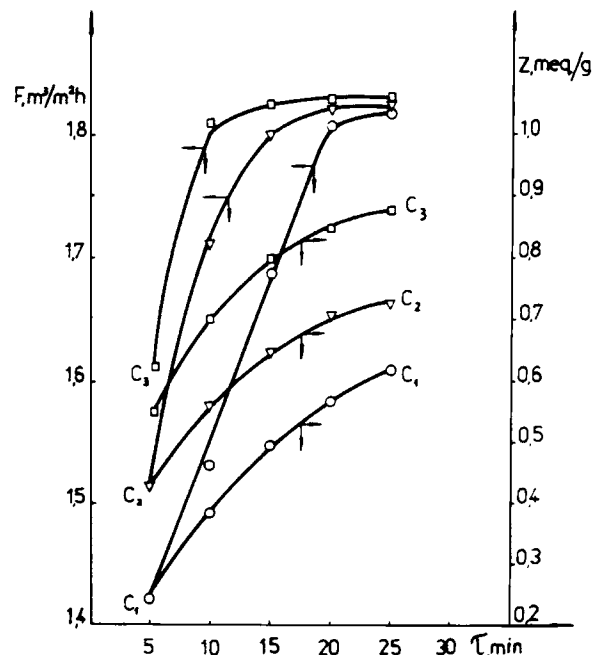
The ion-exchange capacity measured by the method described in the literature<sup>3</sup> was taken as a measure for the degree of sulfonation.

## RESULTS AND DISCUSSION

The investigated polyethylene membranes had a flux of about  $1.9 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$  for ethanol. Under the same



**Figure 1** Influence of reaction time  $\tau$  and temperature ( $t$ ) on the water flux ( $F$ ) and ion-exchange capacity ( $Z$ ) of the polyethylene membranes. Concentration of chlorosulfonic acid = 30 mass %; temperatures ( $^{\circ}\text{C}$ ): ( $\circ$ ) 40; ( $\Delta$ ) 50; ( $\square$ ) 60.



**Figure 2** Influence of reaction time  $\tau$  and concentration ( $C$ ) of chlorosulfonic acid on the water flux and ion-exchange capacity of the polyethylene membranes. Reaction temperature  $50^{\circ}\text{C}$ ; concentration of chlorosulfonic acid (mass %): ( $\circ$ ) 30; ( $\nabla$ ) 40; ( $\square$ ) 50.

conditions, they were practically impermeable to water. Some superatmospheric pressure is to be applied to overcome the capillary repulsive forces towards a nonwetting fluid like water, and then the membrane with a definite pore size will be permeable. For example, the calculated value of the pressure according to Cantor's relationship<sup>4</sup> necessary to initiate water permeation through a hydrophobic membrane with pore radius of  $0.1 \mu\text{m}$  is about 1.4 MPa. After the chemical modification with chlorosulfonic acid, polyethylene membranes are hydrophilized and capillary repulsive forces towards water and aqueous solutions decrease or cease to counteract.

The experimental results are illustrated in Figures 1 and 2. It is evident that an increase in temperature, concentration of the acid, and reaction time favors the sulfonation process. The slopes of the curves of the ion-exchange capacity versus reaction time decrease. This fact may be explained by the decrease in the acid concentration with time and more difficult access of the acid to the bulk material of the membranes. Water permeability is also proportional to the degree of sulfonation, and after a period of time, it approaches a limiting value; i.e. the ion-exchange capacity increases without having any con-

**Table I** Water Flux of Polyethylene Membranes Sulfonated under Different Conditions<sup>a</sup>

Membrane	Temperature of Sulfonation (°C)	Ion-Exchange Capacity Z (meq/g)	Water Flux		Mass Losses after 8 h (%)
			Initial (m <sup>3</sup> m <sup>-2</sup> m <sup>-1</sup> )	After 8 h (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> )	
M1	40	0.35	1.82	1.87	4
M2	50	0.62	1.84	2.10	13
M3	60	0.82	1.82	2.31	20

<sup>a</sup> Reaction time 25 min, sulfonating agent – 30 mass % chlorosulfonic acid.

tribution to an increase in the water permeability. Both figures show that there is not any mutually reversible relationship between the ion-exchange capacity and water permeability far before reaching the limited value. Depending on the conditions of modification, the different values of ion-exchange capacity correspond to a definite value of water flux and vice versa. This fact may be explained with the assumption that water flux depends only on the quantity of sulfonic groups incorporated in the membrane surface and the inner walls of the pores.

Sulfonation in the bulk of the membrane is accompanied by a destruction process. Table I shows that, after 8 h of operation, the membranes lose part of their masses. At the beginning, in spite of their different ion-exchange capacities, water flux is almost the same. During the permeation process, the water flux drains isolated low molecular weight fragments from the membrane matrix as a result of which porosity as well as water flux increases.

It may be concluded that the process of sulfo-

nation should be carried out at a possibly lower concentration of the sulfonating agent and lower reaction temperature in order to perform selectively the sulfonation of the membrane surface and the inner walls of the pore and thus to minimize the destruction process.

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