Iono-molecular Separation with Composite Membranes

I. Preparation and characterization of membranes with polysulfone matrix

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The fast development of these methods in the recent years has been possible due to new materials developing, the boom of nanomaterials in the development of composite and hybrid materials and also due to developing of new techniques and technologies. This paper presents the composite membranes based on polysulfone and performance nanomaterials: polyaniline and magnetic nanoparticles synthesis and characterization. Composite membranes (PSf-PANI and PSf-magnetite) have been produced by phase inversion by immersion - precipitation from a polysulfone in N- methyl pyrrolidone dispersion solution in which were dispersed polyaniline or magnetic nanoparticles. The prepared composite membranes were morphologically and structurally characterized using techniques and specific measurments: FT-IR, SEM, AFM, UV VIS, DSC, dielectric spectroscopy, solvents permeation and bovine serum albumin retention.Membranes pore size indicate their use in micro and ultrafiltration (12% in the case of PSF membrane and 12% for PSf - PANI) or in the field of microfiltration and membrane sensor, 12% for magnetite - PSF membrane. The results show that water flows at 3-4 bar pressure, are increasing in the order: PSf membrane < PSf –magnetite membrane <PSf-PANI membrane. While for alcohols, the dependence is reverse: PSf membrane > PSf –magnetite membrane > PSf-PANI membrane. In the case of alcohols flow, hydrocarbon chain has influence on flows and this correlates with hydrophily of membranes.Following bovine serum albumin retention tests, PSf-PANI membrane has the best performance (R> 95%), which correlates with the higher permeate flows.

Keywords: composite membranes, polysulfone, polysulfone-polyaniline composite, polysulfone - magnetic particles composite, ionic-molecular separations

Current concerns about the removal of ions and / or molecules using membranes and membrane processes have as primarily concern the prevention of environmental pollution by hazardous substances through separation and recovery before reaching into the environment, but also to eliminate polluting technologies and replacing them with others that have strong ecological character [1-5].

The limits regarding materials performances are sometimes a major impediment in the achivement of advanced technologies. Therefore, research on membrane processes and obtaining new membrane materials: composite, hybrid or intelligent, much stronger, more efficient and with lower costs, is an ongoing effort, having as main aim a cleaner environment [6-9] .

Conventional separation methods and techniques (sedimentation, filtration, centrifugation, extraction, absorption) showed their limits, and therefore appeared some new regenerative separation methods based on membranes use: micro-, ultra- , hyper- and nano-filtration, electro- dialysis and electro- ultrafiltration, pervaporation and pertraction[10-15].

The use of these processes has reached industrial scale in areas such as: wastewater treatment, food industry, pharmaceutical industry, chemical industry [16-21].

The fast development of these methods in the recent years has been possible due to new materials developing, the boom of nanomaterials in the development of composite and hybrid materials and also due to developing of new techniques and technologies [22-24].

This paper presents the composite membranes based on polysulfone and performance nanomaterials: polyaniline and magnetic nanoparticles synthesis and characterization.

Experimental part

Methods, materials and apparatus

Polysulfone (PSF) Udel type (Aldrich - M = 22000 Da), was used as basic material for all the variants of membranes prepared from N-methyl pyrrolidone (NMP) (Merck) solutions.

Aniline (A) (Merck), HCl 37%, analysis reagent (Merck) and ammonia peroxydisulphate (Merck) were used for polyaniline generation, while ferric chloride (Merck) and ferrous ammonium sulphate (Merck), HCl 37 % (Merck) and potassium hydroxide (Merck) were the materials leading to the magnetite nanoparticles formation.

Bovine serum albumin (BSA) (Biochemika) was used as a target substance in the prepared membranes retention characterization and its concentration was evaluated by the Lowry method [24-26].

The water required for solution preparation was obtained with a Millipore system and the solvents: acetone and lower aliphatic alcohols (methanol, ethanol and isopropanol) were purchased from Merck.

FTIR analysis was performed on a Nicolet 6700 FT-IR analyzer which records from 400-4000 cm^{-1}. Infrared spectra were carried out using attenuated total reflection (ATR).

Morphological analysis of samples was performed by scanning electron microscopy (SEM). It used a high-resolution microscope, Quanta 3D EGF model with dual beam and equipped with X-ray (EDX) Apollo X energy dispersive detector.

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Atomic force microscopy (AFM) experiments were made using working mode called *intermittent contact* using a Nanosurf® AG Switzerland (EasyScan model 2) apparatus.

The studied membranes UV-Vis spectra were obtained using a Perkin Elmer Lambda 35 spectrophotometer, equipped with integrating sphere.

Gravimetric measurements were performed using a DSC STA 409 PC Luxx (Netzsch) equipment set to 600° C in static air atmosphere with a heating rate of 10 K min.

Dielectric constant measurement was made using an impedance analyzer and a SOLARTRON 1260 A ProboSTAT cell.

Polysulfone solution preparation

In an Erlenmeyer flask with ground glass stopper, the solvent required amount and under magnetic stirring, portions from the purified polymer amount up to the desired concentration (15% polysulfone in solvent mixture NMP: aniline = 95: 5) is inserted.

Using precipitated and dried polymer, the desired polymer solution obtaining occurs within 4 h. Before use, the solution is deaerated by standing in a vacuum ejector for 30 minutes [27-29].

The dispersion of nano species

Magnetic particles prepared by one version of Massart [30-32] method, are dispersed in the polymer casting solution PSf / NMP-A in a concentration of 10% to the polymer by ultrasonication for 4 hours in Branson 1510 sonication bath. A dark brown dispersion is obtained with a 2-5% nanoparticles concentration in the polymer solution.

Membranes formation

A determined amount of polymer solution, 5mL, is deposited on a spectral glass support, and with a chromatographic scraper type is extended to a 250μm standard thick. The polymer film deposited on the glass is submerged in a coagulation bath (I), especially prepared containing lower aliphatic alcohols [33-35].

PSf - aniline membrane functionalization

The crude membrane obtained by immersion - precipitation in accordance with the above procedure is introduced into a tank (S) containing 1M hydrochloric acid and is maintained for 30 min . After this treatment, the membrane is introduced for 4 h in a vat (III) containing ammonium peroxodisulphate solution in hydrochloric acid. In oredr to finalize functionalization (oxidation of aniline to polyaniline - PANI) composite membrane is kept in an acidic solution of persulphate for 24 h [36-38].

Composite membranes were synthesized from the polysulfone - magnetic nanoparticles / NMP / isopropanol dispersed system obtained by membranes coagulation.

Infrared spectroscopy (FTIR)

Infrared spectra were recorded using attenuated total reflection (ATR). In this case, ATR uses multiple reflections of light through a diamond crystal.

Scanning electron microscopy (SEM)

The images were carried out at an accelerating voltage of 15kV, at moderate vacuum (90Pa) using secondary electron detector in moderate vacuum (LVSED). From SEM images are obtained information about morpho - structural characteristics of synthesized materials.

Atomic force microscopy (FAM)

The images of topography and phase contrast are retrieved through scanner with a high resolution of 10 μm x 10 μm and a vertical scale 2μm, having Z axis 0.027 nm and a deviation from linearity in the XY plane of less than 0 6%.

For the measurements made were used needles NCLR (Nanosensors™) type with a spring constant of about 32 N / m and the vibrating frequency of about 166 kHz.

Spectroscopy of diffuse reflectance UV-Vis

The size measured in this case was the reflected radiation by the solid material (membrane). The UV-Vis measurements were made in air at room temperature in the wavelength range of 900-200 nm, using using as a white reflectance standard Spectralon.

Impedance spectrometry (IS)

Dielectric constant measurement was made using an impedance analyzer and a SOLARTRON 1260 A ProboSTAT cells.

The measurement is made in *sandwich*" structure between platinum electrodes.

Determination of water and lower aliphatic alcohols flows

For right circular cylinders membrane pores, perpendicular on the membrane surface, mathematical expression of permeate flow [39,40]:

$$J = \frac{\varepsilon \cdot r^2 \cdot A \cdot DP}{8 \cdot \sigma^2 \cdot \eta \cdot \delta_m} \qquad (1)$$

where:

r - pore radius;

ε - membrane porosity (in general equal to water content);

σ - pore tortuosity factor, s=1;

δ_m - membrane thickness;

A - membrane surface;

η - solvent viscosity;

DP - hydraulic pressure difference.

(10ÚC) = 1.31CP= 1.31 x 10^{-3} Ns/m^2;

The pure water flow or alcohol has been determined by passing through the composite membrane a volume of 100 mL of solvent at a pressure of 2-6 atmospheres, measuring the time required for each experiment [41,42].

Experimental, in order to determine the flows through obtained membranes, a Sartorius installation was used. In the installation tank are introduced 500 mL of pure solvent (water, methanol, ethanol, propanol) and is applied a pressure of 2 up to 6 atmospheres, on the membrane with an area of 10 cm^2. The permeate volume, 100 mL, is measured and timed:

$$J_v = V_p / S_m * \tau \qquad cm^3/cm^2 \cdot min \qquad (2)$$

Determination of bovine serum albumin retention

For the obtained composite membranes, the ultrafiltration of some BSA standard solutions is made [25, 26]. The method consists in performing a series of ultrafiltration experiments calculating the retention time (R) using the equation (3):

$$R = 100 \cdot (1 - c_f / c_a) \qquad (3)$$

where:

c_f – BSA concentration in the filtrate, evaluated by Lowry method;

c_a – BSA in feed evaluated by Lowry method.

Results and discussions

Membranes characterization requires the use of many methods and procedures of which at least three must provide complementary information [43-45].

Next, the results obtained through FTIR, SEM, UV-Vis, thermal analysis (DSC) are highlighted.

FTIR spectroscopy (fig. 1 a - c) shows that characteristic bands in the range 500-1700 cm^{-1} from polysulfone spectrum appear displaced and low in intensity in the case of PSf-PANI and polysulfone with magnetite.

In the case of PSf membrane, specific C - H bond absorption bands appear in plan at 1147 cm^{-1} and remain, but slightly diminished in PANI membrane and in the membrane with magnetite. Also, at 1239 cm $^{-1}$ appears in PSf membrane the specific band for C - N bond, decreasing in intensity for PSf - PANI, and in the one with magnetite is very low and displaced. At 1328 cm^{-1} appears in PSf specific band for SO$_2$ that is found diminished and moved to 1326 cm^{-1} in the magnetite membrane.

Similarly, for specific N - H band from 1583 cm^{-1} falls and moves in the other two membranes. In the case of PSF with magnetite bands from 2851 and 2917 cm^{-1} disappear and appear shifted to lower intensities at 2911 and 2845 cm^{-1}.

The band at 2962 cm^{-1} from PSf membrane disappears. The bands specific HO between 3000-3600 cm^{-1} groups from PSF, the band at 3390 from PSF completely disappears in PANI and appears diminished and moved in MAG at 3336. The whole spectrum area specific to the band situated in the range 2500-3500 cm^{-1} indicates the polymerization of aniline to polyaniline within the polysulfone membrane, which is correlated also with the SEM images from figures 2 a-c.

From SEM images (fig. 2 a - c) are projecting summary information about the characteristics of synthetized materials. So, changes in morphology of PSf by magnetite or PANI addition are observed.

In the case of the first two membrane a porosity is observed, with pore size ranging from 1.20 to 3.23µm (400-800 nm), with a higher incidence of pores in the case of PSf membrane compared to PSf-PANI membrane.

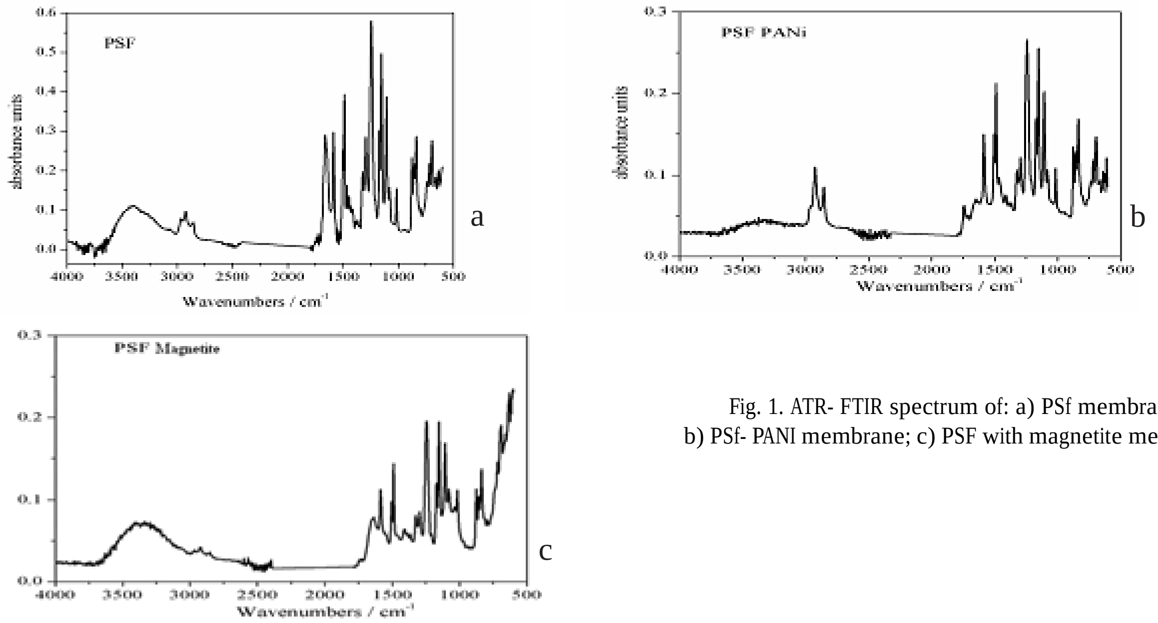

Fig. 1. ATR- FTIR spectrum of: a) PSf membrane; b) PSf- PANI membrane; c) PSF with magnetite membrane

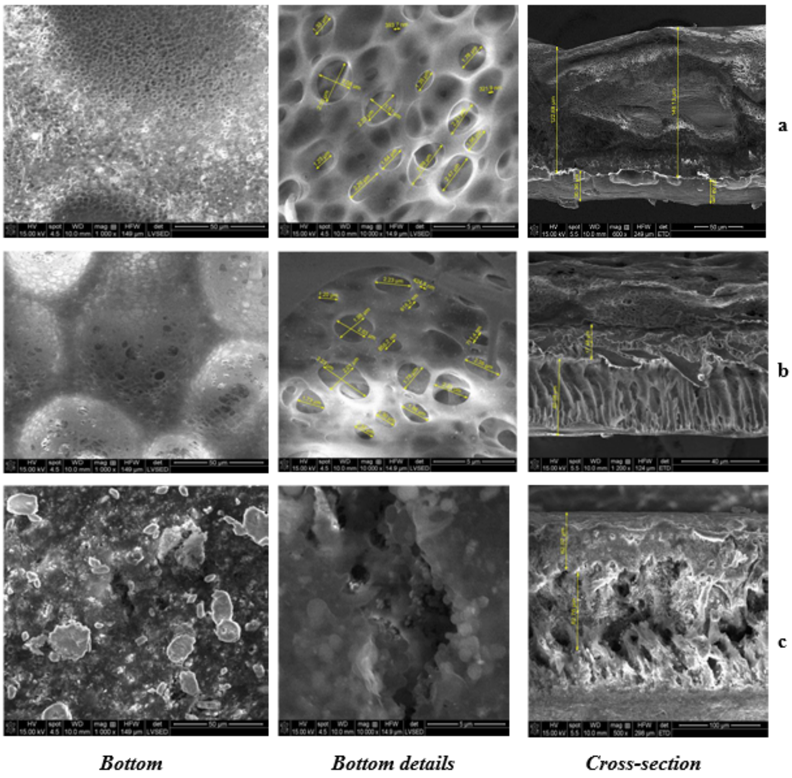

Fig. 2. SEM images a) PSf membrane; b) PSf - PANI membrane; c) PSf with magnetite membrane

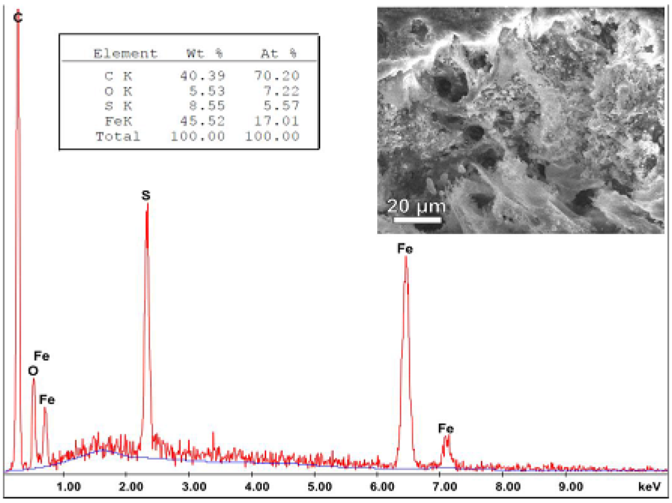

Fig. 3. EDX spectrum for magnetite sample

Unfortunately, polysulfone with magnetite membrane surface could not be measured because of the accentuated relief.

External surface roughness is an important property with role in membrane permeability.

The membrane surface was obtained by measuring the roughness parameters (total roughness Ra) and Rq.

AFM images show *hill and valey* type surfaces more pronounced in the case of PSF PANI membrane (fig. 4b).

Diffuse reflection UV-Vis spectra recorded for the studied membranes (PS, PANI-MAGN, PS-PANI) are shown in figure 5.

The most powerful absorption was recorded for PS-PANI sample. Both polysulfone and polyaniline shows absorption at lower wavelengths of 350 nm, corresponding to π–π * transitions of the benzene ring.

Polyaniline shows two more absorption maxima: at ~ 400 nm, respectively, 550 nm, corresponding to partial protonation of polyaniline chains, respectively benzene rings transition to quinoide rings.

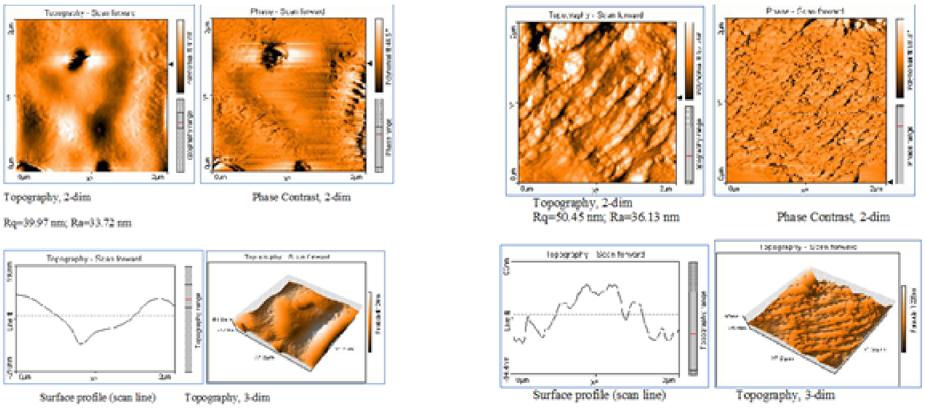

Fig. 4. AFM and 3D images for: *a)* PSf membrane; *b)* PSf - PANI membrane

The membrane with magnetite has a very compact structure, relatively uniform, pore sizes being approximately the same as the magnetite particles.

By PANI or magnetite adding, strong interactions appear at membrane surface, leading to membranes with controlled porosity production.

Homogeneous structure, honeycomb type, of PANI membrane may be linked to the high permeation rates of composite membranes, such that can be used in the separation processes (electrodialysis, electrofiltration, ultrafiltration, nanofiltration) [29-32].

In the case of magnetite, high compaction degree is a first indication for their use in microfiltration [46,47].

The distribution of elements on polysulfone with magnetite membrane surface (fig. 3) was obtained by EDX spectrum which shows the Fe amount distribution in the pores support membrane (PSF) and on the membrane surface.

Unlike the SEM, the AFM have real dimensions in all three directions (x, y, z) from a single scan (fig. 4 a and b).The areas that are scanned are usually contained between several hundred nm and several µm.

It is known that SEM and AFM shows similar lateral resolutions, but there are some situations in which the AFM provides a more detailed representation of the sample surface.

The AFM scanner can measure heights up to 6µm but, for surfaces with heigh variations higher than 5 - 10 µm the most suitable method of investigation is SEM.

The AFM has a vertical resolution <0.5 Å being able to calculate the average roughness of the analyzed surface.

Atomic force microscopy (AFM) was used to characterize the external surface roughness (Ra) of the membranes.

In the PSf - PANI membrane, first band at 580 nm, indicates a charge transfer associated with benzene rings transformation in quinode rings from the highest level of benzenoid rings to the lowest level of quinoide levels (in the literature it was found at 640 nm that appears displaced).

The second band at 320 nm can be also attributed to π-π* transition associated with π electrons of benzenoid nucleus.

For PSf with magnetite membrane central broad absorption band at ~470 nm is associated with the presence of magnetite and comes from the absorption and scattering of UV radiation by magnetic nanoparticles. Normally, this band appears in the region 330-500 nm, the wavelength corresponding to maximum absorption depending on particles size. As the particles are smaller the maximum absorption occurs at smaller wavelengths.

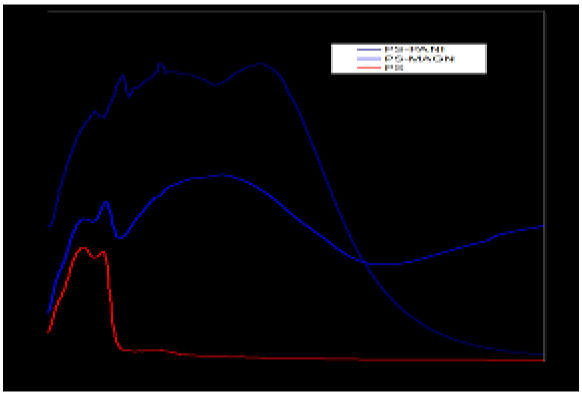

Fig. 5. UV Vis spectrum for membrane: a) PSf, b) PSf-PANI, c) PSf- magnetite

In figure 6 is observed the DSC spectra of the three membranes. Thus, we can see that for polysulfone membrane the decomposition process occurs at 371.82° C, followed by the thermal decomposition, a complex process, as evidenced by multiple peaks seen at 459.9, 490, 500 and 536.7° Celsius.

The PSF PANI thermal decomposition begins at 465° C (associated with PANI) and then there is another peak at 548° C, associated with PSF, after which the thermal decomposition process ends, at polysulfone magnet decomposition process occurs at 244° C (can be a phase transition), the same at 280° C (can be a phase transition). It was found out that the decomposition occurs later, respectively at 476, 525 and 590° C.

The decomposition of membranes proved that membranes thermal stability is very good, these starting to break down after 450° C. This results in a wide range of applications.

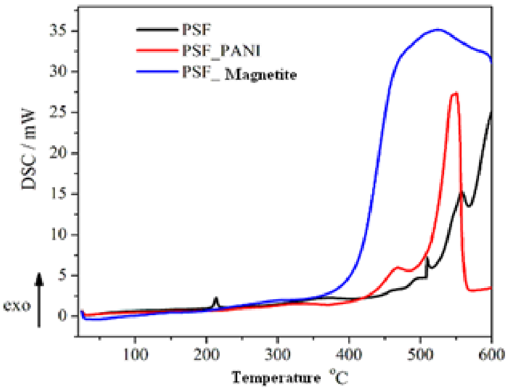

Fig. 6. DSC spectrum for membranes: a) 12%PSf, b) 12% PSf-PANI, c) 13%PSf with magnetite

Impedance spectroscopy is a recent method used for materials electric properties characterization. It can be used to investigate the dynamics of the mobile electrical charges, in-depth or interfacial regions of any type of solid or liquid material: ion semiconductor, mixed (ionic-electronic), or insulator [48].

Commercially available tools, automatically measure the impedance as a function of frequency in the range 1mHz-1MHz and can be easily connected to a laboratory microcomputer. The advantages of this approach are: easy availability of these tools and their use, and the fact that the person that is doing the experiment can control the frequency (easy to analyze the maximum interest domain) [49].

The parameters which are obtained from a IS spectrum fall broadly into two categories: [48,49]:

1. In connection with the material itself, such as: conductivity, dielectric constant, mobility of tasks, etc.

2. In connection with the electrode - material interface such as: capacities of the interface region, diffusion coefficient of neutral species in electrode.

Composite membranes based on polysulfone electrical properties characterization is important because it will be used in ion-molecular separations. The influence of temperature and electric field was investigated by measuring the dielectric constant.

Conductivity and dielectric properties function of temperature, frequency and structure of membranes were investigated.

This kind of researches can provide information about the nature of processes responsible for transition and regrading the temperature-frequency relationship.

The comparison of analyzed data can be useful to identify the properties in order to determine the specific application area.

The dielectric membranes constants were measured, depending on the frequency at room temperature, in air (fig. 7-10).

1. It was observed that PSF-PANI membrane has the highest dielectric constant of the three membranes tested.

2. Dielectric constants were measured every ten degrees in a temperature range (40-100° C) at different frequency values. This comparison showed that PSF-PANI membrane has the highest dielectric constant at all measured temperatures from the three membranes tested.

Dielectric constant increases steadily with temperature increasing due to the increase of total polarization. The fact that the value of the dielectric constant is higher in the case of PSF-PANI membrane can be attributed to the intermolecular interactions caused by PANI.

The characterization of membranes in the chosen process is a useful tool to correlate the permeability and retention (J and R) results with previously determined physical parameter values (fig. 1-6).

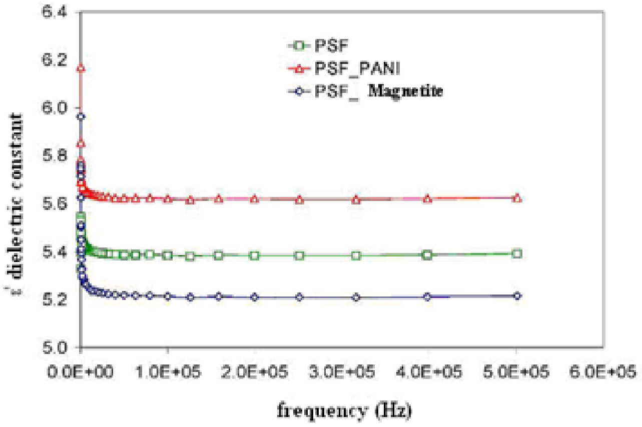

Fig. 7. Dielectric constant vs. Frequency

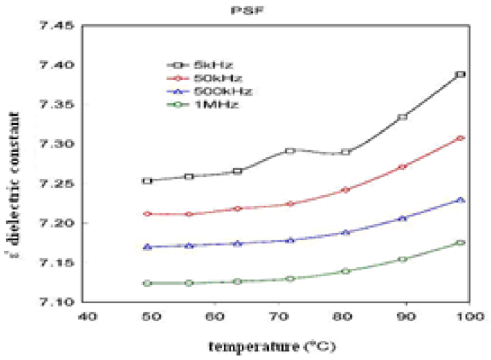

Fig. 8. Dielectric constant for PSf membrane

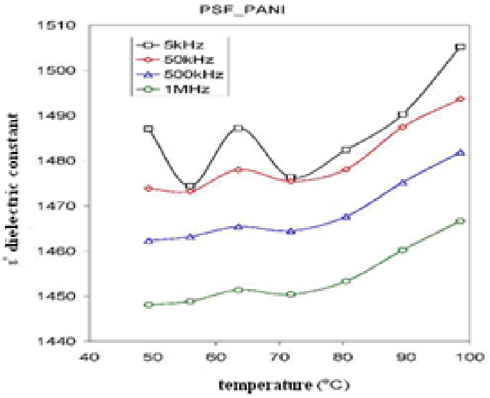

Fig. 9. Dielectric constant for PSf PANI membrane

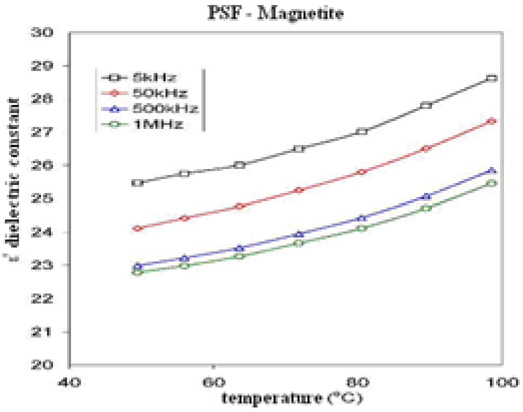

Fig. 10. Dielectric constant for PSf with magnetite membrane

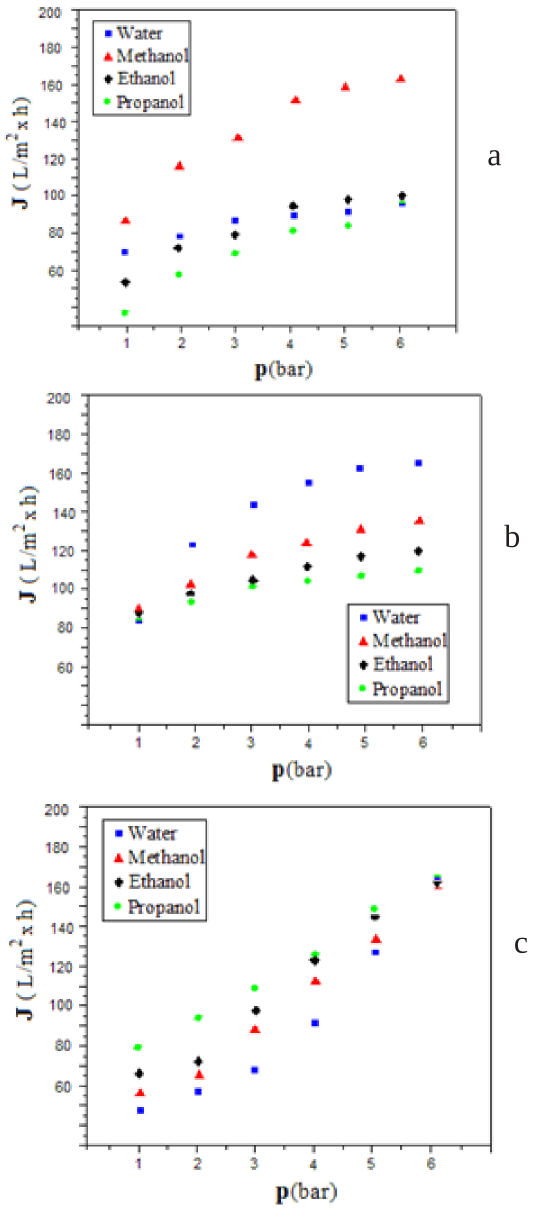

Fig.11. Water and aliphatic *alcohols* flow through: a) PSf membrane b) PSf-PANI membrane ; c) PSf-Magnetite membrane

Determination of water flows and lower aliphatic alcohols

Although there are many studies on modeling, simulation and optimization of membranes performance in various separation processes [50-55] results can not be extrapolated especially when discussing the composite membranes process parameters (J and R).

In particular, membranes characterization is a useful tool for permeability (fig. 11a-c) and retention (fig. 12) results correlation with previously determined physical parameter values (fig. 1-10).

As it can be seen, for membrane PSf (fig. 11) the methanol has a stream much higher throughout the range studied, compared to ethanol, propanol and water.

This fact is explained by the higher swelling capacity that methanol has to the membrane, leading to an apparent increase in pore size and flow permeate simultaneously.

Flow behaviour of the others solvent (ethanol, propanol) is close to that of water (fig. 11a), with the observation that a high pressures, water flow maintains its dependence quasi linear, while in the case of alcohols, increasing the pressure, leads to negative deviation of flow from the linearity. This behavior is known and is caused by membrane compaction [7, 15,16, 56]. PSf - PANI membrane has a different behaviour at solvent flow depending on the pressure applied (fig. 11b).

Due to the increased hydrophobicity, water has a larger volume than all the other solvents, and in the case of alcohols chain growth lowers the permeate flow.

This membrane is therefore indicated for aqueous solutions and polar solvents filtration, togheter with polarity decrease, is drastically decreasing the flow, as in the case o propanol (fig.11.b).

Figure 11c shows how the PSf-magnetite membrane has a contrary behaviour compared to PSf-PANI membrane. Due to pronounced hydrophobicity of the magnetic particles, magnetite - PSf membrane has increasing flows for all four solvents at relatively low pressures.

This time, less polar solvents have a higher flow which correlates with the membrane hydrophobicity. Close flow values for all solvents at high pressures show that membrane - solvent interactions has a minimal influence at high pressures. The results show that water flows at 3-4 bar pressure, are increasing in the order: PSf membrane < PSf –magnetite membrane <PSf-PANI membrane. While for alcohols, the dependence is reverse: PSf membrane > PSf –magnetite membrane > PSf-PANI membrane.

In the case of alcohols flow, hydrocarbon chain has influence on flows and this correlates with hydrophily of membranes.

BSA retention determination

The retention of bovine serum albumin (fig. 12) is dependent on both membrane nature and feed concentration.

The best retention is recorded for PSf - PANI membrane on the whole scale of concentrations tested. PSf membrane presents a slight decrease in retention from 95% to 88%, which is mainly due to larger pores than those encountered in the ultrafiltration of this proteine. PSf-

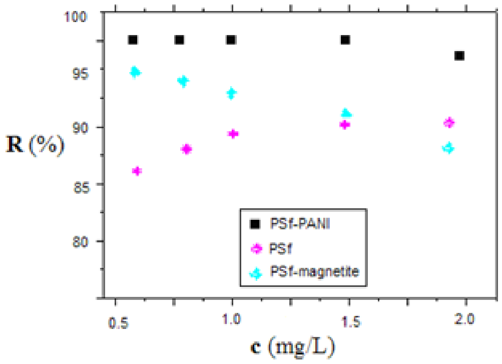

Fig. 12. Bovine serum albumin retention dependence on the concentration of the three types of membranes

magnetite has the lowest performance, both because of pore size and because of lower hydrophilicity reflected in the flow of pure water (fig. 11 c.)

Conclusions

Composite membranes (PSf-PANI and PSf-magnetite) have been produced by phase inversion by immersion - precipitation from a polysulfone in N- methyl pyrrolidone dispersion solution in which were dispersed polyaniline or magnetic nanoparticles.

The prepared composite membranes were morphologically and structurally characterized using techniques and specific measurments: FT-IR, SEM, AFM, UV - Vis, DSC, dielectric spectroscopy, solvents permeation and bovine serum albumin retention.

Membranes pore size indicate their use in micro and ultrafiltration (12% in the case of PSF membrane and 12% for PSf - PANI) or in the field of microfiltration and membrane sensor, 12% for magnetite - PSF membrane. The results show that water flows at 3-4 bar pressure, are increasing in the order: PSf membrane < PSf –magnetite membrane <PSf-PANI membrane. While for alcohols, the dependence is reverse: PSf membrane > PSf –magnetite membrane > PSf-PANI membrane.

In the case of alcohols flow, hydrocarbon chain has influence on flows and this correlates with hydrophily of membranes.

Following bovine serum albumin retention tests, PSf-PANI membrane has the best performance (R> 95%), which correlates with the higher permeate flows.

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