Effect of Coagulation Medium on Properties of Sulfonated Polyvinylidene Fluoride Membranes

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Synopsis

The performance and the structure of sulfonated polyvinylidene fluoride membranes prepared in different coagulation media were investigated. Several pure organic compounds and mixtures of some of them with water were used as coagulation media. The membrane were tested in an ultrafiltration laboratory unit with dextran aqueous solutions. The overall structure of the membranes was examined with the aid of the scanning electron microscope. The effect of temperature of the coagulation medium on the properties of the membranes were also investigated.

INTRODUCTION

In a previous work[1] we studied the effect of some preparation parameters on properties of sulfonated polyvinyiidene fluoride membranes. The parameters investigated were the polymer concentration in the casting solution, the solvent or solvents system, and the evaporation time of the polymer solution before immersion in the coagulation medium.

This paper extends the above work and shows how other parameters during the coagulation step of the casting solution, such as the composition and the temperature of the coagulation medium, can affect the structure and the performance of sulfonated polyvinylidene fluoride membranes.

EXPERIMENTAL

Materials

The sulfonated polyvinylidene fluoride (PVDFS) was obtained by sulfonation of a commercial product (Foraflon 1000 HD, Ugine Kulhmann) as described in an earlier paper.[2] The degree of sulfonation (%) of SO_3H was 2%. Reagent grade *N,N*-dimethylformamide (DMF) was used as solvent for the PVDFS. The coagulation media used for membrane preparation are reported in Table I. Dextran (Dextran T40, Pharmacia Fine Chemicals AB) was used as macromolecular solute for the feed solution in ultrafiltration (UF) experiments. The average molecular weights of the solute were $\overline{M}_w$ = 43,900 and $\overline{M}_n$ = 26,200. The limiting viscosity number in water at 20°C was $|\eta| = 0.22$ dL g^{-1}.

Membrane Preparation

Membranes were prepared as flat sheets from 15,20 wt % polymer solutions. The polymer was dissolved by stirring in DMF at 50°C. The solution

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TABLE I
Coagulation Media Used for Membrane Preparation

Coagulation medium	H_2O (vol %)	CH_3OH (vol %)	C_2H_5OH (vol %)	Glycerol (vol %)	DMF (vol %)	nC_4H_9OH (vol %)	$(C_2H_5)_2O$ (vol %)	CCl_4 (vol %)	$CHCl_3$ (vol %)	Tetrachloro ethylene (vol %)	1,1-2,2-Tetrachloroethane (vol %)
H_2O	100	—	—	—	—	—	—	—	—	—	—
CH_3OH	—	100	—	—	—	—	—	—	—	—	—
H_2O–CH_3OH	90	10	—	—	—	—	—	—	—	—	—
H_2O–CH_3OH	80	20	—	—	—	—	—	—	—	—	—
H_2O–CH_3OH	60	40	—	—	—	—	—	—	—	—	—
H_2O–CH_3OH	30	70	—	—	—	—	—	—	—	—	—
C_2H_5OH	—	—	100	—	—	—	—	—	—	—	—
H_2O–C_2H_5OH	90	—	10	—	—	—	—	—	—	—	—
H_2O–C_2H_5OH	80	—	20	—	—	—	—	—	—	—	—
H_2O–C_2H_5OH	60	—	40	—	—	—	—	—	—	—	—
H_2O–C_2H_5OH	30	—	70	—	—	—	—	—	—	—	—
Glycerol	—	—	—	100	—	—	—	—	—	—	—
H_2O–glycerol	90	—	—	10	—	—	—	—	—	—	—
H_2O–glycerol	80	—	—	20	—	—	—	—	—	—	—
H_2O–glycerol	60	—	—	40	—	—	—	—	—	—	—
H_2O–glycerol	30	—	—	70	—	—	—	—	—	—	—
H_2O–DMF	90	—	—	—	10	—	—	—	—	—	—
H_2O–DMF	80	—	—	—	70	—	—	—	—	—	—
H_2O–DMF	60	—	—	—	40	—	—	—	—	—	—
H_2O–DMF	40	—	—	—	60	—	—	—	—	—	—
nC_4H_9OH	—	—	—	—	—	100	—	—	—	—	—
$(C_2H_5)_2O$	—	—	—	—	—	—	100	—	—	—	—
CCl_4	—	—	—	—	—	—	—	100	—	—	—
$CHCl_3$	—	—	—	—	—	—	—	—	100	—	—
Tetrachloro-ethylene	—	—	—	—	—	—	—	—	—	100	—
1,1-2,2-Tetrachloro-ethane	—	—	—	—	—	—	—	—	—	—	100

was cooled at room temperature and filtered. The polymer solution was cast onto a glass plate using a casting knife with a thickness of 200 μm. After 30 s in a controlled room (temperature 20°C, humidity 60%) the plate was immersed in the coagulation medium for 10 min. Unless otherwise specified, the temperature of the coagulation medium was 4°C. The membrane was then easily removed from the plate and leached overnight under running water before testing.

Scanning Electron Microscope Investigations

The structure of the membrane was examined with the aid of a Cambridge 250 K scanning electron microscope. The membranes were carefully dried using a Balzers Union critical point dryer. Cross sections were obtained by fracturing the membrane at liquid nitrogen temperature and coating with gold.

Ultrafiltration Experiments

Ultrafiltration experiments were carried out in a laboratory-scale pilot plant with a 0.1% aqueous solution of dextran. The unit had two flat UF cells assembled in parallel. Each cell could operate independently. The membrane surface was 5×10^{-3} m^2; the clearance was 2 mm. The recirculation rate at the membrane surface was 5 m/s. The operating conditions were 40°C and 200 kPa. Further details on the ultrafiltration unit are reported in another paper.[3] Dextran in feed and permeate was determined by colorimetric method.[4] Permeate fluxes and dextran rejections were measured after 1 h. The rejection was calculated as follows:

$$R = (1 - C_p/C_f) \times 100$$

where C_p is the dextran concentration in the permeate and C_f the concentration in the feed.

RESULTS

Effect of Different Alcohol–Water Mixtures and Some Pure Organic Compounds as Coagulation Media

The scanning electron micrograph of the cross section of a membrane obtained by immersion in water is shown in Figure 1(a). The membrane exhibits a large number of macrovoids and fingerlike cavities in a porous structure. Figures 2–4 reproduce scanning electron micrographs of cross sections of membranes obtained by immersion in pure alcohols and alcohol–water mixtures of different alcohol content.

Increasing the concentration of the alcohol in the coagulation medium, the formation of a porous structure composed of polymeric globules is observed, and the macrovoids and fingerlike cavities tend to disappear. Methanol–water (Fig. 2) or ethanol–water (Fig. 3) mixtures containing 40 vol % alcohol are enough to obtain membranes without voids. By using glycerol–water mixtures macrovoids and fingerlike cavities occurs up to 40 vol % glycerol concentration (Fig. 4). Membranes obtained by immersion in pure

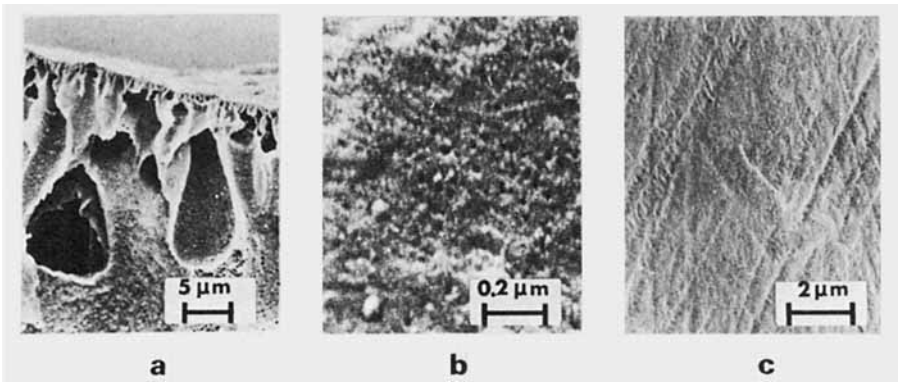

Fig. 1. Scanning electron micrographs of a membrane obtained by immersion in pure water: (a) cross section; (b) top surface; (c) top surface. Casting solution, 20 wt % PVDFS in DMF.

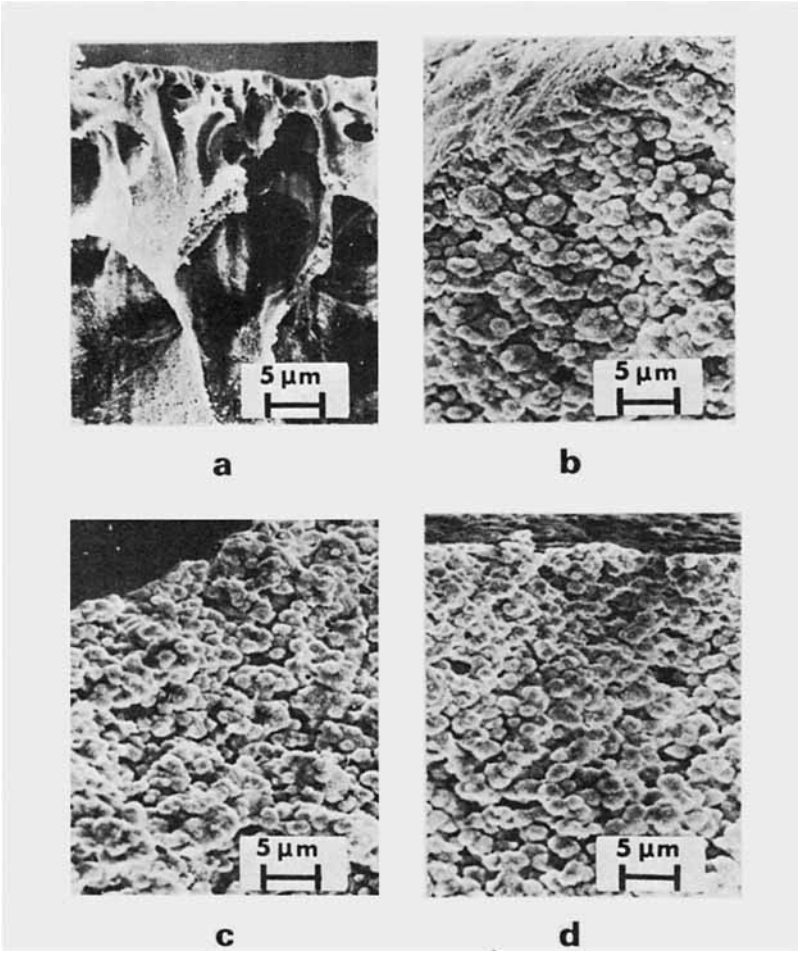

Fig. 2. Scanning electron micrographs of cross section of membranes obtained by immersion in methanol–water mixtures of different methanol content or pure methanol. Casting solution, 20 wt % PVDFS in DMF. Methanol content in the coagulation mixture (vol %), (a) 20; (b) 40; (c) 70; (d) 100.

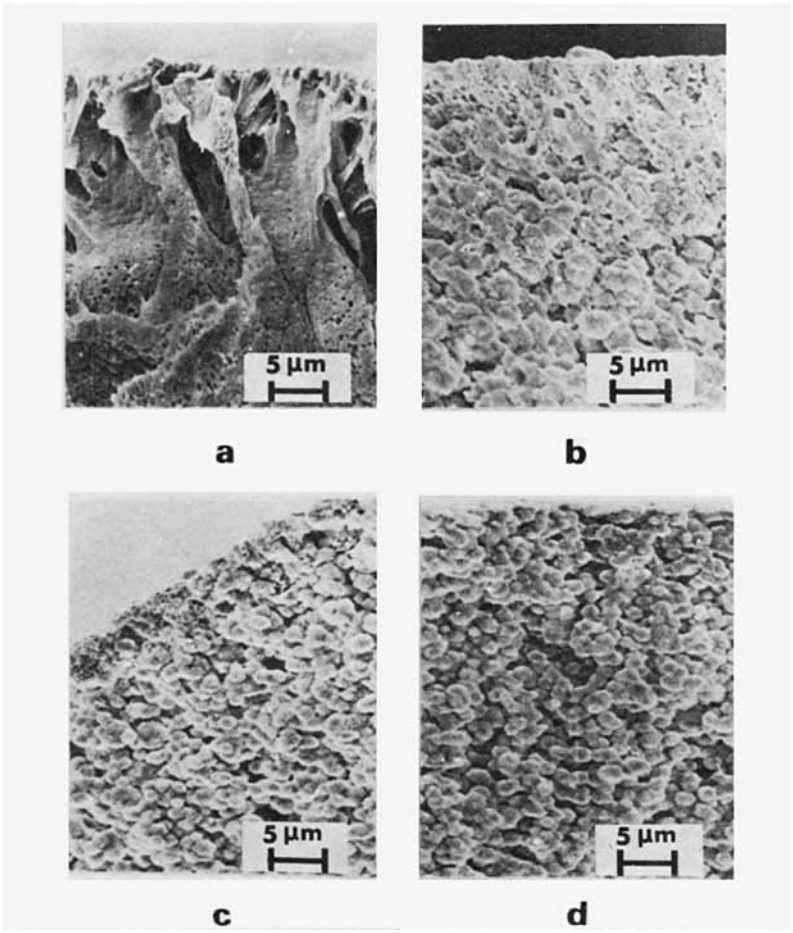

Fig. 3. Scanning electron micrographs of cross sections of membranes obtained by immersion in ethanol–water mixtures of different ethanol content or pure ethanol. Casting solution, 20 wt % PVDFS in DMF. Ethanol content in the coagulation mixture (vol %), (a) 20; (b) 40; (c) 70; (d) 100.

alcohols exhibit a symmetric globular structure over the whole cross section. A similar structure is formed by using *n*-butanol, diethylether, chloroform, carbontetrachloride, 1,1-2,2-tetrachloroethane and tetrachloroethylene as coagulation agents, as can be seen, for example, from the scanning electron micrographs reported in Figure 5.

The effect of concentration of methanol, ethanol, and glycerol in the coagulation medium on the performance of the membranes is shown in Figure 6. The flux of permeate decreases, increasing the alcohol concentration. The lowest fluxes and the best rejections are obtained with glycerol. The rejection, at approximately 20 vol % alcohol, passes through a maximum.

Up to 40 vol % of above alcohols or into pure alcohols as coagulation media, the membranes become brittle and difficult to handle. None of the membranes has significant dextran rejection. A similar behavior shows the membrane precipitated in *n*-butanol, dyethylether, and the halogenated organic compounds above mentioned.

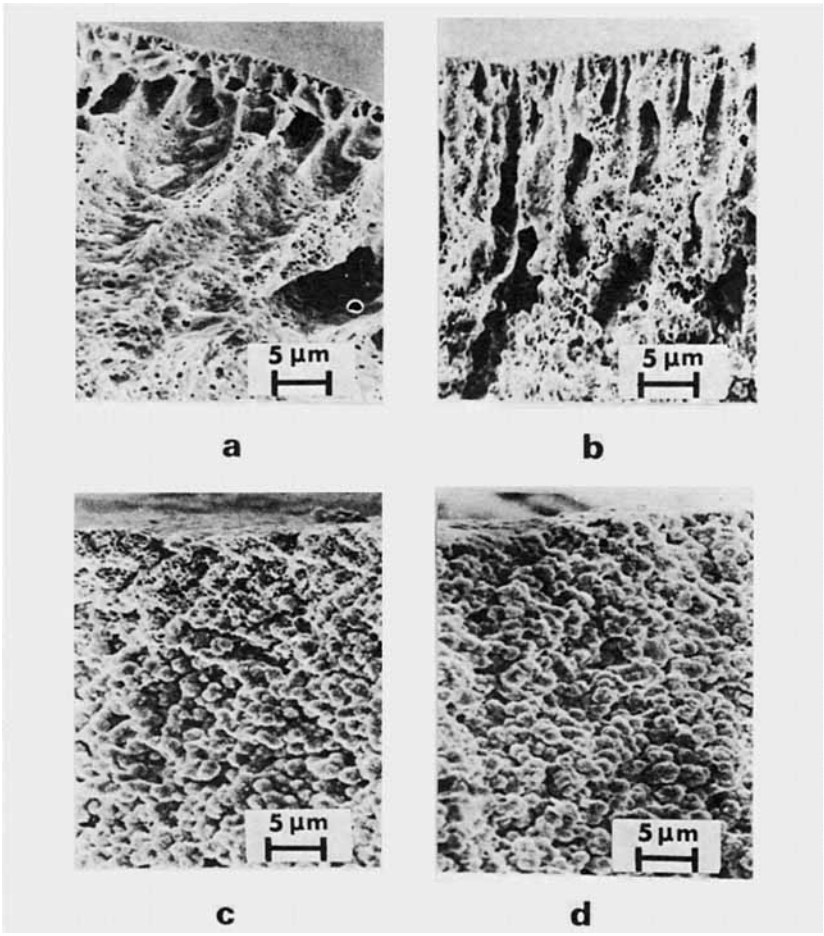

Fig. 4. Scanning electron micrographs of cross sections of membranes obtained by immersion in glycerol–water mixtures of different glycerol content or pure glycerol. Casting solution, 20 wt % PVDFS in DMF. Glycerol content in the coagulation mixture (vol %): (a) 10; (b) 40; (c) 70; (d) 100.

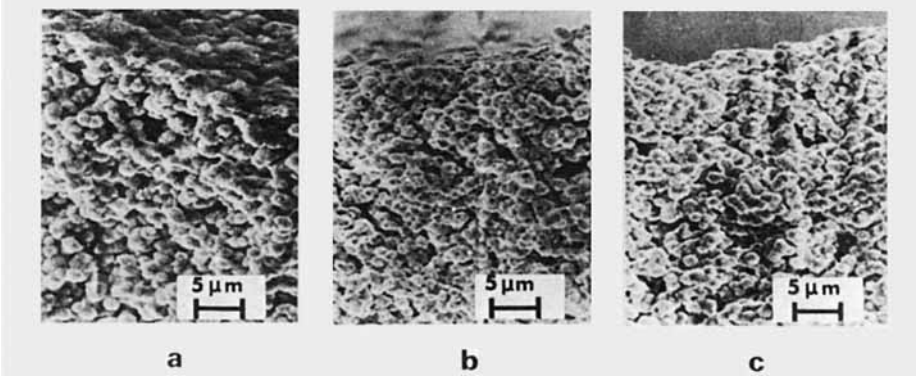

Fig. 5. Scanning electron micrographs of cross sections of membranes obtained by immersion in different pure organic compounds: (a) *n*-butanol, (b) diethylether; (c) carbontetrachloride. Casting solution, 20 wt % PVDFS in DMF.

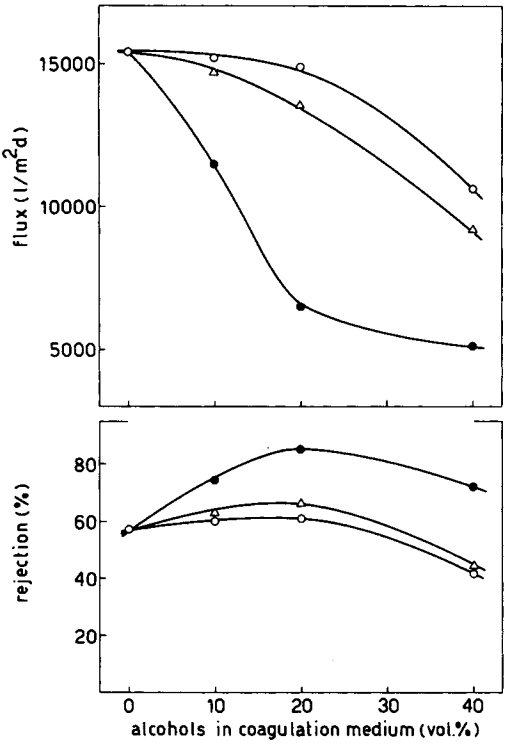

Fig. 6. Effect of alcohols concentration in the coagulation medium on flux and rejection of membranes. Casting solution 20 wt % PVDFS in DMF. Alcohol in the coagulation medium: (○) methanol, (△) ethanol; (●) glycerol.

Scanning electron micrographs of top surface of membranes obtained by immersion in water [Figs. 1(b), (c)] or pure alcohols and alcohol-water mixtures [Figs. 7–9] present remarkable differences. At low magnification the surface of the membranes obtained in water and water-rich mixtures are homogeneous while the surface of the membranes obtained in alcohol rich mixtures or pure alcohols present large defects. Only at high magnification in the former can fine substructures and pores be observed.

Effect of DMF–Water Mixtures as Coagulation Media

The effect of the presence of DMF, in the coagulation medium on the performance of the membranes, is shown in Figure 10. When the concentration of DMF increases, the flux of permeate decreases while the rejection passes through a maximum. The trends are similar to those shown in Figure 6. With a content of DMF of 60% the membranes become brittle and cannot be used for ultrafiltration experiments.

Figure 11 reproduces scanning electron micrographs of cross section of membranes obtained by immersion in a coagulation medium containing a different amount of DMF. As the concentration of DMF is increased, a porous globular structure is formed, and the macrovoids and fingerlike cavities disappear.

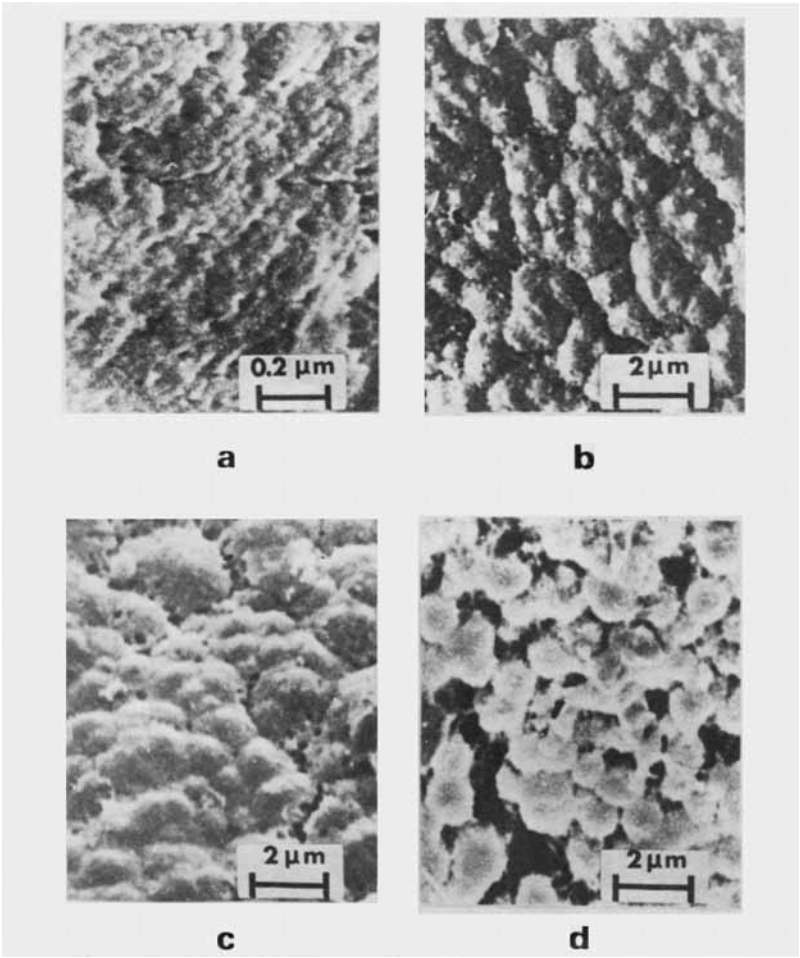

Fig. 7. Scanning electron micrographs of top surfaces of membranes obtained by immersion in methanol–water mixtures of different methanol content or pure methanol. Casting solution, 20% PVDFS in DMF. Methanol content in the coagulation mixture (vol %): (a) 20; (b) 40; (c) 70; (d) 100.

Effect of Temperature of Coagulation Medium

The performance of membranes prepared by immersion in a 40 vol % DMF–water mixture at different temperature is reported in Figure 12. The results show that the flux of permeate slightly decrease while the corresponding rejection remains practically constant decreasing the temperature of the coagulation medium.

From Figure 13 it appears that as the temperature increases the size of the fingerlike cavities becomes bigger. Figures 14(a)–(c) reproduce scanning electron micrographs of membranes obtained by immersion in water at different temperatures. The increase of the temperature affects the size of the cavities as well as the morphology of the porous structure inside the walls of the cavities. As can be clearly seen, the membrane precipitated in water at 20°C [Fig. 14(a)] exhibits a porous structure formed by polymeric globules while the membrane precipitated at 70°C [Fig. 14(c)] exhibits a

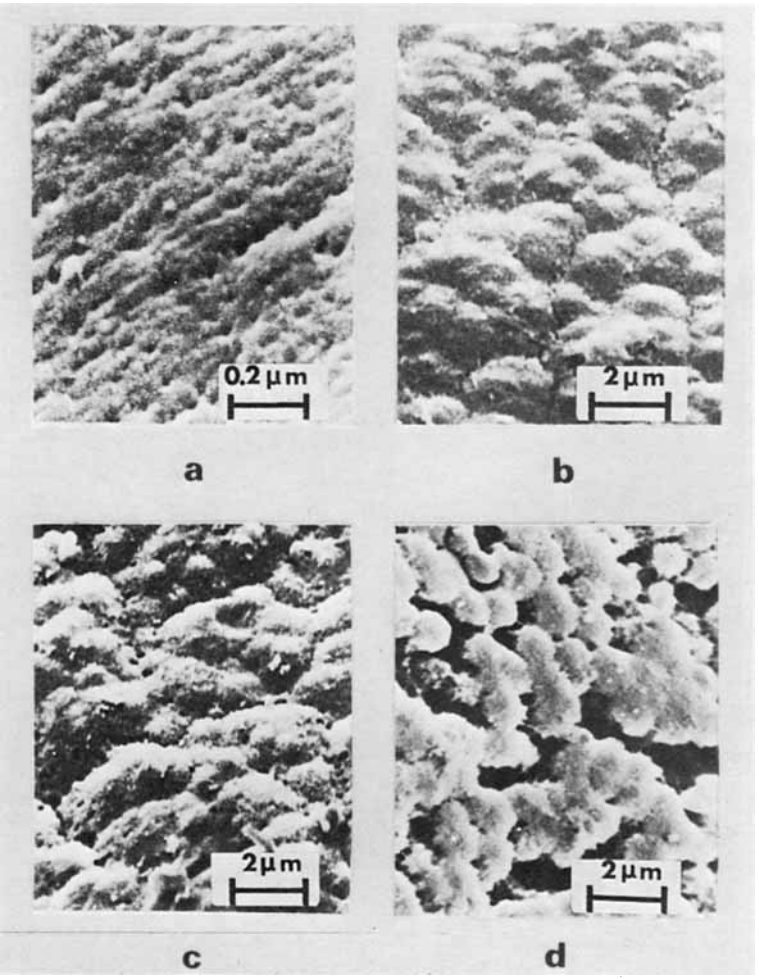

Fig. 8. Scanning electron micrographs of top surfaces of membranes obtained by immersion in ethanol–water mixtures of different ethanol content or pure ethanol. Casting solution, 20 wt % PVDFS in DMF. Ethanol content in the coagulation mixture (vol %): (a) 20; (b) 40; (c) 70; (d) 100.

porous alveolar structure. The membrane precipitated at 40°C [Fig. 14(b)] exhibits an intermediate structure where both polymeric globules and alveoli appear.

DISCUSSION

Scanning electron microscopy studies show that a large variety of membranes with different morphological structures can be obtained by varying the experimental condition during the coagulation step. Similar structures have been observed by several authors for other polymeric systems and for a variety of membrane preparation variables.[5–30] This indicates that the different structures obtained with our experiments are not a function of our particular systems investigated. When the casting solution is immersed in the coagulation medium a depletion of the solvent from the surface of the solution occurs and a formation of a dense skin layer takes place. This

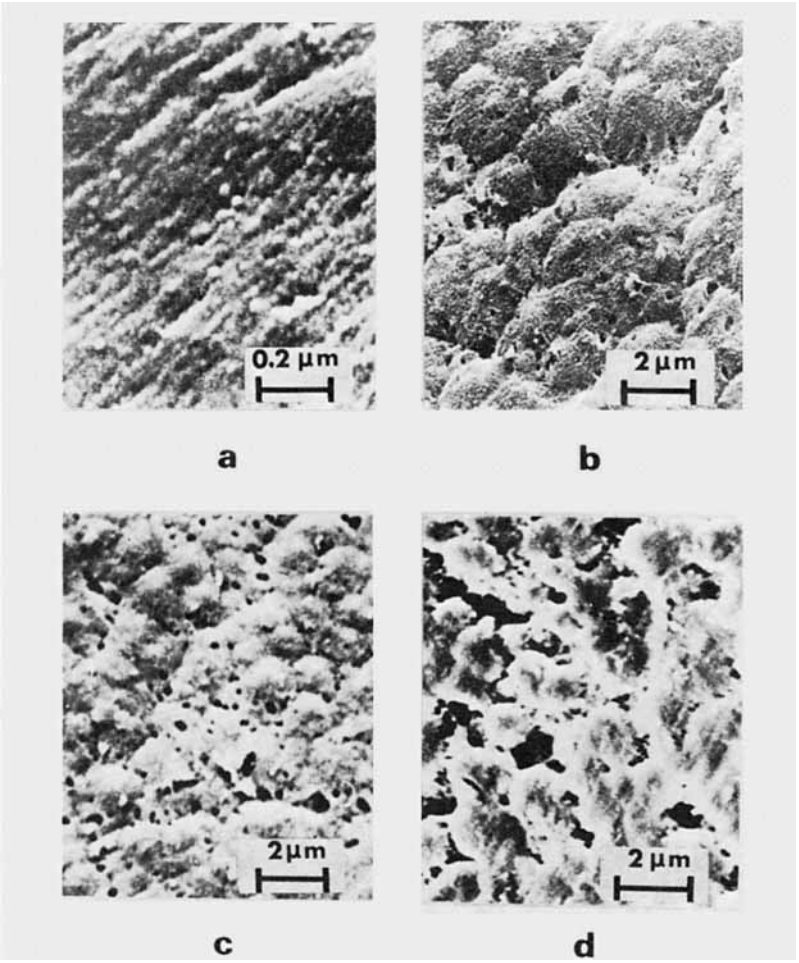

Fig. 9. Scanning electron micrographs of top surfaces of membranes obtained by immersion in glycerol–water mixtures of different glycerol content or pure glycerol. Casting solution, 20 wt % PVDFS in DMF. Glycerol content in the coagulation mixture (vol %), (a) 10; (b) 40; (c) 70; (d) 100.

skin acts as a barrier for the diffusion of the coagulation medium (inwards) and the casting solvent (outwards). Because of the dilution of the coagulant by the entraped casting solvent, the coagulation of the solution beneath the skin layer occurs slowly, and a porous sublayer is formed.

This porous sublayer can be globular or alveolar or can exhibit an intermediate structure where both polymeric globules and alveoli appear. The formation of macrovoids and fingerlike cavities is a well-known phenomenon not only in membrane coagulation processes. Very similar cavities were early observed in the wet spinning process of synthetic polymer fibers.[31–35] Some of the mechanism proposed for the formation of cavities in wet spun fibers[32,34] have been extended to membranes prepared by coagulation techniques.[9,20,22] Several experimental evidences[5,9,13,19,21,26] show that the formation of macrovoids and fingerlike cavities in the membrane is associated with high rates of coagulation of the casting solution upon im-

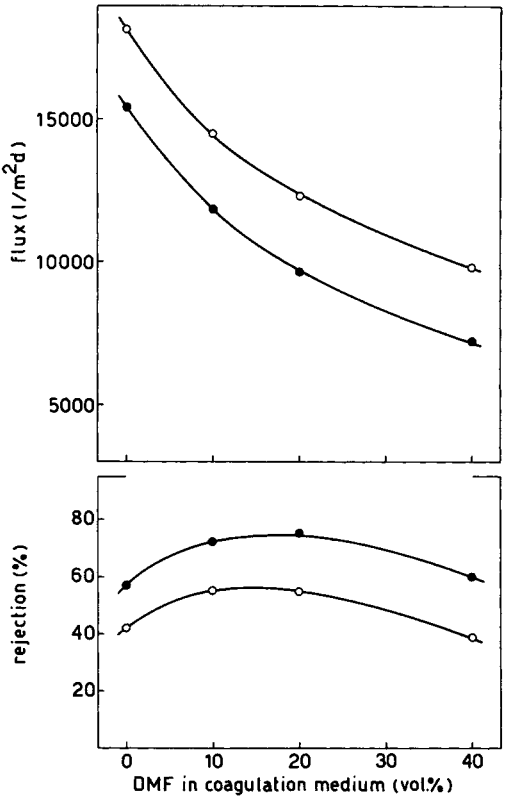

Fig. 10. Effects of DMF concentration in the coagulation medium on flux and rejection of membranes. Casting solution: (○) 15 wt % PVDFS in DMF; (●) 20 wt % PVDFS in DMF.

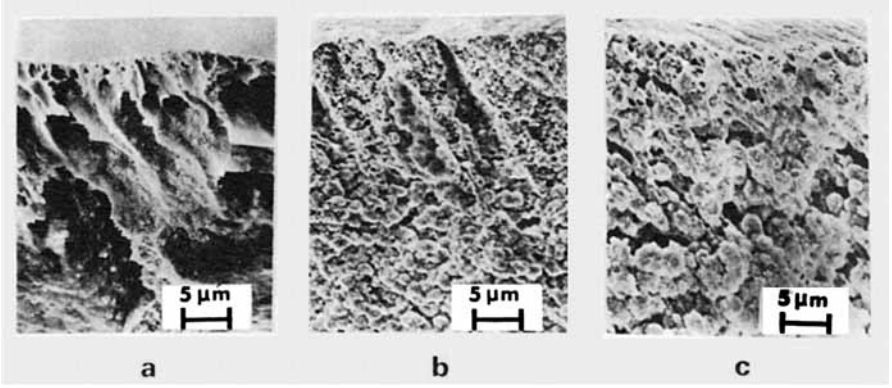

Fig. 11. Scanning electron micrographs of cross sections of membranes obtained by immersion in DMF–water mixtures of different DMF content. DMF content in the coagulation mixture (vol %): (a) 20; (b) 40; (c) 60. Casting solution 20 wt % PVDFS in DMF.

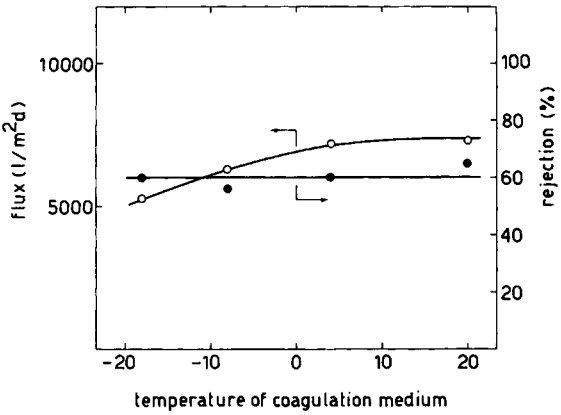

Fig. 12. Effect of the temperature of coagulation medium on flux and rejection of membranes. Casting solution, 20 wt % PVDFS and DMF. Coagulation medium, 40 vol % DMF in H_2O.

mersion in the coagulation medium. On the other hand, porous structures without cavities are formed by slow coagulation. Our results are in agreement with above experimental evidences. Water is a strong coagulant and produces membranes with large macrovoids and fingerlike cavities. Lowering the rate of exchange between the casting solvent and the coagulation medium, i.e., substituting gradually water with poor coagulants such as alcohols or DMF, the macrovoids and fingerlike cavities become progressively smaller until they disappear when alcohol- or solvent-rich mixtures or pure alcohols are used as coagulation media. In these latter cases, as mentioned in the Results section, an entirely porous globular structure, with globules of polymer badly connected, is formed. Similar results are obtained precipitating the membrane in *n*-butanol, diethylether, or the mentioned halogenated compounds which are poor coagulation media. The decrease of the number and the size of cavities causes a decrease of the fluxes while the formation of large surface defects and irregularities causes

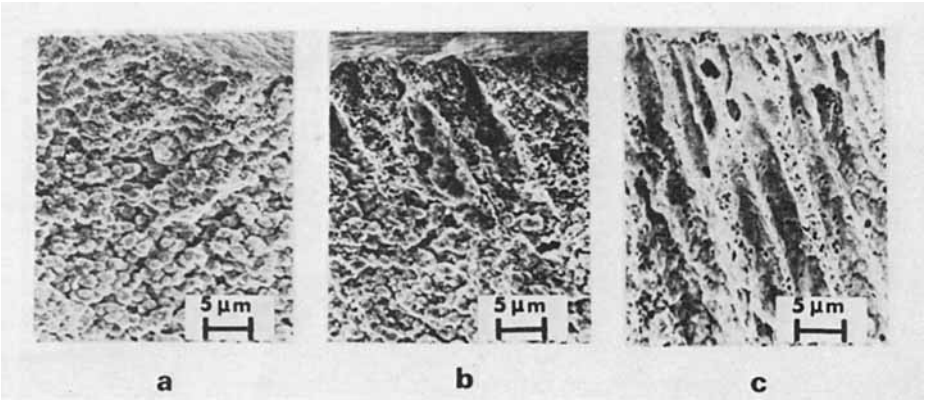

Fig. 13. Scanning electron micrographs of cross sections of membranes obtained by immersion in 40 vol % DMF–water mixtures at different temperatures. Casting solution, 20 wt % PVDFS in DMF. Temperature of coagulation mixture (°C): (a) −17; (b) 4; (c) 20.

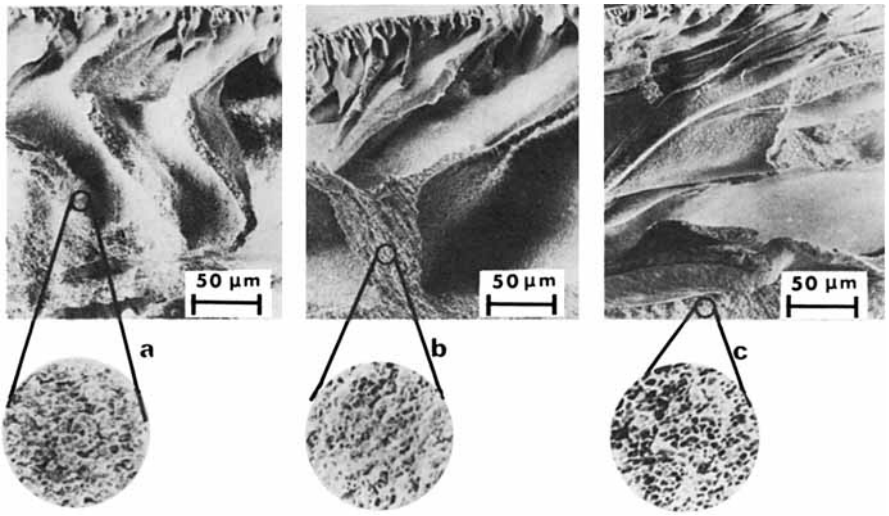

Fig. 14. Scanning electron micrographs of cross section of a membrane obtained by immersion in pure water at different temperature. Casting solution, 15 wt % PVDFS in DMF. Temperature of the water (°C): (a) 20; (b) 40; (c) 70.

the loss of selectivity and the brittleness of the membranes. Another way to affect the rate of exchange between the casting solvent and the coagulation medium is to change its temperature. Temperature tends to increase both the rate of exchange and the solubility of the polymer. However, the effect of temperature on the former is higher; therefore, the membrane precipitate rapidly and the size of macrovoids and fingerlike cavities become bigger. Moreover, an increase in temperature affect the morphology of the porous structure inside the walls of the cavities. Lowering the temperature of the coagulation medium the flux slightly decreases while the rejection does not seem affected at all. In this case the performance of the membrane is determined mainly by the high DMF content in the coagulation medium, and the effect of temperature is, therefore, minimized.

CONCLUSIONS

The effect of several coagulation media on the performance and structure of sulfonated polyvinylidene fluoride membranes was investigated. All the organic compounds used as coagulants yielded membranes with uniform porous structure over their entire cross section. These membranes were extremely brittle and could not be used for ultrafiltration experiments. Mixtures of water and methanol, ethanol, glycerol, and DMF yielded membranes whose properties were strictly related to the concentration of alcohols and DMF in the mixture. Increasing their concentration the flux of permeate of the membranes decreased and a rejection passed through a maximum, while, from a morphological point of view, the trend towards the formation of a globular porous structure was observed. When the concentration of alcohols and DMF rose to 70 and 60 vol %, respectively, the membranes became brittle, and their performance was damaged. The structure of these membranes was entirely porous. A trend towards the elimi-

nation of macrovoids and fingerlike cavities was also observed by lowering the temperature of coagulation medium.

Although the performance of the membranes precipitated in media different from water does not seem particularly attractive for practical ultrafiltration application, we think that this study provides new and further information for a better knowledge and understanding of the parameters governing the mechanism of formation of membranes prepared by coagulation technique.

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