ROMANIAN JOURNAL OF INFORMATION SCIENCE AND TECHNOLOGY
Volume **12**, Number 3, 2009, 410–422

Synthesis and Characterisation of Ionic Conductive Polysulfone Composite Membranes

Ştefan Ioan VOICU[1], Nicoleta Doriana STANCIU[2],
Aurelia Cristina NECHIFOR[1], Dănuţ Ionel VAIREANU[1],
Gheorghe NECHIFOR[1]

[1] *Politehnica* University Bucharest,
Faculty of Applied Chemistry and Materials Sciences,
Str. Gheorghe Polizu 1–7, Bucharest 011061, Romania

E-mail: `svoicu@gmail.com`

[2]Centre for Organic Chemistry *Costin D. Neniţescu*, Romanian Academy,
202B Spl. Independenţei, CP 35-108, Bucharest 060023, Romania

Abstract. In order to combine the advantages of polysulfone (PSf) as a membrane material and the requirements of an enhanced selectivity to that of polyaniline as a conductive polymer, this paper reports the results obtained for synthesis of polysulfone-polyaniline composite membranes by a new technique consisting in phase inversion by immersion precipitation accompanying by chemical reaction followed by the activation of polyaniline with sulfonated β-cyclodextrine and p-sulfocalix[4]arene. The above synthesized membranes were structurally characterized using Scanning Electron Microscopy, FT-IR spectroscopy, thermal analysis. The ionic conductivity and electrochemical characteristics were also determined by Electrochemical Impedance Spectroscopy.

Key words: composite membranes, polysulfone, polyaniline, electrochemical characteristics.

1. Introduction

Membrane technology is presently an established part of several industrial processes and presents a significant relevance in the food industry, in the manufacture of dairy products as well as in the automotive industry for the recovery of electropainting baths, electronic industry for solvent purification or other important industrial processes [1].

Among the conducting polymers family, polyaniline (PANI) has been extensively studied due to its environmental stability, oxidation or protonation-adjustable electrical properties and its potential use as a component of e.g. light-emitting or electrochromic devices, sensors, separation membranes and antistatic coatings [2]. It is one of the most useful conducting polymers due to its facile and cheap synthesis and simple behaviour of chemical doping/dedoping, and can be readily prepared in bulk by the chemical oxidative polymerization of aniline. Compared with granule polyaniline synthesized by conventional chemical methods, nanostructure polyaniline exhibits superior chemical sensing and unique photothermal effect [3].

Between the very well known membrane polymeric materials, like cellulose derivatives, polyamides, aromatic polymers with etheric, esteric, imidic and iminic groups, polysulfones are extensively studied [4–8]. The constant interest of the membrane scientists for polysulfone is due to its excellent characteristics [9–11] such as: solubility in a large range of aprotic polar solvents (dimethylformamide, dimethylacetamide, dimethylsulfoxide, halogen derivatives, nitrobenzene), high thermal resistance (150–170°C), chemical resistance on entire pH range, resistance in oxidative medium (hypochlorite 5–7%, hydrogen peroxide 3–5%), high mechanical resistance of the films (fracture, flexure, torsion), moderate reactivity in aromatic electrophile substitutions reactions (sulfonation, nitration, chloromethylation, acylation, etc.). Good solubility allows all preparation methods for polysulfone membranes especially phase inversion by immersion precipitation, chemical resistance allows the sterilization (thermal and chemical), biocompatibility and moderate reactivity allows functionalization by aromatic electrofile substitution or other reactions. However the polysulfones exhibit two main disadvantages, the hydrophobic character and the low resistance to UV radiation. The first one can be cancelled by chemical modification of polysulfones (e.g., introducing sulfonic, hydroxyl-ethyl, carbonylic or carboxymethylic groups) which will also give a decrease of the basic properties of polymer. The synthesis of completed polysulfone membranes with hydrophilic functions is competing with the synthesis of composite membranes including a support consists in a polysulfone membrane and an active layer made from functional polysulfone.

This paper reports the results obtained for synthesis of polysulfone-doped polyaniline composite membranes by a new technique seldom reported in the literature consisting in phase inversion by immersion precipitation accompanying by chemical reaction. The obtained membranes were tested by Electrochemical Impedance Spectroscopy in order to verify their electrochemical performances.

2. Methods

Polymer (polysulfone-PSf) was supplied by BASF (Ultrason S3010). The polymer was further purified by re-precipitation from chloroform with methanol and dried in vacuum at 60°C. As solvents for polysulfone, aniline (Merck) and chloroform (Fluka) were used and as non-solvent, cyclohexanol (Merck) was used. In experiments, ammonium peroxodisulfate (Fluka), hydrochloric acid (HCl), p-sulfocalix[4]arene and β-cyclodextrin sulfated sodium salt (Aldrich) were used. The β-cyclodextrin sulfated sodium salt was treated with an aqueous solution of acetic acid (5%) in order to obtain sulfonated β-cyclodextrin.

The reactions for aniline polymerization to polyaniline, respectively the dopping reaction of polyaniline with sulfated β-cyclodextrin are schematically represented in Fig. 1.

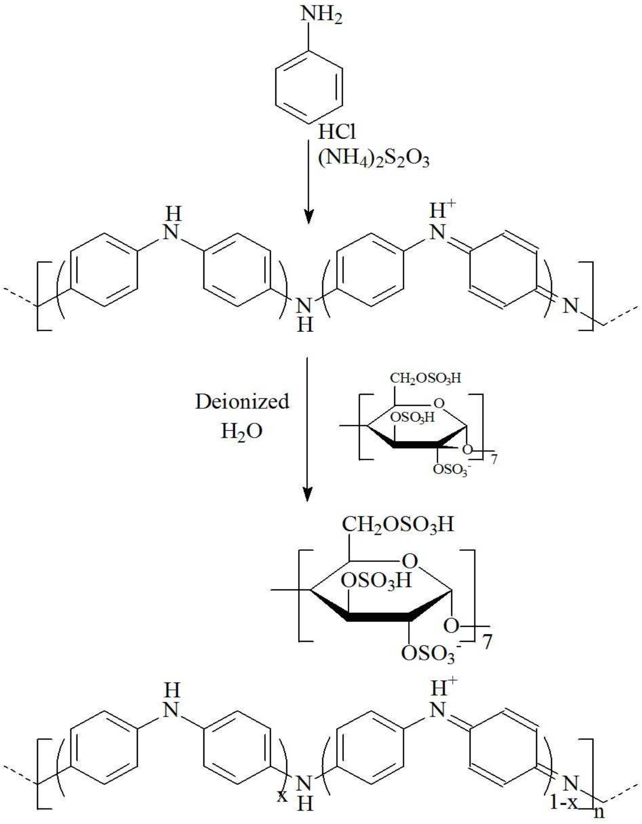


Fig. 1. Schematic representation for polyaniline synthesis and dopping reaction with sulfated β-cyclodextrin inside the polysulfone membrane pores.

2.1. Composite membrane synthesis

A schematic representation for molecular structure of obtained composite membrane is represented in Fig. 2.

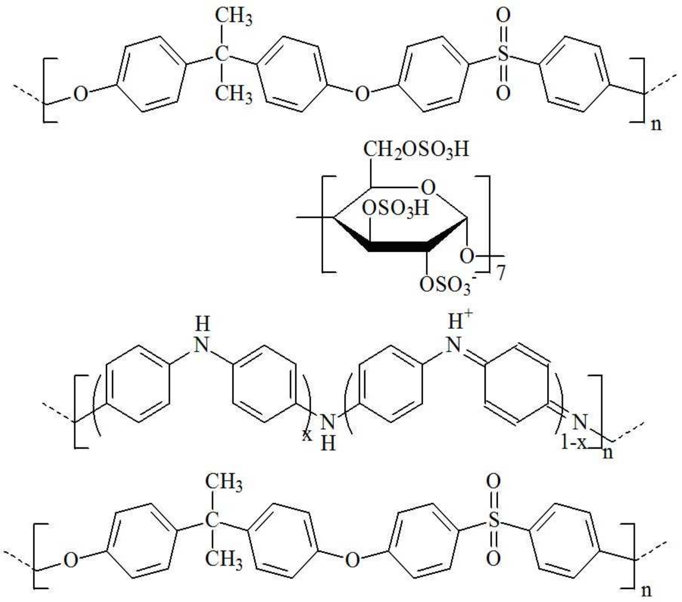


Fig. 2. Schematic representation for molecular structure of synthetized polysulfone- sulfated β cyclodextrine doped polyaniline composite membrane.

The required amount of solvent (aniline) is introduced into an Erlenmeyer glass and small portions of polymer are added under magnetic stirring until the desired concentration (15% polymer in aniline) is achieved. The air is then removed from solution into a desicator under vacuum for 30 minutes. 5 ml of polymer solution is deposited onto a spectral glass and fixed at a standard thickness of 250 μm. The polymer film deposited on glass is immersed into the coagulation bath (I) which contains 200 mL cyclohexanol. The crude membrane obtained by immersion precipitation (from first coagulation bath with cyclohexanol) is introduced into a tank (II) containing hydrochloric acid 1M and is maintained in this solution for 30 minutes. After this treatment the membrane is introduced into a tank (III) with ammonium peroxodisulfate solution in chloride acid for 4 hours.

In order to finish the functionalization (aniline oxidation at polyanilne) the composite membrane is kept into a persulfate acid solution for 24 hours. The obtained membranes are kept in water:methanol solution 1:1.

2.2. Doping of polyaniline from composite membranes

The polyaniline from polysulfone-polyaniline composite membranes was doped with sulfonated β-cyclodextrin or p-sulfocalix[4]arene [12, 13]. A surface of 10 cm^2 of a polysulfone-polyaniline composite membrane is immersed in deionized water with 1 g of sulfonated β-cyclodextrin or p-sulfocalix[4]arene and the solution is stirring for 24 h. After this, the membrane is washed with deionized water for residual sulfonated β-cyclodextrin or p-sulfocalix[4]arene removal.

The obtained membrane was characterized by FT-IR spectroscopy, TGA analysis, SEM microscopy and electrochemical characteristics were determined by Electrochemical Impedance Spectroscopy spectroscopy.

3. Results

Relatively a small number of papers and researchers reports until now phase inversion with chemical reaction. The regenerated cellulose films are made by cellulose xantogenate spinning (Cell-O-CS S^-Na^+) into a coagulation bath which contains sulfuric acid as main reagent and sodium sulfate, or in the last years zinc sulfate and surfactant [14, 15]. Mulder et al. have tried to promote reactive systems in phase inversion by immersion precipitation using poly benzimidazole/sulfuric acid, alkaline solution, this technique didn't too much develop and it was beated by other methods of phase inversion.

One of the arguments that may still maintain the atractivity of this technique consists in the fact that from polymer/solvent/non solvent system, even if a chemical reaction between solvent and non solvent exists, the membrane is formed from initial dissolved polymer in solution: polysulfone, polyamide or poly benzimidazole.

The reported tentative [8] related to *in situ* functionalization of the polymer by phase inversion in Polysulfone/DMF solvent and $POCl_3$ system (Vilsmeyer-Haak reaction) giving as a result the formylated polysulfone membrane had not yet the expected impact. This is the reason for which in this paper the results related to polysulfone and polysulfone/polyaniline membranes synthesis using a relatively new system [16-18], PSf/aniline are presented. This system exhibits the following advantages: polysulfone in aniline solutions (5–15%) are stable for very long time, showing a favorable consistence for films formation, films are adherent on different surfaces-glass, steel, copper, aluminum, Teflon, and finally, the solution presents compatibility with different nano-species, such as carbon nanotubes, magnetic nanoparticles, colloidal silver, micro- and nano- disperse gold and copper and polymeric nano-powders. Aniline is miscible with alcohols, halogen derivatives, ethers, esters, and this fact allows the approach of phase inversion in many ways for the polysulfone/aniline/non solvent system. As an alkaline chemical species (pKa $\approx$ 9), the aniline allows on one hand phase inversion with chemical neutralization reaction, but on the other hand, and on the other hand different organic reactions such as oxidation and condensation.

Polysulfone membranes preparation from polysulfone/solvent/non solvent systems is well known. One should find the adequate non solvent so that starting from a known polymer concentration in solvent to be able to obtain a membrane for micro-, ultra-, nano-filtration or pervaporation. An experimental test for phase inversion in polysulfone/aniline/non solvent system was performed. The used non solvents were: cyclohexanol, acetone, propanol, ethylether, ethylacetate and octanol, and some mixtures of these solvents. In additional study polysulfone solutions in aniline at three concentrations (7%, 11% and 15%) were used. A small number of obtained membranes may be used in a membrane process, most of all presenting surface damages and non-homogeneity which may be explained only by formation of solvent-non solvent synergic mixtures which interact with polymer and cause resolubilization, swelling and local agglomeration of the polymer film. Among all studied systems, the polysulfone/anyline/cyclohexanol system exhibits the best results because it allows good membranes synthesis at all three concentrations, suitable for further use.

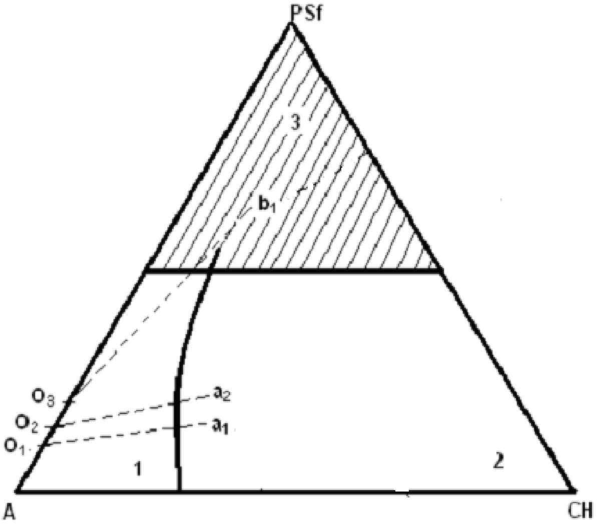


Fig. 3. Coagulation arrows in polysulfone(PSf)/aniline(A)/ cyclohexanol(CH) system ternary system: 1. mono phase, 2. two-phase system, 3. gel region (O_1–7% PSf, O_2–11% PSf, O_3–15% PSf).

After phase inversion in polysulfone /aniline/cyclohexanol system, membranes with a significant amount of aniline in their structure were obtained, no matter what way O-a and O-b was followed (Fig. 3). Classical interpretation for membrane formation in polysulfone/solvent/non solvent system can be considered the most appropriate for the goal of this paper. Aniline concentration from coagulation bath gives information about the aniline quantity which still remains in polysulfone membrane's pores (Fig. 4).

It was disregard the non solvent volume which penetrates the polymer film for membrane coagulation.

According with previous considerations enough aniline quantity remains in membrane which can be transformed *in situ* (within the crude membrane) in polyaniline by oxidation. The formed membrane will be made by a polysulfone matrix which contains polyaniline.

The SEM images (FESEM Hitachi S4500) (Fig. 5) for obtained membrane reveals a homogenously structure with a well determined structure for polyaniline crystals (1–1.5 µm length and 100 nm diameter) and a very pronounced active layer.

The formation of polysulfone-polyaniline composite membrane was also demonstrated by thermal analysis (Fig. 6) with a maximum loss point at 561.49°C for polyaniline.

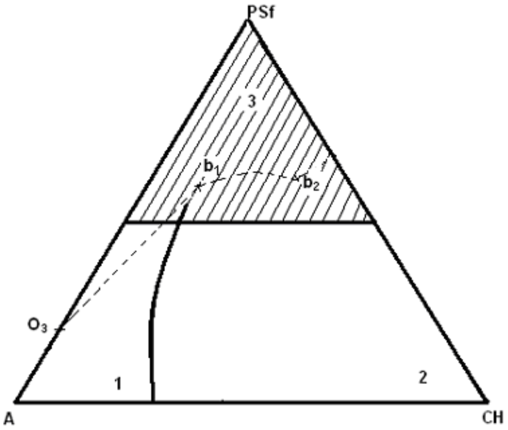
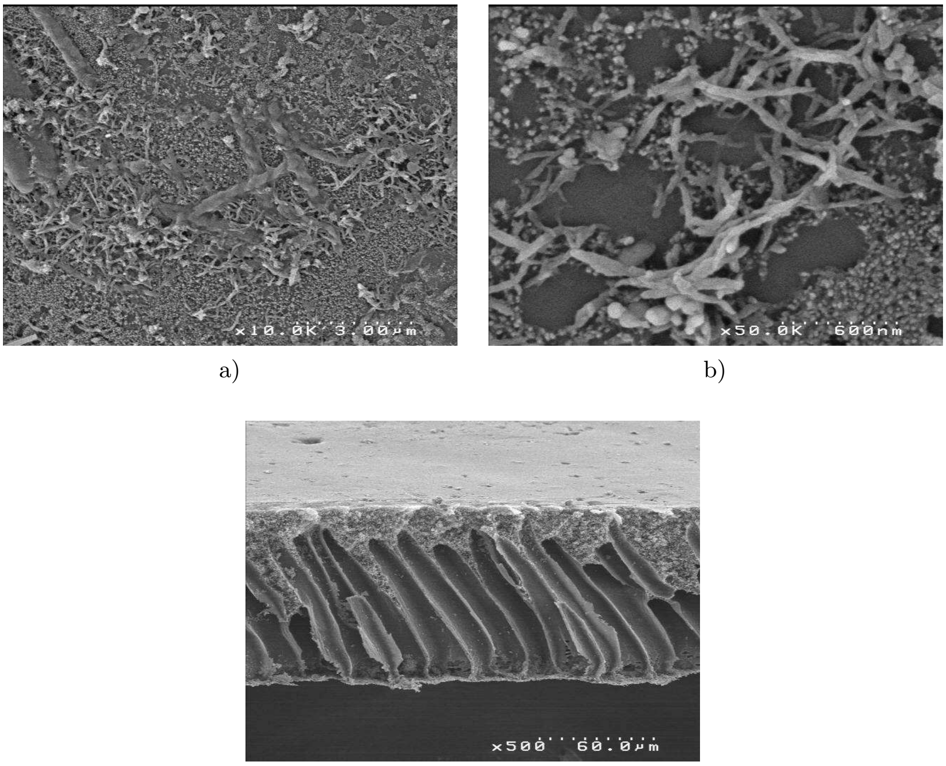


Fig. 4. Coagulation arrows in polysulfone(PSf)/aniline(A)/ cyclohexanol(CH) system ternary system: $O_3 \rightarrow b_1$(aniline extraction) and $b_1 \rightarrow b_2$ (in situ polymerization by oxidation).



a) b)

c)

Fig. 5. SEM images of obtained composite membrane: a)-top surface (×10k), b)-top surface (×50k) and c)-cross section (×500).

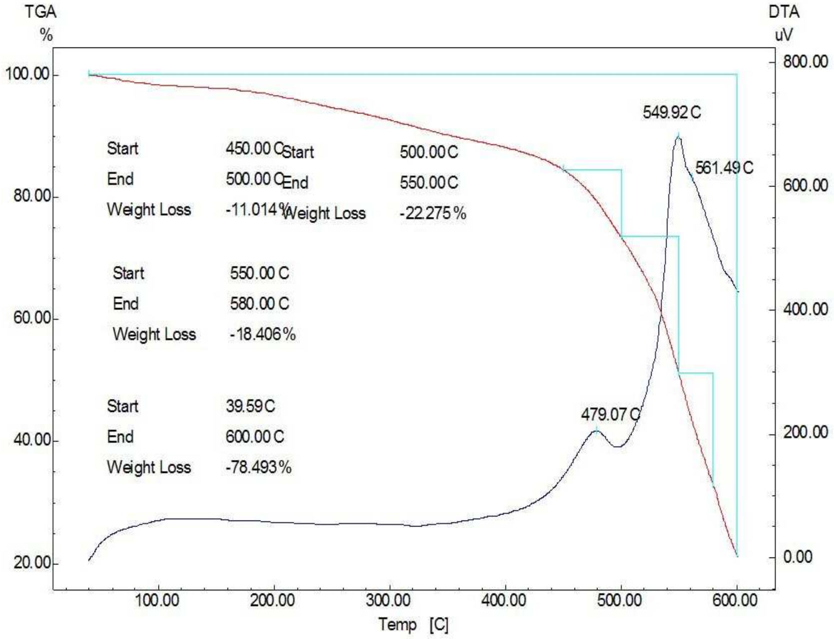


Fig. 6. TGA spectra for polysulfone-polyaniline composite membrane.

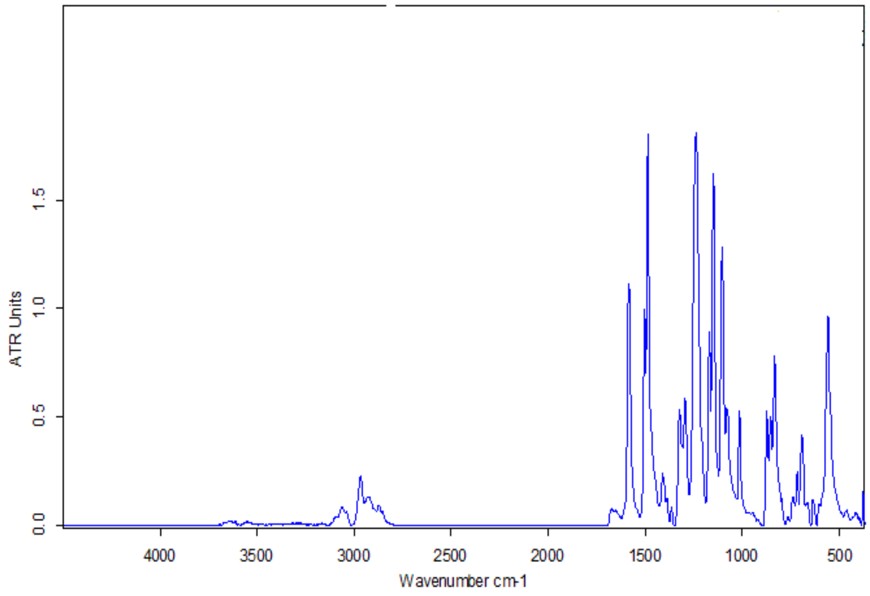
Nitrogen atoms from polyaniline are protonated during the doping reaction. Figure 7 shows the FTIR spectra of polysulfone-doped polyaniline composite membranes.

The reaction between sulfonated β-cyclodextrine or p-sulfocalix[4]arene and the polyaniline backbone is confirmed by FTIR spectra.

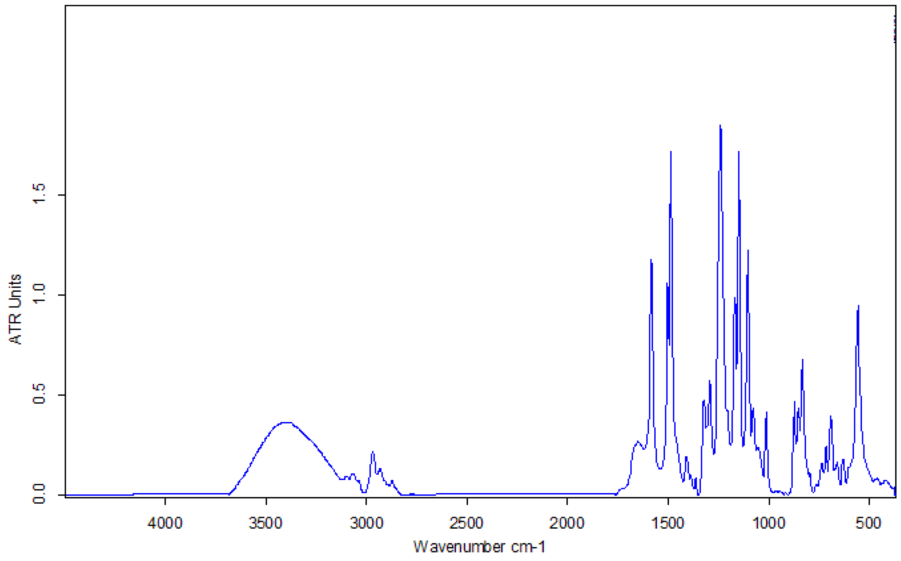
The 1594 cm^{-1} band, which is attributed to quinone ring in the undoped polyaniline, suffers a shift to 1583 cm^{-1}. Also, the band of benzene ring deformation at 1487 cm^{-1} is shifted with about 7cm^{-1}. A peak seems to manifest in the domain 2500–3000 cm^{-1} and it could be attributed to the specific imonium group ($\mathrm{C} = \mathrm{N}^+{-}\mathrm{H}$), which occurs by protonation of imine nitrogen.

The ionic conductivity and capacitance for obtained membranes were determined by Electrochemical Impedance Spectroscopy. The measurements were made using a platinum cell with two platinum electrodes with a specific surface of 0.9503 cm^{-2} in frequency range 100 kHz–100 mHz at 25°C. The obtained EIS spectra are presented in Fig. 8.

At a medium membrane thickness of 124.4 μm, the measured capacitance was $\mathrm{C} = 2.816\ \mu\mathrm{F/cm}^2$ and the ionic conductivity was $\sigma = 1.76 \cdot 10^{-4}\ \mathrm{S/cm}^{-1}$ for the membrane doped with p-sulfocalix[4]arene. In the case of polysulfone-polyaniline composite membrane doped with sulfated β-cyclodextrine, at a medium membrane thickness of 128 μm the measured capacitance was $\mathrm{C} = 2.345\ \mu\mathrm{F/cm}^2$ and the ionic conductivity was $\sigma = 2 \cdot 10^{-4}\ \mathrm{S/cm}^{-1}$. Due to the presence of the four sulfonic groups on the supramolecular architecture of the 4-sulfo-calixarene (which ionize in aqueous solution), respectively 21 sulfonic groups in the case of sulfated β-cyclodextrine these two molecules could be considered as polydopants. This is the reason for better ionic conductivity in the case of polysulfone- sulfated β-cyclodextrine doped polyaniline composite membrane.

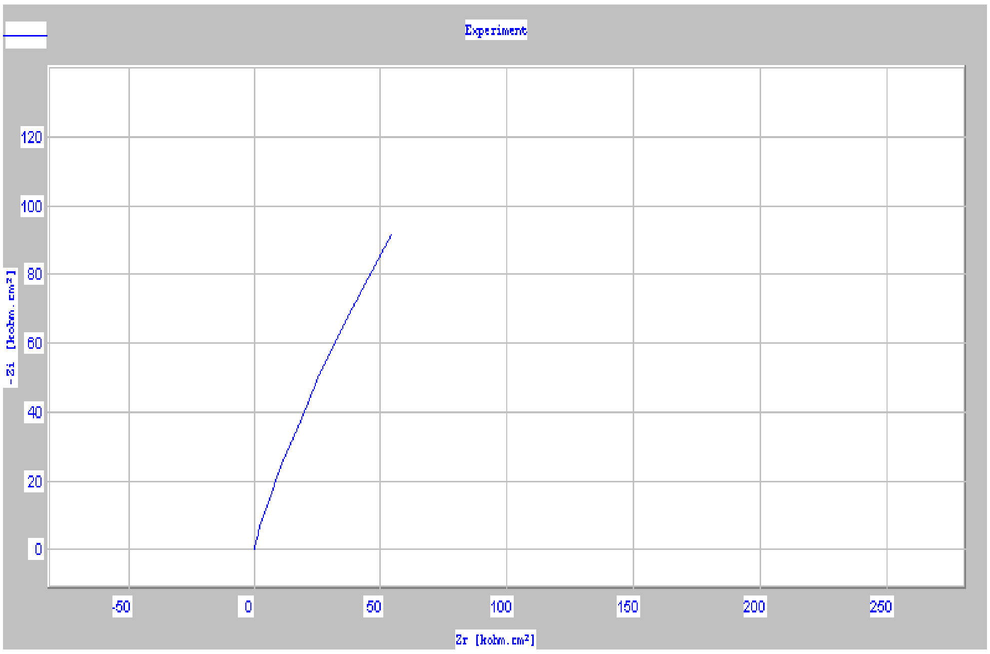


a)

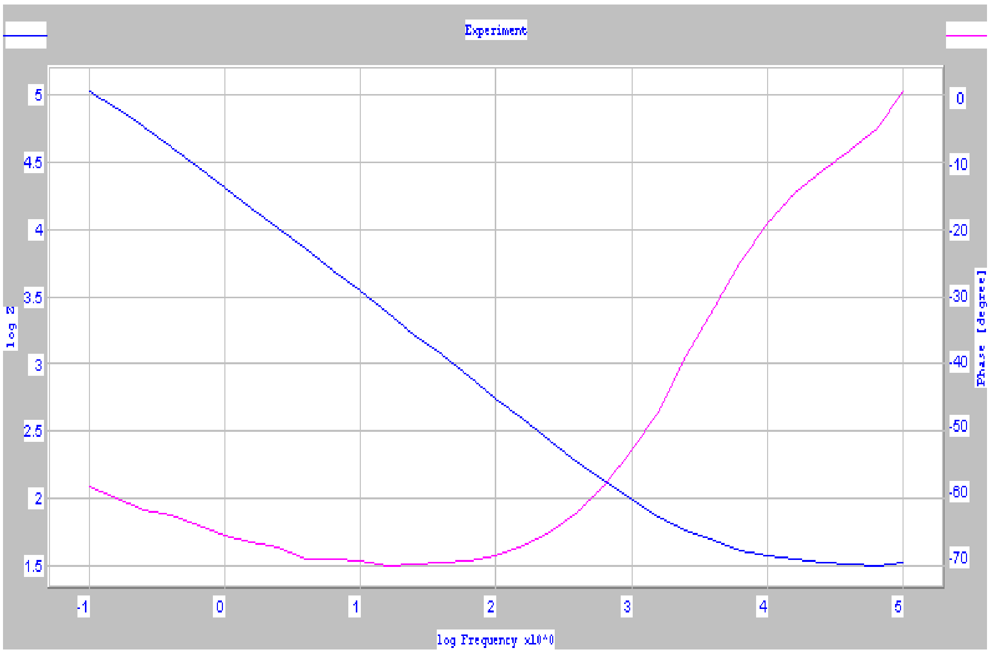


b)

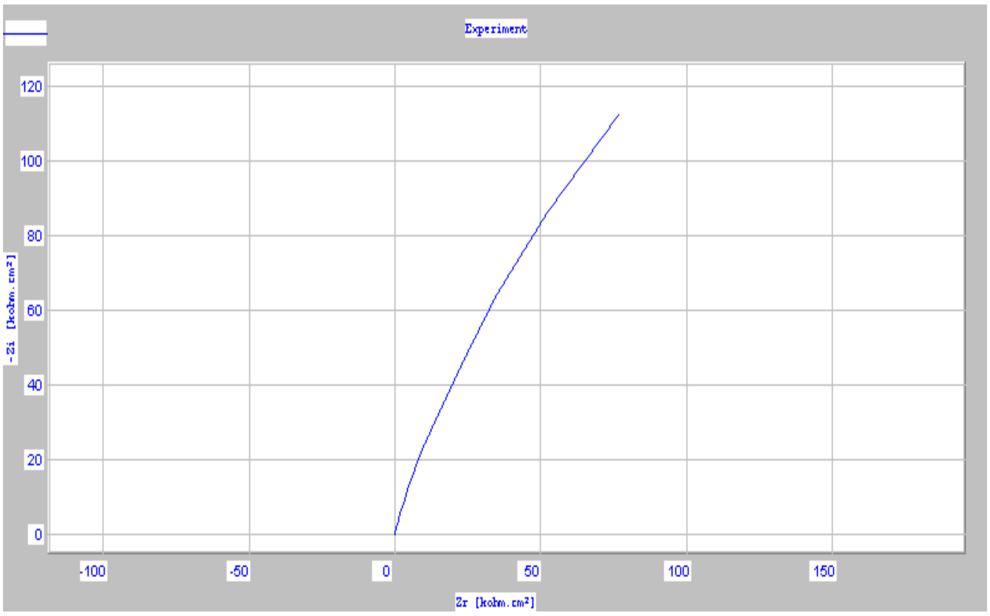
Fig. 7. FT-IR spectra for polysulfone-doped polyaniline composite membrane with sulfated β-cyclodextrin and p-sulfocalix[4]arene.


Experiment
-Zi [kohm.cm²]
120
100
80
60
40
20
0
-50
0
50
100
150
200
250
Zr [kohm.cm²]

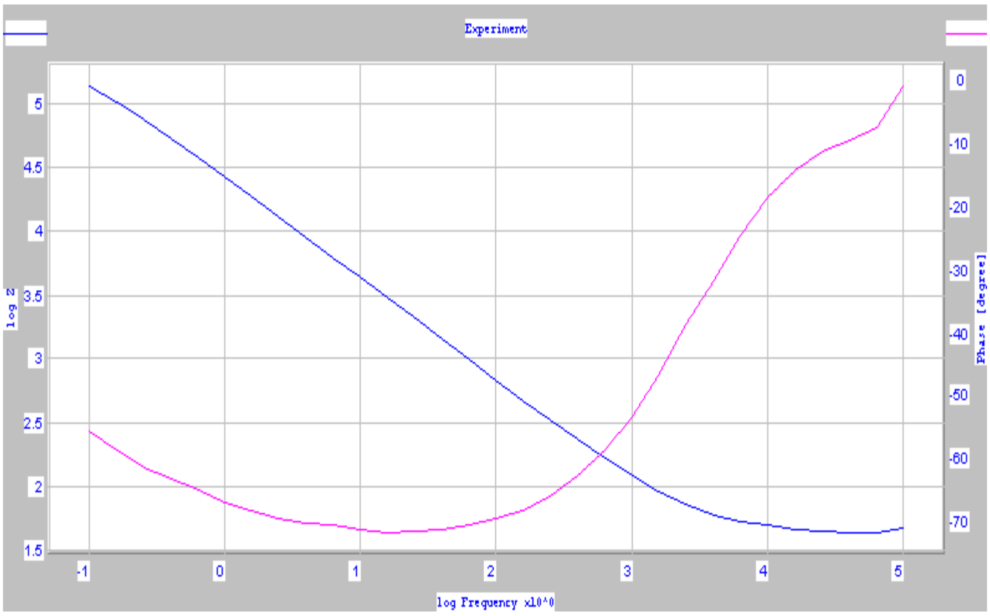
a)


Experiment
log Z
5
4.5
4
3.5
3
2.5
2
1.5
Phase [degree]
0
-10
-20
-30
-40
-50
-60
-70
-1
0
1
2
3
4
5
log Frequency x10^0

b)



c)



d)

Fig. 8. EIS spectra for polysulfone-doped polyaniline composite membrane:with sulfated β-cyclodextrine [Nyquist representation (a) and Bode representation (b)]and p-sulfocalix[4]arene [Nyquist representation (c) and Bode representation (d)].

These values and properties indicate possible applications for this material like micro-capacitors, support for different sensor devices, electronic and optic use solvents purification, colorants and proteins nanofiltration.

4. Conclusions

PSf-aniline system may lead to membrane formation through phase inversion by immersion precipitation into a coagulation bath which contains cyclohexanol (cyclohexanol gives the best results in comparison with other oxygenated organic solvents such as inferior alcohols, esthers, ethers, ketones), followed by immersion precipitation in cyclohexanol and ammonium persulfate (acid solution) oxidation which leads to polysulfone-polyaniline composite membranes. The polyaniline from obtained membranes can be reversible doped with sulfated β-cyclodextrin and p-sulfocalix[4]arene in order to increase the ionic conductivity and to improve the electrochemical characteristics for new synthesized material. The measured capacitance was C = 2.816 μF/cm^2 and the measured ionic conductivity was $\sigma = 1.76 \cdot 10^{-4}$ S/cm^{-1} for polysulfone - p-sulfocalix[4]arene doped polyaniline composite membrane, respectively the measured capacitance C = 2.345 μF/cm^2 and the measured ionic conductivity $\sigma = 2 \cdot 10^{-4}$ S/cm^{-1} for polysulfone – sulfated β-cyclodextrine doped polyaniline composite membrane.

Acknowledgements. Ovidiu Cojocaru and Dr. Ruediger Bhlum from BASF are kindly acknowledged for providing the polysulfone material. Mr. Didier Cot from European Institute of Membranes in Montpellier is acknowledged for SEM images. The authors also gratefully acknowledge the financial support of this research by the PNII 71-025, PNII 71-034 and PNII 71-062 research projects and CNCSIS TD 025/2007 research grant.

References

[1] *Membrane Technology in the Chemical Industry*,eEdited by S. P. Nunes, K.-V. Peinemann, Wiley-VCH Verlag GmbH, 2001.

[2] SARAVANAN C., PALANIAPPAN S., CHANDEZON F., *Synthesis of nanoporous conducting polyaniline using ternary surfactant*, Materials Letters, **62**, pp. 882–885, 2008.

[3] LI X., ZHUANG T., WANG G., ZHAO Y., *Stabilizer-free conducting polyaniline nanofiber aqueous colloids and their stability*, Materials Letters, **62**, 2008, pp. 1431–1434, 2008.

[4] PETERSEN R. J., *Composite reverse osmosis and nanofiltration membranes*, J. Mem. Sci., **83**, p. 81, 1993.

[5] LUNDY K. A., CABASSO I., *Analysis and construction of multi-layer composite membranes for the separation of gas mixtures*, Ind. Engng. Chem. Res., **28**, p. 742, 1989.

[6] DAI Y., GUIVER M. D., ROBERTSON G. P., BILODEAU F., KANG Y. S., LEE K. J., JHO J. Y., WON J., *Modified polysulfones 5: synthesis and characterization of tetramethyl polysulfones containing trimethylsilyl groups and their gas transport properties*, Polymer, **43**, p. 5369, 2002.

[7] NECHIFOR G., VOICU S. I., NECHIFOR A. C., GAREA S., *Nanostructure hybrid membrane polysulfone-carbon nanotubes for hemodyalisis*, Desalination, in press, 2009.

[8] VOICU S. I., NECHIFOR A. C., SERBAN B., NECHIFOR G., MICULESCU M., *Formylated Polysulphone Membranes for Cell Immobilization*, Journal of Optoelectronics and Advanced Materials, **9**(11), pp. 3423–3426, 2007.

[9] MULDER M., *Pervaporation – separation of ethanol-water and of isomeric xylenes*, Ph.D. Thesis, Twente University, Enschede, Netherlands, pp. 81–104, 1986.

[10] RAUTENBACH R., ALBRECHT R., *Membrane Processes*, John Wiley, New York, 1989.

[11] RODEMANN K., STAUDE E., *Synthesis and characterization of affinity membranes made from polysulfone*, J. Mem. Sci., **88**, p. 271, 1994.

[12] SERBAN B., BERCU M., VOICU S. I., MIHAILA M., NECHIFOR G., COBIANU C., *Calixarene-Doped Polyaniline for Applications in Sensing*, *Proceedings of International Semiconductors Conference (CAS)*, p. 257, 2006.

[13] SERBAN B., BERCU M., VOICU S. I., NECHIFOR A. C., COBIANU C., *Sinteza şi caracterizarea unei noi polianiline dopată cu sulfat acid de ciclodextrină*, Revista de Chimie, **57**, p. 978, 2006.

[14] HIGUCHI A., IWATA N., TSUBAKI M., NAKAGAWA T., *Surface-modified polysulfone hollow fibers*, Journal of Applied Polymer Science, **36**, p. 1753, 1988.

[15] HIGUCHI A., MISHIMA S., NAKAGAWA T., *Separation of proteins by surface modified polysulfone membranes*, J. Mem. Sci., **57**, p. 175, 1991.

[16] HU Z. A., REN L. J., FENG X. J., WANG Y. P., YANG Y. Y., SHI J., MO L. P., LEI Z. Q., *Platinum-modified polyaniline/polysulfone composite film electrodes and their electrocatalityc activity for methanol oxidation*, Electrochemistry Communications, **9**, p. 97, 2007.

[17] YANG Y., SHANG X., KONG C., ZHAO H., HU Z., *Preparation of PANI/PSF conductive composite films and their characteristics*, Frontiers of Chemistry in China, **1**, p. 484, 2006.

[18] HU Z.-A., SHANG X.-L., YANG Y.-Y., KONG C., WU H.-Y., *The electrochemical synthesis of polyaniline/polysulfone composite films and electrocatalytic activity for ascorbic acid oxidation*, Electrochimica Acta, **51**, p. 3351, 2006.