CHARACTERIZATION OF POLYTETRAFLUOROETHYLENE MEMBRANES IMPREGNATED WITH CALIX[n]ARENES (n=4, 6 AND 8) AND ACETATECALIX[n]ARENES FOR USE IN TREATMENT OF RADIOACTIVE WASTE USING THE SUPPORTED LIQUID MEMBRANE TECHNIQUE

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ABSTRACT

In the nuclear industry the separation processes have been to the long of those years of great importance in what refers to the production of nuclear materials used as fuels, having assumed fundamental paper in the strategy of decontamination of decommissioned nuclear installations and potentially in the disposition of liquid radioactive waste. Those wastes are produced continually, varying considerably in volume, radioactivity and chemical composition. In the treatment of these wastes different techniques have been used as the chemical treatment, the adsorption, the filtration, the ion exchange and the evaporation. Those techniques are limited to remove all the pollutants, and in the case of the evaporation they end up generating secondary solid wastes. In the last decades the technology of membranes has been a lot used mainly in the nuclear area to recover metal ions of radioactive liquid waste. This work presents the characterization of the PTFE membranes with pore size ranging between 0.45 and 5 μm for use in the recovery of metal ions in processes using the SLM technique. The membranes were characterized for: thickness and porosity, thermogravimetric analysis, infrared spectroscopy (IR), scanning electron microscopy (SEM) and luminescence spectroscopy with Eu(III) ions.

1. INTRODUCTION

The use of supported liquid membranes (SLMs), porous supports impregnated with an organic solution containing the carriers or extractor agents, they have been receiving growing attention in the last years, due its potential for use in the separation and removal of metal ions [1-3]. Instead, its industrial application is still limited, mainly, by the slow dissolution of the carrier impregnated in the pores of the membrane, what causes loss of the stability of SLM and decrease of its acting. That degradation mechanism is still being investigated by researchers, and among them they are mentioned the absorption of water of the polymeric support by the aqueous phases and the solubilization of the carrier in the interface of the solutions [4].

SLMs based on the principles of liquid–liquid extraction. The basic principle of SLM technique is that two aqueous phases, the feeding and stripping solutions, are separated by a hydrophobic membrane. Within the pores of this membrane an organic phase, comprised of an appropriate extractor agent with low solubility in water, is adsorbed. The analyte is transported from one aqueous phase (feeding solution) through the organic phase to the

stripping solution. The driving force of this transport might be pressure, pH or concentration gradients [5, 6].

The function of a membrane is illustrated in Figure 1, which shows the transport of a component *X* from feeding solution (4) through a SLM (1) into the stripping solution (5) due to a driving force. The driving force in this example is the concentration gradient.
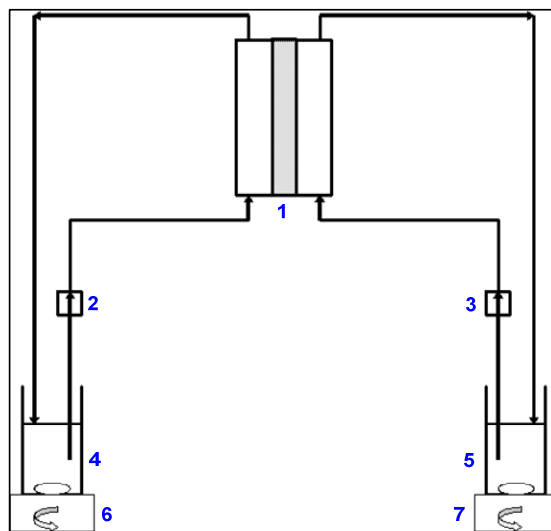

Figure 1. Schematic representation of the transport module containing the SLM
(1) SLM; (2) and (3) peristaltic pumps; (4) feeding solution; (5) stripping solution;
(6) and (7) magnetic stirrers

The mass transfer in the SLM technique depends mainly on the concentration difference of the analyte in the two aqueous solutions [3, 5, 6].

The permeability of a certain component in a membrane is determined by its concentration and its mobility in the membrane structure. In a porous structure, the concentration of a component in the membrane is determined by its size and by the pore size of the structure. The concentration of a component in the membrane often can be increased by a selective carrier.

The major advantage of SLM technique is that membrane and carrier can be optimized as well as the conditions in the feeding and stripping solutions for every application, allowing separations with good selectivity. In addition, the SLM process offers lower capital and operating costs [3].

Membranes are made of various materials, including metals, ceramics, polymers, and even liquids. Their structures include dense films and porous media that can have cylindrical pores or just a sponge-type structure. The membranes can be symmetric which are made of one material with an identical structure throughout the thickness of the membrane. To ensure sufficient mechanical strength, the membrane has to be of suitable thickness to withstand hydraulic pressures, or they can be asymmetric which consists of a very thin skin supported on a very open spongeous substructure, these membranes are capable of combining good

separation characteristics with very high flux rates and long useful lifetimes in all pressure driven membrane mass separation processes [1, 2].

Polytetrafluorethylene membranes (PTFE) are characterized by a combination of properties that make it unique, as its chemical, physical and anti-adherence properties. PTFE is chemically inert and only fluorine (chlorine trifluoride or oxygen difluoride) and molten alkali metals can change its physical and chemical structure. It has high resistance to temperature, resistant to 533 K in continuous employment, and for limited periods supports up to 633 K with consequent loss of mechanical properties. This means that the PTFE membranes do not release fragments or degradation products of the surrounding environment.

The objective of this study was to characterize PTFE membranes to use in treatment of liquid radioactive waste using the SLM technique.

2. EXPERIMENTAL PROCEDURE

2.1 Reagents and membranes

The supports used for the liquid membranes (organic phase) in the experiments were polytetrafluorethylene membranes (PTFE) manufactured by SARTORIUS, Germany. This support has high porosity, thin thickness and is hydrophobic. Supports were used with 47 mm diameter and pore size of 1.2 µm.

The liquid membranes *p-tert*-butylcalix[n]arenes (n = 4, 6 and 8) were obtained from Sigma-Aldrich (purity >99%) and the acetatecalix[n]arenes were synthesized by acetylation reaction by method described in the literature [7].

Chloroform was used as diluent. The stock solution of europium(III) nitrate for was prepared from the dissolution of 1.1780 g of europium(III) oxide in appropriate amount of HNO_3 6 mol L^{-1} and final concentration of the solution was 6.7×10^{-3} mol L^{-1}. The working solutions were prepared by diluting. This solution was used with the aim of confirming the complexation of the Eu(III) on with the extractor agents in the interface of the membranes in the emission and excitation spectra.

2.2 Preparation of supported liquid membranes (SLM)

The SLMs was prepared by soaking overnight (24 h) the PTFE film in 10 mL of the *p-tert*-butylcalix[n]arene and acetatecalix[n]arene solution in chloroform (Figure 2) and after immobilization, the excess organic liquid was blotted with paper tissue.
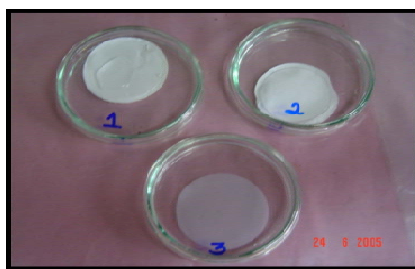

Figure 2. Impregnation of the SLMs

2.3   Characterization of PTFE membranes and supported liquid membranes (SLM)

The thickness of the membranes was measured by using a micrometer which defines the mean thickness of the membranes measured in five different areas of the membrane. The porosity in membranes was determined by measuring the volume of dodecane that the membrane absorbed in their pores by methodology described by ZHANG *et al.* [8].

2.3.1   Thermogravimetric analysis

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained in a thermobalance Mettler-Toledo model 851, using crucibles under conditions of dynamic air atmosphere1 system. The experiments were performed in a dynamic atmosphere of oxygen (50 mL min^{-1}), sample mass in the 2–13 mg range and heating rate at 10 ºC min^{-1} in the range from 30 to 700 ºC.

2.3.2   Infrared absorption spectroscopy

Fourier transform-infrared spectra were performed between 4000 and 600 cm^{-1} using NICOLET 520 infrared spectrometer equipped with ATR of germanium. Among a sample and other the crystal was clean and dry with absorbent paper. The obtained signs were expressed as absorbance.

2.3.3   Scanning Electron Microscopy

For analysis of scanning electron microscopy the membranes were fixed on a metallic support and coated with graphite by sputtering technique. The micrographs were obtained with a scanning electron microscope PHILIPS XL-30 of the Materials Science and Technology Centre-IPEN-CNEN/SP.

2.3.4   Luminescence spectroscopy

The spectra of luminescence (emission and excitation) of membranes impregnated with calixarenes were recorded at room temperature (~ 298 K) in the spectral range from 250 to 720 nm using a spectrofluorometer (SPEX-FLUOROLOG 2) with 0.22 nm double grating monochromator (SPEX 1680) and a 450 W Xenon lamp as excitation source. All spectral data were collected at an angle of 22.5º (front face) using a detector mode correction.

3.   RESULTS AND DISCUSSION

3.1   Characterization of the PTFE membranes

Before the preparation of supported liquid membranes the mean thickness of the PTFE membranes was measured with a micrometer and the porosity was determined measuring the volume of dodecane absorbed in its pores. The polymer supports were weighed and the porosities calculated by the differences of masses. The values of porosity obtained in this work agree with the values obtained by SRIRAM *et al.* [9] (Table 1), thus confirming that the

values obtained for the PTFE membranes are consistent with the literature, even using different techniques of characterization.

Table 1: Characterization of polymeric support

POLYMER SUPPORT	THIS WORK		SRIRAM *et al.* [9]
	THICKNESS (cm)	POROSITY	POROSITY
PTFE 1.2 μm	0.0095±0.0001	0.740±0.003	0.74

The curves TGA/DTG (Figure 3) show that the decomposition of the PTFE membranes show only one event of decomposition with mass loss of about 99.5% for the thermal decomposition of PTFE polymer that begins in 470 ºC and ends at approximately 600 ºC.
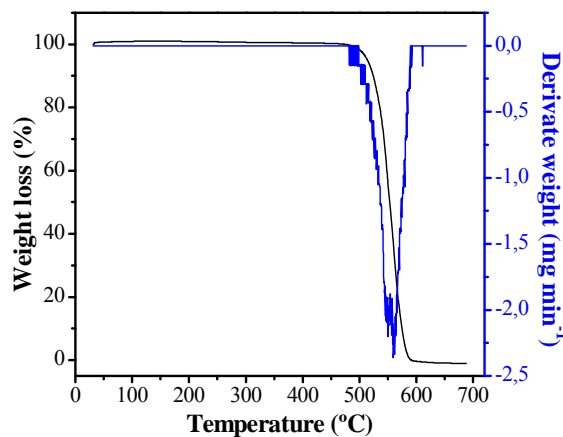
Figure 3. TGA/DTG curves of PTFE polymer

3.2 Characterization of the supported liquid membranes

The supported liquid membranes impregnated with the *p-tert*-butylcalix[n]arenes and acetatecalix[n]arenes were analyzed after impregnation in order to ensure the complete filling of the membrane pores by liquid membranes to verify their homogeneous distribution.

All thermal analysis measurements in this work were performed under exactly the same experimental conditions. From the TG curves of *p-tert*-butylcalix[n]arenes the weight losses occurred from 470 ºC, because there are no substituted groups. The temperature range 470–580 ºC corresponds the loss of methanol in the structure, and the other values are the decomposition stages. The decomposition which starts at 250 ºC and ends at 350ºC is the stage which is probably the mass of *tert*-butyl groups [10]. From 470 °C the decomposition process is rapid up to 580 °C, remaining stable up to 700 ºC.

Already the membranes impregnated with the acetatecalix[n]arenes decompose in three stages. The first decomposition occurs between 120–150 ºC for acetatecalix[4]arene, between and 190–230 ºC for acetatecalix[8]arene. But the acetatecalix[6]arene stable until 320 ºC. The

first event could be attributed to residual moisture still present after the drying procedure in the acetatecalix[n]arenes (n = 4 and 8). A second event observed was attributed to weight loss of the acetatecalix[n]arenes and probably corresponds to the mass of *t-butyl* groups. The third decomposition from 300 °C corresponds to decomposition of acetate groups and subsequent decomposition of PTFE.
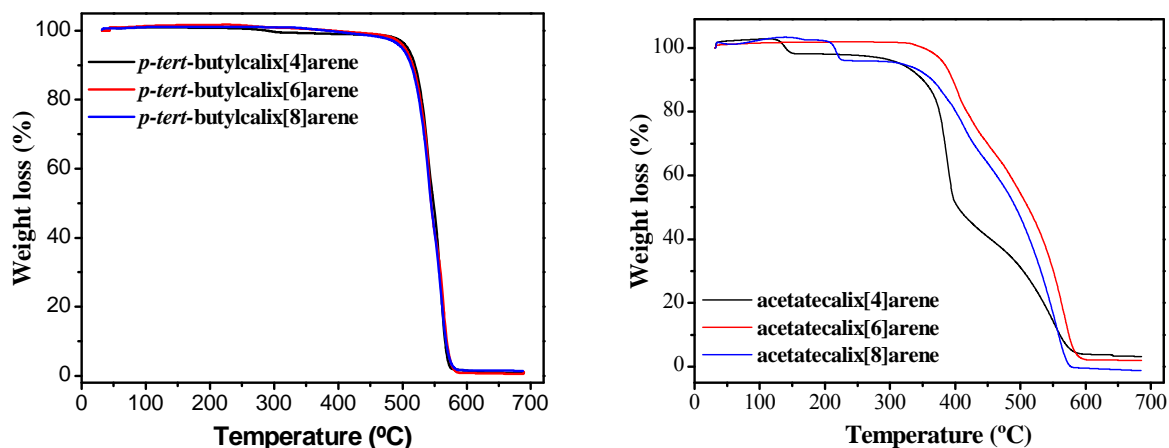

Figure 4. TGA curves of PTFE membranes impregnated with *p-tert*-butylcalix[n]arenes (left) and acetatecalix[n]arenes (right)

Through the spectra (Figure 5) can be observed that the spectrum of PTFE is very similar to that found in the literature. Most species CF_X (CF, CF_2 and CF_3), the main characteristic of fluorinated films, show two intense bands in the region of 1000–1300 cm^{-1} [11]. The marked peak at 1751 cm^{-1} is assigned to the C=O stretching mode (carbonyl group inserted in the molecule of *p-tert*-butylcalix[4]arene). The spectra of other *p-tert*-butylcalix[n]arenes and acetatecalix[n]arenes (not shown) also showed the same characteristics of Figure 5 in the infrared region.
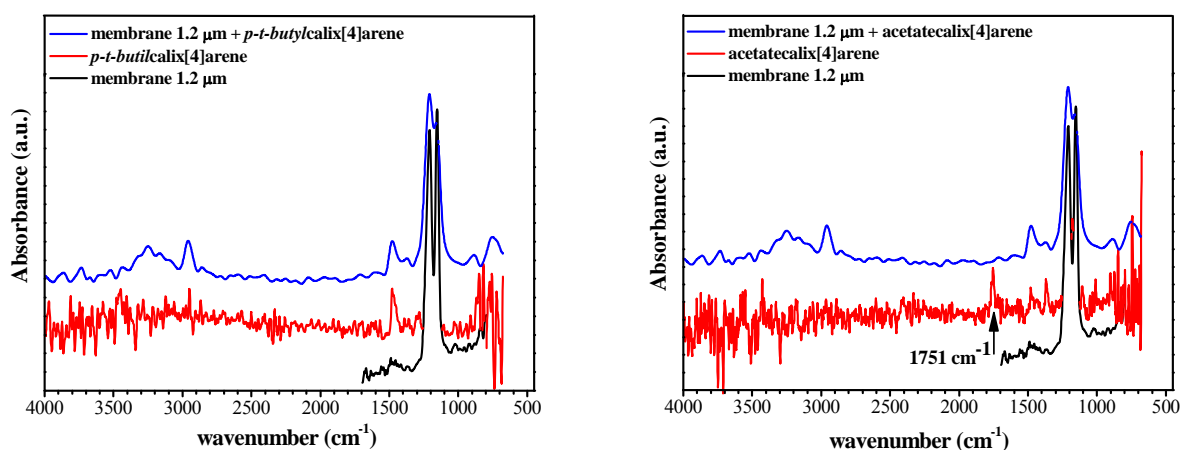

Figure 5. Infrared spectra of the PTFE membranes with *p-tert*-butylcalix[4] arene (left) and the acetatecalix[4]arene (right)

The micrographs (Figure 6) showed that the impregnation of the membranes in the systems of extraction of *p-tert*-butylcalix[4]arene in chloroform did not alter the structure of the polymer. Although, dilatations are observed small pores. It was also observed that the larger the average size of pores, they are more rigid. The membranes impregnated with the acetatecalix[4]arene showed similar behavior to membrane impregnated with *p-tert*-butylcalix[n]arene. The other micrographs obtained (not shown) showed the same morphology of the micrographs presented in Figure 6.
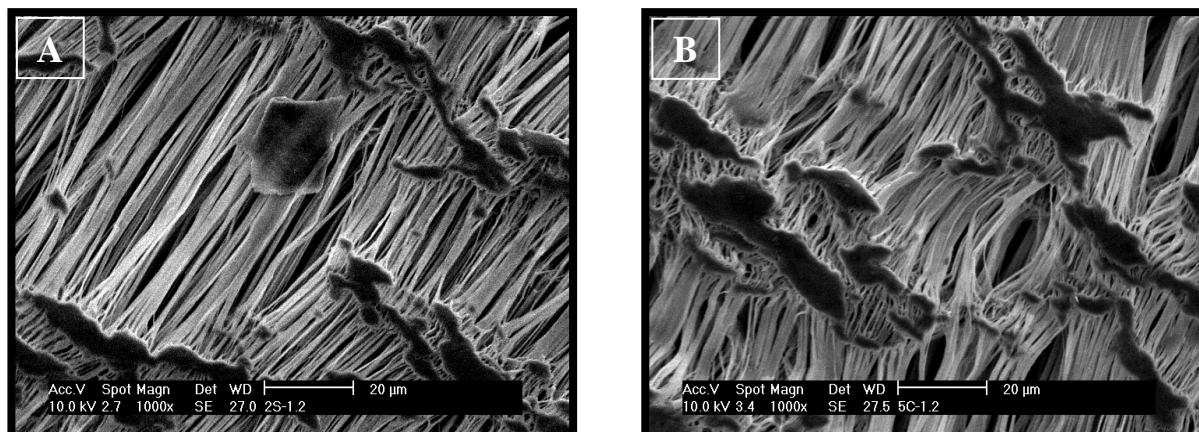

Figure 6. Scanning electron micrographs of porous PTFE membrane (A) without the agent extractor and (B) impregnated with *p-tert*-butylcalix[4]arene

The luminescence spectra of the membranes with the systems *p-tert*-butylcalix[n]arenes and acetatecalix[n]arenes were made with the aim of confirming the complexation of the rare-earth ion with the extractor agents in the interface of the membranes.

The excitation spectra were monitored in the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ (~ 613 nm). While the emission spectra were obtained with excitation in the rare-earth ion (~ 394 nm) in the interval from 420 to 750 nm, corresponding to the transitions intraconfiguracionais $^5D_0 \rightarrow {}^7F_{0-4}$. It is important to point out, that there were not significant differences among the spectra registered 298 K.

Figure 7 shows the excitation spectra of the complexes of HTTA in alcohol with the *p-terc*-butylcalix[n]arenes and the acetatecalix[n]arenes as ligands. In the region from 250 to 410 nm, the spectra present a wide band with maxima around 340 nm associated to the allowed transition $S \rightarrow S_0$ belonging to the ligand HTTA. The fine bands originating from of the transitions intraconfiguracionais $4f^6 \rightarrow 4f^6$, $^7F_0 \rightarrow {}^5G_6$, $^5H_4$ and $^5L_6$ have a overlap with the large bands of the ligands. You should know that thin bands with lower intensities are observed around 468, 482 and 492.5 nm, which are attributed to the transitions $^7F_0 \rightarrow {}^5D_2$, and $^5D_1$ of the Eu(III) ion.
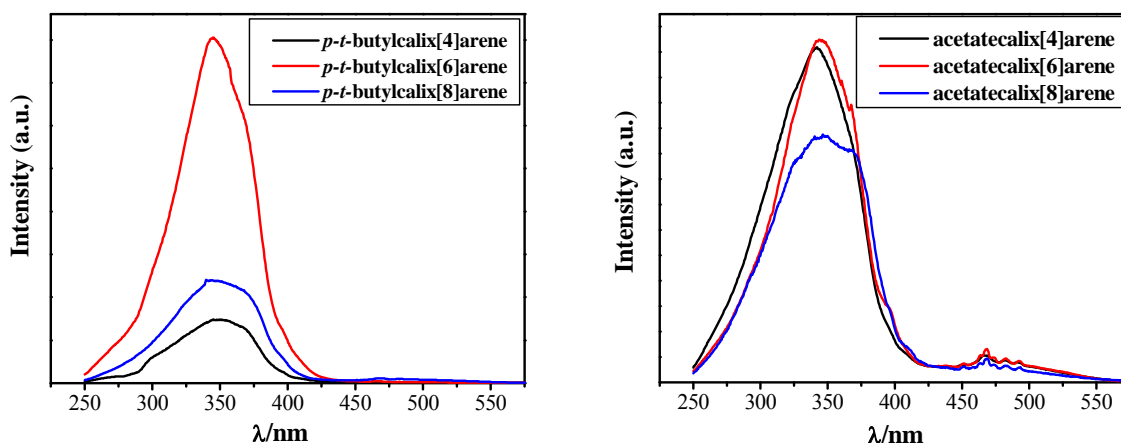
Figure 7. Excitation spectra of the PTFE membranes impregnated with
p-tert-butylcalix[n]arenes (left) and acetatecalix[n]arenes (right) containing europium nitrate
and revealed with an alcoholic solution of HTTA

The emission spectra of the PTFE membranes impregnated with $Eu(TTA)_3(H_2O)_2$ illustrated in Figure 8 were recorded in the range from 420 to 720 nm, at 298 K, with excitation in the europium ion (~ 394 nm). These spectra show fine bands assigned to transitions $^5D_0 \rightarrow {}^7F_J$ (where J = 0, 1, 2, 3, 4) and hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ more intense.

Unlike the $Eu(TTA)_3(H_2O)_2$ complex (Figure 8) of the PTFE membranes (Figure 9) impregnated with *p-tert*-butylcalix[n]arenes and acetatecalix[n]arenes they didn't present the bands originating from of the transitions $^5D_1 \rightarrow {}^7F_0$ (~ 532 nm), $^5D_1 \rightarrow {}^7F_1$ (~ 539 nm) and $^5D_1 \rightarrow {}^7F_2$ (~ 558 nm), in the spectral region from 500 to 570 nm and that are observed for the hydrated complex.
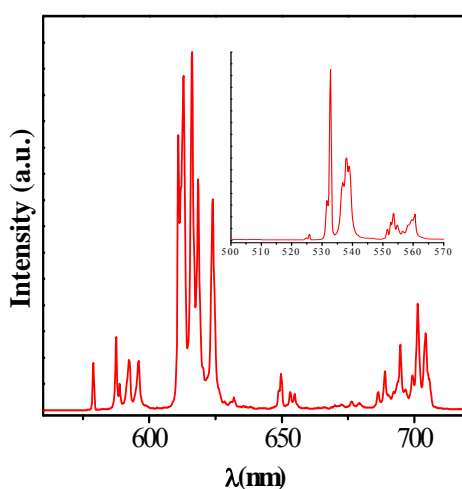

Figure 8. Emission spectra of the hydrated $Eu(TTA)_3(H_2O)_2$ complex
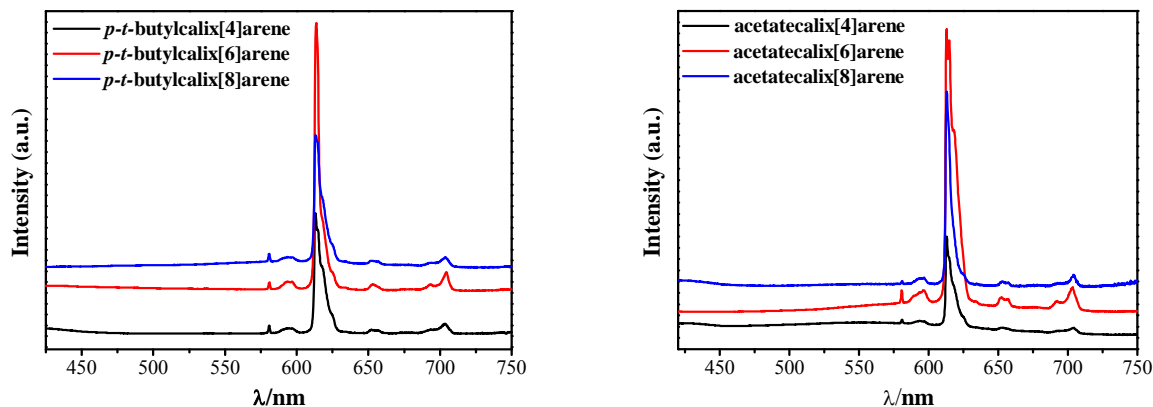l_{exc} = 394 nm

Figure 9. Emission spectra of the PTFE membranes impregnated with
p-tert-butylcalix[n]arenes (left) and acetatecalix[n]arenes (right) containing europium nitrate
and revealed with alcoholic solution of HTTA
$l_{exc} = 394$ nm

4. CONCLUSIONS

The study was made for supported liquid membranes impregnated with *p-tert*-butylcalix[n]arenes and acetatecalix[n]arenes. The analysis was made in PTFE membranes without and with impregnation of the extractor agents.

PTFE membranes impregnated with the *p-tert*-butylcalix[n]arenes and the acetatecalix[n]arenes showed a homogeneous distribution of the extractor agents inside the pores. The results of characterization lead to conclusion that the impregnation of extracting agents in the pores of the membranes is effective as a mobile carrier for the treatment of radioactive waste. This can be confirmed mainly by the infrared spectra and the luminescence spectra of the membranes before and after impregnation.

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