

Cationic surfactants-controlled geometry and dimensions of polymeric membrane pores

S.I. VOICU^{a*}, A. DOBRICA^a, S. SAVA^a, A. IVAN^a, L. NAFTANAILA^a

^aUniversity Politehnica from Bucharest, Faculty of Applied Chemistry and Materials Sciences, 1-7 Gheorghe Polizu, Bucharest, 011061, Romania

The use of polymeric membranes is well known and irreplaceable in various areas such as hemodialysis, filtration and water purification, food or pharmaceutical industry. The efficiency of any of these processes depends on membrane pore size and distribution of the active layer of membrane. In order to control this parameter, this article presents the results obtained from modeling a porous polysulfone membrane using four cationic surfactants as additives in the polymer solution. The obtained membranes were characterized by SEM microscopy and specific tests for membranes and membrane processes (solvent permeation, retention of proteins).

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1. Introduction

In the last years, the synthesis and characterization of functional materials due to its multiple applications has attracted a large interest from scientists [1-5]. Between different types of materials, the polymeric membranes constitute a wide studied domain due to their uses in biomedicine, environmental techniques, electronics, sensors, food and pharmaceutical industry [6-9].

Membrane separation processes are more effective, more economical in time and energy and focused on clean technologies. The main advantages of membrane processes are high selectivity and separation ability which solves the fractionation and concentration of biological products that are involved in medicine, biology, biotechnology, pharmaceutical and organic chemistry. Development of membrane separation processes was based on both, technical factors (separation selectivity, reliability technology, productivity and energy efficiency) and economic factors (the cost of facilities and equipment, operating and maintenance costs and raw material costs).

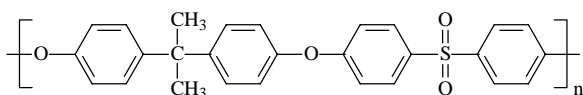


Fig. 1 Molecular structure of aromatic polysulfone

Aromatic polysulfones (Fig. 1) has several key features such as high value glassy transition point (T_g - generally greater than 170°C) and high thermal oxidative stability. Because of their nature and chemical structure these polymers present also optical transparency.

Due to the structure of aromatic functions, these ether polymers are resistant to hydrolysis in hot water or steam at medium temperature. In addition, present resistance to acids and bases in a wide range of concentrations and temperatures [10-13].

The performances of a polymeric membrane are directly influenced by the dimensions, geometry and distributions of pores. Some previous works have studied the influence of anionic surfactants related to desired membrane pores synthesis [14-16].

On this paper, the effect of four different cationic surfactants at the synthesis of a polymeric membrane are presented and their influence through the geometry and dimensions of this pores are discussed. The obtained membranes were characterized by SEM microscopy and specific tests for membranes and membrane processes (solvent permeation and proteins retention).

2. Experimental

2.1 Materials

The polysulfone was provided by BASF (Ultrasonic S3010). As solvent for polysulfone was used N-methyl pyrrolidone - NMP (Merck) and as non-solvent for phase inversion an iso-propanol (Fluka)-deionized water (Fluka) mixture was used. As cations for the study, dimethyl dioctadecyl ammonium bromide (Merck), alkyl benzyl dimethyl ammonium chloride (Merck), Hyamine 10-X (Fluka) and N-dodecylpyridinium chloride (Merck) were chosen. The proteins for specific retention tests, were purchased from Merck (myoglobin, hemoglobin and albumin) and Fluka (bovine serum albumin).

2.2. Methods

The polymer was purified by re-precipitation from chloroform and dried in vacuum at 60°C. Into an Erlenmeyer flask with glass stopper the polymer was dissolved in solvent under magnetic stirring until the desired concentration was achieved (12% polysulfone mixed in NMP). Using dried and re-precipitated polymer the solution is obtained within 4 hours. Before use, the air is removed from the solution into a vacuum desiccator for 30 minutes. Into a cylinder a small amount of surfactant (calculated concentration of 10-5M) was added to 4 mL of NMP. After this, the surfactant solution is mixed with 20 ml of polysulfone solution and shake vigorously in order to disperse the surfactant in all the volume of polymer solution. For the membrane formation, a small quantity of polymer solution is deposited on a glass substrate and is extended to a standard thickness of 250µm. The polymeric film deposited on glass is immersed in coagulation bath and the membrane is formation by the precipitation of the polymer. After the synthesis, the membrane is washed with distilled water and kept in a mixture of water and iso-propanol. Solvent permeation tests were performed using deionized water and alcohols at different temperatures. the tests were performed using a Sartorius module with 500 mL of solvent at atmospheric pressure. Scanning Electron Microscopy was performed with a FEI ESEM microscope (samples were covered with gold, in order to be performed analyzes at higher magnitude).

3. Results and discussion

The membrane formation through phase-inversion process involves a coagulation of a polymeric film (dissolved polymer into a proper solvent) with a non-solvent (with respect of a very important rule - the solvent of the polymer and the non-solvent of the polymer are completely miscible). The schematic representation of this process is presented in Fig. 2.

The miscibility between solvent and non solvent is extremely important because determine the speed of coagulation and consequently the dimensions and geometry of membrane pores. These dimensions and geometry affect directly the membrane performances due to specific fluxes and retention properties of these materials. This study was performed in order to demonstrate that the membrane performance related to pores properties can be lead and manipulated by the use of surfactants added in the polymer solution. The action of surfactants is explained by the interaction of these molecules (at the micellar critical concentration) with the solvent molecules and polymer molecules. The presence of the surfactants can 'accelerate' or 'brake' the speed of the non-solvent at the membrane formation. The representation of this process is presented in Fig. 3.

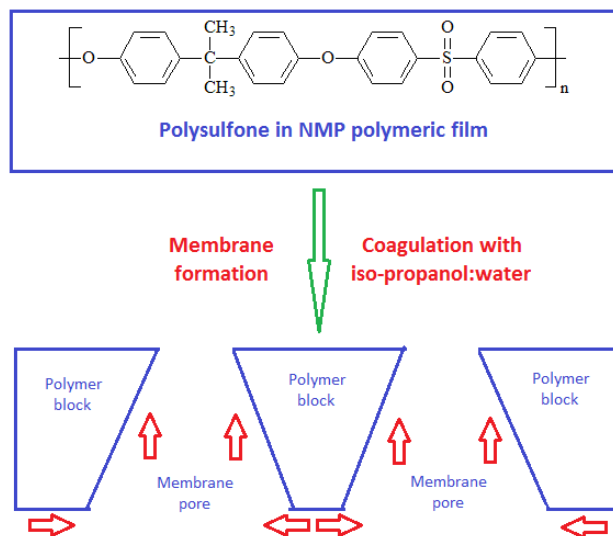


Fig. 2 The schematic representation of membrane formation through phase inversion

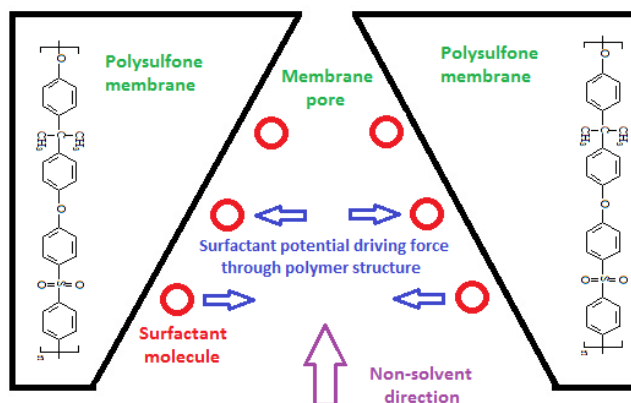


Fig. 3 The schematic representation of surfactant molecules action through polymeric block at the membrane pores formation

The micellar critical concentration (MCC) is a critical factor which determine the results of the entire process. A concentration below MCC will not be very effective during phase inversion process and a concentration that will exceed the MCC will have as result the appearance of agglomerated surfactants structures that will affect negatively the membrane structure by the determination of large volume cavities.

The membranes were characterized by Scanning Electron Microscopy (Fig. 4). First observation can be made related to the thickness of the membranes. The membrane with dimethyl dioctadecyl ammonium bromide present a thickness in cross section of 50-58 µm, the membrane with alkyl benzyl dimethyl ammonium chloride 90-99 µm, the membrane with Hyamine 10-X 131-132 µm and the membrane with N-dodecylpyridinium chloride

144-154 μm . This can be explained by the stronger or lighter interaction of surfactant with the coagulation mixture. A stronger interaction determine a high speed of

coagulant through polymer film and as a consequence a very short time of membrane formation (with a small thickness of the membrane).

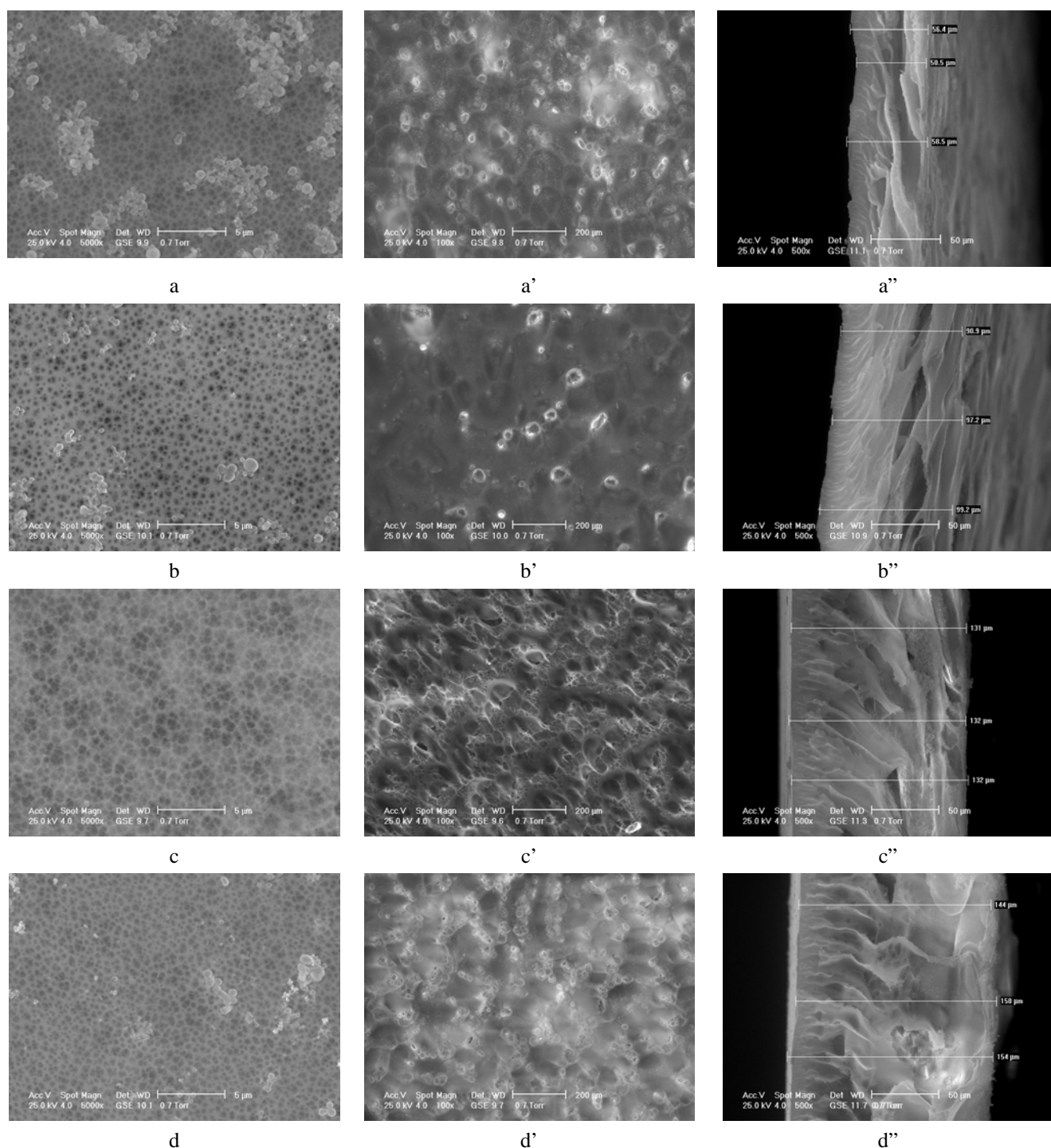


Fig. 4 SEM micrographs of synthesized membranes using the following surfactants: dimethyl dioctadecyl ammonium bromide (a), alkyl benzyl dimethyl ammonium chloride (b), Hyamine 10-X (c) and N-dodecylpyridinium chloride (d). a, b, c, d represent the active surface (X5000), a', b', c', d' represent the porous surface (X100) and a'', b'', c'', d'' represent the cross section of the membranes (X500)

The dimension of cross section increase with the decreasing of the coagulation speed in the following order: dimethyl dioctadecyl ammonium bromide < alkyl benzyl

dimethyl ammonium chloride < Hyamine 10-X < N-dodecylpyridinium chloride. These results are also

correlated with the dimensions and geometry of the membrane pores.

In the case of dimethyl dioctodecyl ammonium bromide used as surfactant, the pores on the active surface of the membrane present a round shape with a diameter around 0.52 μm . Also, at the surface of this membrane some polymer agglomeration can be observed due to the fast route of the iso-propanol through polymer film. In the case of alkyl benzyl dimethyl ammonium chloride, the pores also present a round shape with a diameter of 0.38 μm , but the amount of polymer agglomeration at the surface is lower than the previous membrane. The following two membranes (with Hyamine 10-X respectively N-dodecylpyridinium chloride) present hexagonal pore shapes with a diameter of 0.48 and 0.28 μm . The membrane obtained with Hyamine 10-X has no polymer agglomerations being the membrane with the cleanest active surface.

The specific water fluxes at different temperatures through synthesized membranes were measured in order to evaluate the membrane performances for a specific process or application. The results are presented in Table 1.

Table 1. Specific water fluxes at different temperatures for synthesized membranes

Used surfactant	Flux ($\text{L}/\text{m}^2 \text{ h}$)			
	30°C	40°C	50°C	60°C
Dimethyl dioctodecyl ammonium bromide	117.12	118.91	121.67	123.67
alkyl benzyl dimethyl ammonium chloride	118.32	120.02	122.76	124.95
Hyamine 10-X	121.45	124.34	128.31	132.50
Dodecylpyridinium chloride	119.44	122.67	123.78	125.50

The results obtained indicate the membranes can be used in ultrafiltration process with specific application for hemodialysis, dialysis or proteins retention. The highest fluxes obtained with the increasing of temperature can be explained by the expansion of the membrane pores. These results present a practical value due to the modelling of a polymeric membrane for a certain process especially for biomedical applications. For the hemodialysis application, the use of membrane with Hyamine 10-X is the optimum choice because due to the high flux of blood, the coagulation is prevented and the addition of anticoagulants is lower. The membranes obtained with dimethyl dioctodecyl ammonium bromide, alkyl benzyl dimethyl ammonium chloride, N-dodecylpyridinium chloride are characterized by the comparable values of fluxes and necessitate different additives in the case of this application.

The fluxes of water at 40, 50 and 60°C show that a separation or a retention process can be manipulated by the temperature of feed solution in situations where the heat does not affect the quality of the separated chemical species.

Table 2. Specific alcohols (methanol, ethanol, iso-propanol) fluxes for synthesized membranes

Used surfactant	Flux ($\text{L}/\text{m}^2 \text{ h}$)		
	Methanol	Ethanol	i-Propanol
Dimethyl dioctodecyl ammonium bromide	68.23	62.31	50.34
alkyl benzyl dimethyl ammonium chloride	69.00	65.34	57.12
Hyamine 10-X	72.31	67.21	55.98
Dodecylpyridinium chloride	69.44	66.21	58.04

The specific alcohols fluxes, presented in Table 2, indicates the potential use of membranes in the domain of fuel cells. The data are important in order to calculate the mobility of protons inside the membrane (the alcohols are the cheapest sources for H^+ as fuel for polyelectrolyte membranes).

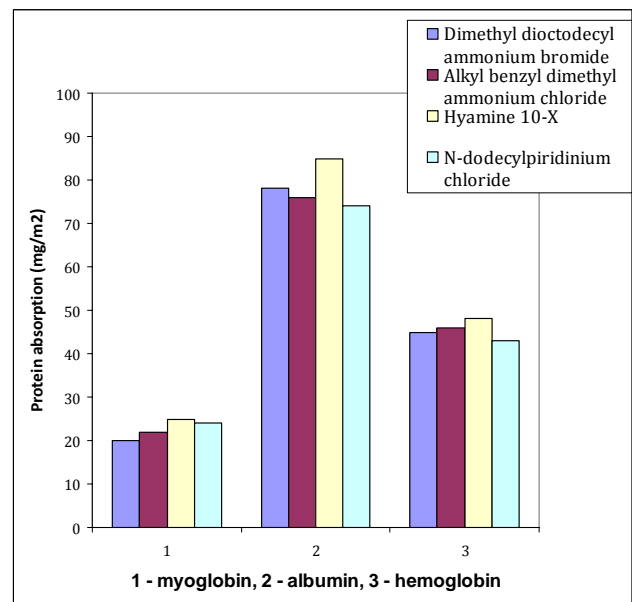


Fig. 5 Myoglobin, albumin and hemoglobin retention on synthesized membranes

If the membranes are designed to be used for hemodialysis, the separation of different proteins from blood is presented in Fig. 5. The tests were performed with myoglobin, albumin and hemoglobin from synthetic solutions at a standard concentration at 10^{-5} M with a feed solution of 1L. The retained quantity of proteins in

membrane structure was determined by UV-VIS spectroscopy analyzing the feed solution and the permeate after the recirculation for 30 min.

The small amount of separated myoglobin can be probably explained by the dimensions of this protein (larger than albumin and hemoglobin, fact which lead to a fast fouling of the membrane). The values of retention are situated in range of 20 to 25 mg/m² of membrane for myoglobin, 74 to 85 mg/m² of membrane for albumin and 43 to 48 mg/m² of membrane for hemoglobin. the best retention for all types of proteins was obtained with the membrane obtained with Hyamin 10-X as additive. All the membranes can be used for protein retention and other biomedical applications because this values don't affect the quality of a dialysis process (imbalance of physiological processes or excessive retention of biological interest proteins).

For the evaluation of fouling capacity of membranes, a standard test of Bovine Seric Albumin was performed at a standard concentration at 10⁻⁵ M with a feed solution of 1L for 100 min. The results are presented in Fig. 6.

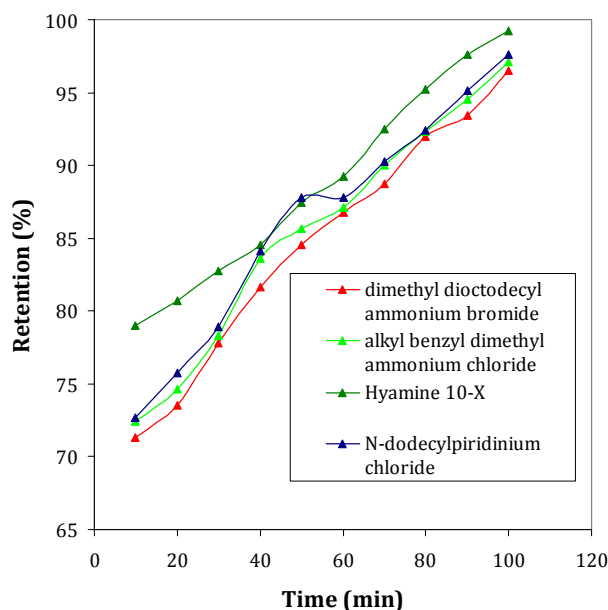


Fig. 6. Retention of Bovine Seric Albumin through synthesized membranes

The data are completely correlated with the retention of myoglobin, albumin and hemoglobin. The best performances were shown by the membrane synthesized using Hyamine 10-X. After 100 min, almost 100% from the entire protein quantity. The results are not so different between membranes, but the properties can be harness for sensitive processes were very precise amounts of chemical species must be separated or fractionated.

4. Conclusions

The use of cationic surfactants demonstrated that the polysulfone membranes can be designed at the level of

geometry and membrane pores for specific applications. Dimethyl dioctodecyl ammonium bromide, alkyl benzyl dimethyl ammonium chloride, Hyamine 10-X, N-dodecylpyridinium chloride used as additives lead to different polysulfone membranes with thicknesses between 50 and 154 μm and pore diameters between 0.28 and 0.52 μm . The specific water fluxes are situated in a wide range 117.12 - 132.5 L/m²h which indicate a versatile method for the design of polymeric membranes for targeted applications. The retention tests performed for three different biological interest proteins shown a membrane capability of retention between 20 to 25 mg/m² for myoglobin, 74 to 85 mg/m² for albumin and 43 to 48 mg/m² for hemoglobin, values that recommend these membranes for dialysis or hemodialysis separation processes.

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*Corresponding author: svoicu@gmail.com