Pervaporation of Volatile Amine Solutions Using Polysulfone-C$_{60}$ Nanocomposite Membranes

Aurelia Cristina Nechifor$^1$, Stefan Ioan Voicu$^2$, Eugenia Eftimie-Totu$^2$, Alina Mihaela Dima$^3$, Vlad Mihai Voicu$^3$, Gheorghe Nechifor$^2$

$^1$National Institute for Microtechnologies IMT Bucharest, 126A Str. Erou Iancu Nicolae, 077190 Bucharest, Romania

$^2$Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Sciences, 1-7 Gheorghe Polizu St., Bucharest, 011061, Romania

$^3$Academy of Economic Studies Bucharest, 6 Piata Romana, Bucharest, Romania

Abstract
The development and implementation of new technologies for separation processes represents one of the great challenges of membranology. The pervaporation of the aromatic amine solutions presents particular importance, with applications especially in the pharmaceutical, dyes industry and environment protection upon the purification and separation of the residue resulted from the synthesis of aromatic intermediates. The synthesis of new polysulfone - C$_{60}$ fullerene membranes used for the pervaporation of the aromatic amine solutions is presented in this paper. The synthesized materials were characterized by FT-IR spectroscopy, TGA-DTA thermal analysis and SEM microscopy. For the aniline pervaporation tests, the obtained membranes were used, as well as a polysulfone membrane obtained from chloroform without fullerene. Best results were obtained for the polysulfone membrane with fullerenes obtained from chloroform.

Key Words: pervaporation, polysulfone membrane, nanostructured materials, composite membranes, environment protection,

1. Introduction
The polysulfones constitute the most extensively studied class from the commonly used polymeric membrane materials: cellulose derivatives, polyamides, aromatic polymers with ether, ester, imide and imine groups [1, 2].

The physical and chemical characteristics of polysulfones allowed to apply all the membrane preparation methods, especially the phase inversion by immersion precipitation [3] which provides the possibility of (thermal and chemical) sterilization, the achievement of biocompatibility, and its functionalization by aromatic electrophilic substitution [4-9].

Fullerenes are polyhedral carbon cages, in which the sp$^2$ hybridized carbon is directly linked to other three carbon atoms in an arrangement of rings made up of five, respectively six atoms. From all synthesized fullerenes up to the present, the most studied one is C$_{60}$ due to the fact that it is one of the few known molecular structures being part of the I$_h$ symmetry class [10, 11]. The applications of fullerenes nowadays are of high scientific and technical interest [12], but they appeared sporadically in the membrane field.

The obtaining of the polysulfone - nanospecies composite membranes, in particular polysulfone - fullerene membranes, supposes the preparation of polymer homogenous solutions including the fullerenes [13]. The complete solubilization of the fullerenes within the polymeric solution is difficult, although it is much easier when compared to the inclusion of the carbon nanotubes. There is a wide range of solvents which may solubilize these species. The solvation of C$_{60}$ fullerenes requires the disruption of interfacial between the solvent molecules, interactions which may not be fully compensated by the interactions between the solvent and fullerene due to its rigid geometry and its electric dipole moment value. The C$_{60}$ molecules are completely insoluble in protic or aprotic dipolar solvents, such as MeOH, MeCN, tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO). The solubility of fullerenes in alkanes is superior to that one in protic solvents, increasing from pentane to decane. The halides
are excellent solvents for fullerenes (with best results for chloroform, tetrachloroethylene and 1,1,2,2 - tetrachlorethan). However, the aromatic amino-derivates such as aniline, N-methylaniline and N,N' dimethyl aniline proved to be the best solvents [14-16].

The fullerene-based membrane materials using polyphenylenoxide as polymer have been recently obtained by Sterescu and Wesling [17, 18].

The polysulfone / fullerene composites laying at the basis of asymmetric membrane formation are studied in this paper. The obtained membranes were used for the pervaporation of aniline from aniline : N-methylaniline mixture. The use of aniline and its derivatives in colorants and dyes industry present a major impact for environment and usually, the small amounts or traces of un-reacted aniline are difficult to be removed applying conventional methods.

2. Experimental

2.1. Preparation of the polysulfone solution in N, N’-dimethylformamide

The required amount of polymer (polysulfone - PSf offered by BASF, Ultrason S3010 sort) is introduced under magnetic stirring in a flask filled with N, N’-dimethyl formamide (DMF) as solvent until the desired concentration (15% PSf in DMF) is achieved. Using the reprecipitated and dried polymer, the preparation of the desired polymeric solution takes place within maximum 24 hours. Before use, the solution is deaerated by standing in the vacuum drier for 30 minutes.

2.2. Preparation of the polysulfone solution in chloroform

Similar to the preparation of the solution in DMF, a polysulfone solution in chloroform was prepared (10% polysulfone in chloroform). The dissolution is faster, only 12 hours being necessary to obtain the solution.

2.3. Dispersion of the fullerenes in the polymer solution

After the formation of the polymer solution, the fullerenes (98% pure C60) are added in a proportion of 5% related to the polymer. The fullerene solution in the solubilized polymer is kept in ultrasoning for 48 hours for homogenization purposes.

2.4. Membrane formation

A determined quantity of polymer solution, 5mL, is deposited on a spectral glass support, and it is extended to a standard thickness of 250µm. The polymer film placed on glass is immersed in a coagulation bath containing an aqueous solution of isopropanol (50%) (in the case of the polymer solution in DMF). After coagulation, the membrane is washed using distilled water and methanol in order to remove the traces of solvent and coagulant. In the case of the membranes obtained from chloroform, the coagulation is performed with methanol, using the same procedure of subsequent washing.

2.4. Membrane characterization

The synthesized materials were characterized by FT-IR spectroscopy (Bruker Vertex 70), DSC thermal analysis, TGA-DTA (TA Instruments 2950) and scanning electron microscopy (SEM) (Hitachi S 4500). The pervaporation tests were carried out into a standard laboratory apparatus. The volume of feed tank was 200 ml, the temperature of feed was controlled using a thermal circulating bath and the unit was operated with continuous circulation of feed. The tests were performed using a mixture of aniline : N-methylaniline in volume ratio 1:10. The disc membranes for tests had a standard diameter of 9 cm.

3. Results and Discussions

The solutions obtained from polysulfone and fullerenes, for the synthesis of membranes by phase inversion, were prepared in dimethylformamide and chloroform, after prolonged homogenization in ultrasound field. In order to study the morphology and structure of the obtained membranes there were performed high resolution scanning electron microscopy, infrared spectroscopy and thermal analysis.

The carbon nanotubes are superior to the fullerene ones from the electric properties point of view. However, due to the fullerenes symmetry and their functionalization possibility, they are ideal candidates for sensing applications.

In the FT-IR spectra of the characterized membranes (Figure 1), both for the material obtained from chloroform (Figure 1a), and that obtained from dimethylformamide (Figure 1b), a 3-5 cm⁻¹ shift of the polymer-specific absorption bands towards higher values is observed. This is most probably due to the electrostatic interactions taking place between the polymer and fullerenes.

The specific absorption band for SO₂ group is shifted from 1325 cm⁻¹ in the polysulfone membrane to 1321 cm⁻¹ in polysulfone – C60 fullerene composite membrane in chloroform, respectively to 1323 cm⁻¹ in the polysulfone – C60 fullerene composite membrane in N, N’ dimethyl formamide. The specific absorption band for -CH₃ group is shifted from 1470 cm⁻¹ for the polysulfone membrane
to 1483 cm\(^{-1}\) for polysulfone – C\(_{60}\) fullerene composite membrane in chloroform, respectively to 1487 cm\(^{-1}\) for the polysulfone – C\(_{60}\) fullerene composite membrane in N, N’ dimethylformamide. It could be observed that the specific absorption bands for electro-negatively charged groups are shifted towards lower values, while the specific absorption bands for other groups are shifted towards higher values.

![FT-IR spectrum](image1.png)

**Figure 1.** FT-IR spectrum of the PSf-C\(_{60}\) composite membrane obtained from chloroform (a) and N, N’-dimethylformamide (b).

The thermal analysis was performed only on the PSf-C\(_{60}\) composite membrane obtained in dimethylformamide (Figure 2).

From the DSC diagrams a change of the glass transition point (T\(_g\)) of polysulfone from 188 to 182.6°C is observed. Such small modification is due to the low content of fullerenes. Thus, out of the 5% initial concentration of fullerene related to the polymer, a percentage of only 2.2% fullerene remains in the formed membrane. This could be explained by the relatively big size of the membrane pores related to the fullerene sizes, which results in their partial extraction during the coagulation process of the membrane formation.

![DSC and TGA-DTA](image2.png)

**Figure 2.** Thermal analysis spectrums for the PSf-C\(_{60}\) membrane obtained from dimethylformamide (a – DSC and b - TGA-DTA)

The scanning electron microscopy - SEM (Figure 3) of the polysulfone - fullerene composite membranes reveals a very compact structure for the membranes obtained from chloroform (Figures 3-1a and 3-1b). Such membranes could be potentially used in pervaporation or gas separation their absorption performances being amplified by fullerenes. For the membranes obtained from DMF (Figures 3-2a and 3-2b) a more relaxed structure, is observed. However, they have a higher compact degree than the polysulfone membranes. The second type of membranes could be used in filtration processes based on the adsorption property at the surface of fullerenes of the various organic chemical species or metallic ions. The performance of a separation process of a liquid mixture, similar to the separation of gases, requires operating pressures of over 40 atm.
Figure 3. SEM surface images of the polysulfone - fullerene composite membranes obtained from chloroform (1a – x1000, 2b – x10000) and from N,N’ – dimethyl formamide (2a – x1000, 2b – x10000).

The inconvenience of the use of high pressures in the separation of the volatile compound solutions was solved by applying the pervaporation. The vaporization of the desired component may be made in vacuum – vacuum pervaporation, or by entrainment using an inert gas – entrainment pervaporation. The pervaporation performances are amplified if the volatilized component has low vaporization heat (ethers, esters or hydrocarbons). Thus, the water-alcohol azeotrope is separated by water removal, and the halides – alcohol mixtures by alcohol vaporization. Lately, the economic aspects imposed the reorientation of the pervaporation towards the removal of the volatile compounds from the waste water.

The current tendency in the separation of gases and pervaporation underlines the use of composite membranes based on the high selectivity polymers.

For the aniline pervaporation tests, both types of obtained membranes were used, as well as a polysulfone membrane obtained from chloroform without fullerene. Best results were obtained for the polysulfone membrane with fullerenes obtained from chloroform. Such results is explained by the compact structure of the membrane and by the properties of the fullerenes. The results are presented in Figure 4.

Figure 4. Aniline pervaporation flows for the selected membranes

The possibility of aniline removal from aniline aqueous solutions by pervaporation is highly dependent on the pH (Figure 5). The use of an alkaline pH increases considerably the efficiency of aniline pervaporation from the solution, whereas a pH below 6 makes the process practically inefficient, irrespective of the membrane type. It is absolutely reasonable to consider that the \( \text{Ar-NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ar-NH}^+ + \text{H}_2\text{O} \) balance should be shifted to the left, so that aniline may solubilize in the membrane and then diffuse to the vacuum compartment and be removed from the system.

Figure 5. Removal of aniline retention versus pH for a 100 ppm aniline solution (R=retention)

Practically, in its ionic form the aniline is actually insoluble in the membrane and its impermeability does not allow the development of the pervaporation process.

The development and implementation of new technologies for separation processes represents one of the great challenges of membranology. The pervaporation of the aromatic amine solutions presents particular importance, with specific applications in the pharmaceutical and dyes industry for the purification and separation of the residues resulted from the syntheses of aromatic intermediates.
The membrane procedures are actually during an important evolution period, the technical issues being still doubled by economic considerations as well.

It should be known that the economic optimization of these procedures is complex as consequence of an increased number of parameters: operating pressure, crossing velocity, nature of the processed solution, conversion degree.

4. Conclusions

New C\textsubscript{60} polysulfone - fullerene composite membranes were synthesized by phase inversion, chloroform, respectively N, N'- dimethylformamide being used as solvents. The C\textsubscript{60} polysulfone - fullerene composite membrane presented excellent results in the pervaporation process of the aniline residual solutions resulted from syntheses in the pharmaceutical, respectively dyes industries.

For the aniline pervaporation tests, both types of obtained membranes were used, as well as a polysulfone membrane obtained from chloroform without fullerene. Best results were obtained for the polysulfone membrane with fullerenes obtained from chloroform. The obtained aniline pervaporation flow for polysulfone - C\textsubscript{60} fullerene membrane was 9·10\textsuperscript{-6} g/s·cm\textsuperscript{2}, which is much higher than the bvalue of the polysulfone membrane (2.3·10\textsuperscript{-6} g/s·cm\textsuperscript{2}).

5. Acknowledgements

Ovidiu Cojocaru and Dr. Ruediger Bluhm 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. Authors recognise financial support from the European Social Fund through POSDRU/89/1.5/S/54785 project: “Postdoctoral Program for Advanced Research in the field of nanomaterials” and also the financial support from project POSDRU/89/1.5/S/63700, 2010-2013, „Human Resource Development by Postdoctoral Research on Micro and Nanotechnologies”.

6. References