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Preparation and characterization of nano-porous Polyacrylonitrile (PAN) membranes with hydrophilic surface

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ABSTRACT

Polyacrylonitrile (PAN) membranes with nano-porous surface and high hydrophilicity were fabricated by addition of polyoxyethylene (40) nonylphenyl ether (IGEPAL) as an additive in the casting solution. The membranes were prepared from PAN/IGEPAL/1-Methyl-2-pyrrolidone (NMP) via phase inversion induced by immersion precipitation technique. Pure water was used as coagulation medium. The effects of adding IGEPAL and the PAN concentration on the morphology, wettability, and permeability of the prepared membranes were studied. The morphological studies were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). In addition, the wettability and permeability of membranes were examined by contact angel measurements and permeation experiments. The contact angle measurements indicate that the hydrophilicities of membrane enhanced by the addition of IGEPAL surfactant and decreasing the PAN concentration in the casting solution. According to SEM and AFM analysis, it was found that the addition of IGEPAL and change concentration of polymer have a significant influence on structure of the membrane top surface and the sub-layer. In addition, it was found that decreasing the PAN concentration and addition of IGEPAL resulted in the formation of membranes with high permeability.

Keywords: *Polyacrylonitrile (PAN); Membrane preparation; Immersion precipitation; Nano-porous; Hydrophilic surface.*

INTRODUCTION

Membrane filtrations are extensively used for product recovery and pollution control in chemical, electronic, metal plating as well as in food, pharmaceutical, water treatment and biotechnological industries [1]. Polymeric membranes are used for a wide range of industrial separation applications extending from microfiltration to reverse osmosis [2]. For the preparation of synthetic polymeric membranes, the phase inversion method has been widely used [3].

The phase inversion technique via immersion precipitation is the common method to preparation of the most polymeric microfiltration and ultrafiltration and some of nanofiltration membranes, which used for separation processes. In this technique, a film of homogenous polymeric solution is cast on a suitable substrate (glass, polyester or polyethylene non-woven fabric, metal, Teflon). The cast film is immediately after immersed in a non-solvent bath where the exchange between solvent and non-solvent and the precipitation of polymer take place [4].

The separation performance depends on the properties of the membrane, such as hydraulic permeability, membrane material and surface charge, membrane thickness, pore size and operating conditions such as pressure, filtration time and feed concentration [1]. Various factors responsible for governing membrane structure and porosity during its preparation by phase inversion method include dope solution concentration, solvent used for dope solution preparation, additives present in the dope solution, evaporation time, solvent and non-solvent composition, coagulation temperature, etc [5].

Polyacrylonitrile (PAN) membrane has attracted much attention due to their excellent characteristics of thermal stability, tolerance to most solvents and commercial availability [6]. PAN has also good resistance against chlorine, and cleaning agents such as sodium hypochlorite, sodium hydroxide [7].

Generally, the anti-fouling property of membrane can be promoted by improving its hydrophilicity. Based on this idea, various modification strategies for PAN membrane such as blending, copolymerization and surface modification were reported [8]. The additive may be inorganic salts, surfactants, polymer, water, low molecular weight organics, mineral fillers, non-solvents type and etc[4, 5]. To sum up, the role of these additives is to suppress and/or excite the formation of macrovoids, enhance and/or decline pore formation and improve pore interconnectivity and/or hydrophilicity[4].

In the previous study [9], for the first time, the effects of adding the IGEPAL surfactant as a hydrophilic additive were investigated to improve the permeation and hydrophilic properties of PAN membranes.

In this study, the effects of adding IGEPAL and changing the PAN concentration on the morphology, wettability, permeability, thickness, and surface properties of the PAN membranes were investigated.

EXPERIMENTAL

Material

To prepare the casting polymer solutions, the Polyacrylonitrile (PAN) with an average molecular weight 150,000 g/mol (Aldrich, USA) was used. 1-Methyl-2-pyrrolidone (NMP) with an analytical purity of 99.5% (Merck) and distilled water were used as the solvent and the non-solvent agent, respectively. IGEPAL CO-890 (polyoxyethylene (40) nonylphenyl ether, HLB=17) was used as a nonionic surfactant additive in the casting solution. The chemical structure and properties of IGEPAL are presented in Figure 1 and Table 1, respectively.

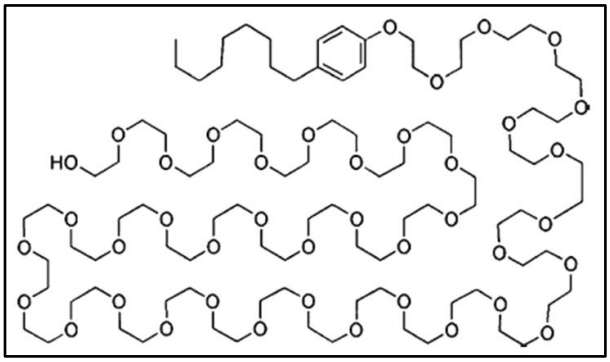

Fig. 1. Molecular structure of IGEPAL.

Table 1. Properties of IGEPAL (used during membrane preparation).

Property	Value
Molecular weight	1980 g/mol
Density	0.96 g/cm^3
HLB number	17
Melting point	47 °C
Boiling point	>200 °C
Linear formula	$(C_2H_4O)_n.C_{15}H_{24}O$ (n=40)

Preparation of the membranes

For the preparation of the casting solutions, the mixtures PAN/NMP were prepared first. Subsequently, surfactants added to each mixture. Their compositions are presented in Table 2. The mixtures were stirred at room temperature for about 12 h to ensure the complete dissolution of the polymer. After a homogeneous solution had formed, the dope solution was held at ambient temperature for around 8 h to remove the air bubbles.

Table 2. Compositions of the casting solutions.

Membrane Name	PAN (wt.%)	IGEPAL (wt.%)
8-4	8	4
10-4	10	4
12-4	12	4
12-0	12	0

Prepared homogeneous solutions were cast using a casting knife with 250 μm clearance gap on a glass plate substrate at room temperature. The cast films and the glass plates together were immersed in coagulation baths containing water as a non-solvent at 25^{0}C temperature. During gelation, the formed membranes peeled off from the glass plates spontaneously. After primarily phase separation and formation, the membrane was stored in water for 24 h to guarantee complete phase separation. This allows the water soluble components in the membrane to be leached out. Finally, the membranes were kept between two sheets of filter paper for 24 h and dried at room temperature.

Membrane characterization

The prepared flat-sheet membranes have been characterized as follows:

- **Scanning Electron Microscope (SEM)**

The membrane top surface and cross section were examined by a scanning electron microscope (SEM, Philips microscope at 25 kV). First, the membrane samples were fractured in liquid nitrogen, then were placed adequately over a support and coated with gold under vacuum conditions. The thickness of the membranes has been determined from the obtained SEM cross-sectional images.

- **Pure Water Flux (PWF)**

Permeation flux studies were carried out in a batch mode. A flat sheet membrane module made from stainless steel was used in all experiments. Effective area of the membrane in the module was 20 cm^2. The schematic representation of set-up is shown in Figure 2. The PWF measurement was carried out in transmembrane pressure of 1 MPa. PWF was calculated using the following equation:

$$Flux = \frac{Q}{A.\Delta t} \qquad (1)$$

Where Q is the quantity of permeate (L), A is the effective membrane area (m^2), and Δt is the sampling time (h).

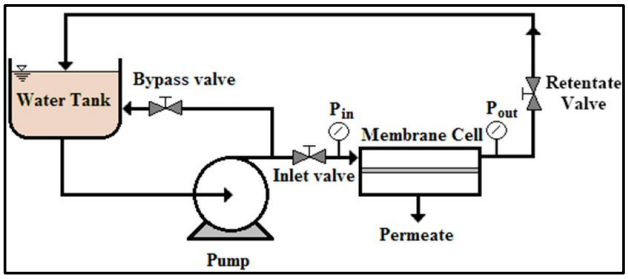

Fig. 2. Schematic diagram of the experimental setup.

- **Contact Angle**

The contact angle between water and the membranes was directly measured using a contact angle measuring instrument (OCA15plus, Data Physics, Filderstadt, Germany) for the membranes hydrophilicity evaluation. De-ionized water was used as the probe liquid in all the measurements.

- **Atomic Force Microscopy**

Atomic force microscopy was employed to analyze the surface morphology of membranes. The AFM apparatus was DualScope™ scanning probe-optical microscope (DME model C-21, Denmark). The small squares of the prepared membranes (approximately 1 cm^2) were cut and glued on glass substrate. The membrane surfaces were examined in a scan size of 1 μm×1 μm. Mean pore sizes of the membranes were calculated from height profile of AFM images using SPM software.

RESULTS AND DISCUSSION

The Effect of PAN and IGEPAL concentration on Morphology and thickness

The SEM images of top surface of membranes are observed in Figure 3. With respect to this figure, the surface morphology declines with the increase of additive (Figure 3a, b). However, virgin membrane surface (Figure 3c) is uniform and film revealed a smooth surface without pores. By increasing the IGEPAL/PAN concentration ratio in polymeric solution, the content of IGEPAL in the skin layer of membrane is increased.

Membranes prepared from the casting solution, resulted compact surfaces with small surface pore sizes. In fact, the pore sizes on top layer of membranes are commonly in the size of nanometer. It is difficult to see the pore structure of membrane surface using scanning electron microscopy.

Figure 3 depict the AFM images of surfaces of PAN membranes ready with different concentrations of PAN and IGEPAL in the casting solution. Also, Figure 4 (a, b, c) represents the 3-Dimension AFM images of membranes.

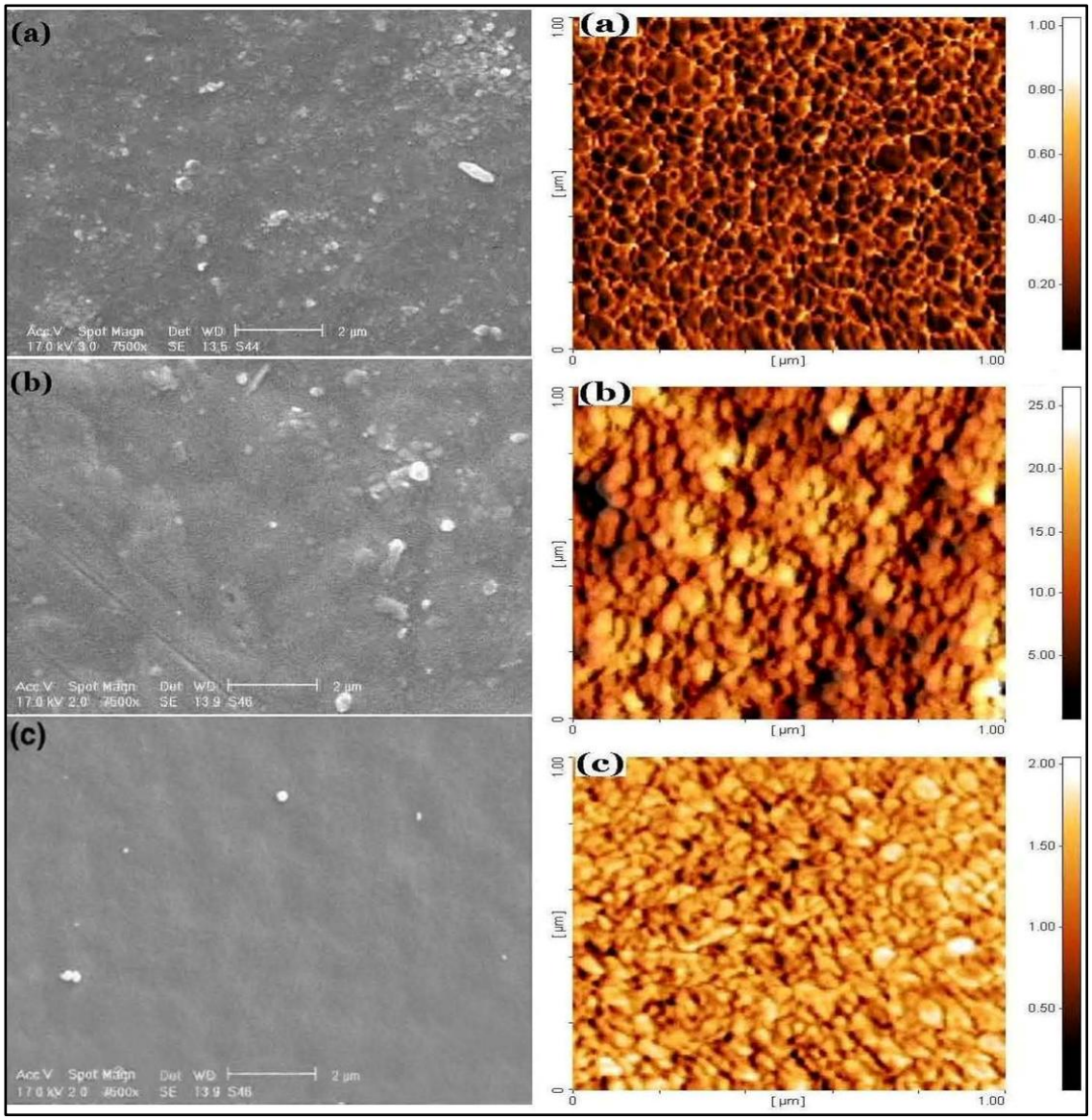

Fig. 3. Top surface SEM (Left) and AFM (Right) images of different membranes: (a) 8 wt% of PAN and 4 wt% of IGEPAL, (b) 12 wt% of PAN and 4 wt% of IGEPAL, and (c) 12 wt% of PAN.

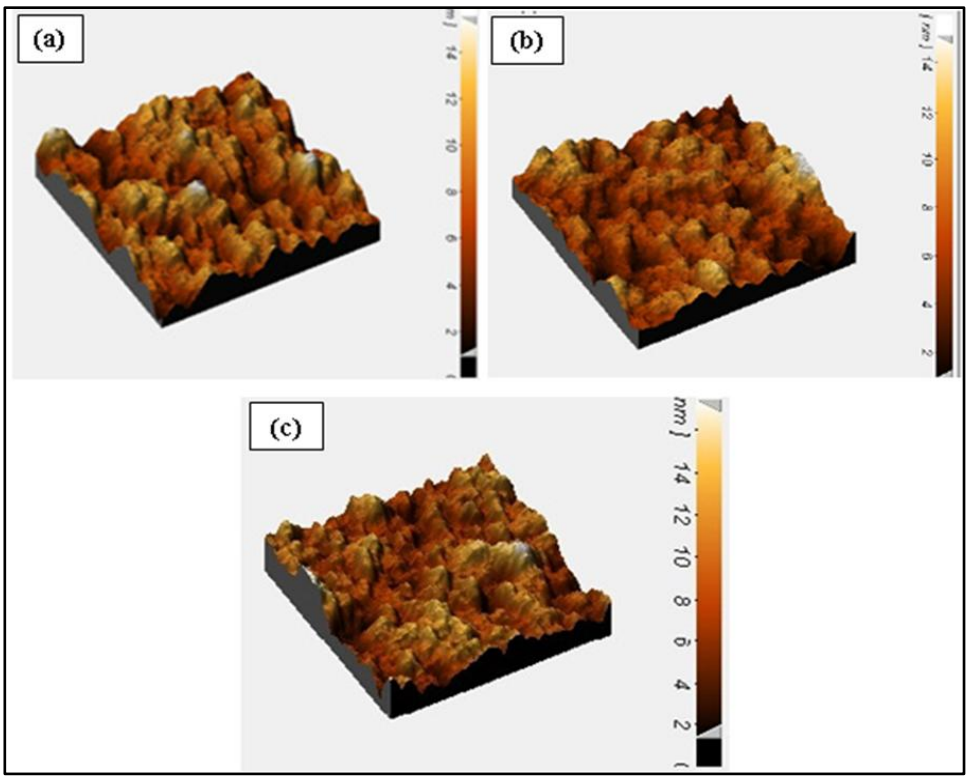

Fig. 4. 3-Dimension AFM images of (a) 8 wt% of PAN and 4 wt% of IGEPAL, (b) 12 wt% of PAN and 4 wt% of IGEPAL, and (c) 12 wt% of PAN.

In these images, the brightest area presents the highest point of the membrane surface and the dark regions show valleys or membrane pores. The mean pore size of membrane surfaces were obtained from AFM images [4]. The sizes of 30 pores in 1 μm ×1 μm area of membrane surface were measured from height profile of two dimensional AFM images using SPM software and the average value is reported in Table 3. It seems that the size and number of surface pores are increased with PAN concentration decrement from 12 to 8 wt.% and adding IGEPAL to the casting solution.

Table 3. Mean pore size calculated from AFM images.

Membrane Name	Mean pore size (nm)
8-4	37
12-4	28
12-0	21

The effect of PAN and IGEPAL concentration on membrane thickness and cross-sectional morphology of the prepared membranes is presented in Figures 5, 6 and 7. As it is observed from the SEM images, results of increase in PAN concentration from 8 wt.% to 12 wt.% are as followings:

1- Cross section of the prepared membranes become more dense (Figure 5 a, b, c).

2- Increase in the thickness of dense top layer (Figure 6 a, b, c).

3- A slight decrease in the thickness of the prepared membranes (Figure 5 and 7).

Also, results of increase in IGEPAL concentration from 0 wt.% to 4 wt.% are:

1- Greater formation of macrovoids and more porous structure in the sub-layer/top layer (Figures 5 c, d and 6 c, d).

2- Increase in the thickness of the prepared membranes (Figures 5 and 7). The average thickness of the membranes increases from 76 to 85 μm, when the concentration of IGEPAL in the casting solution increases from 0 to 4 wt.%.

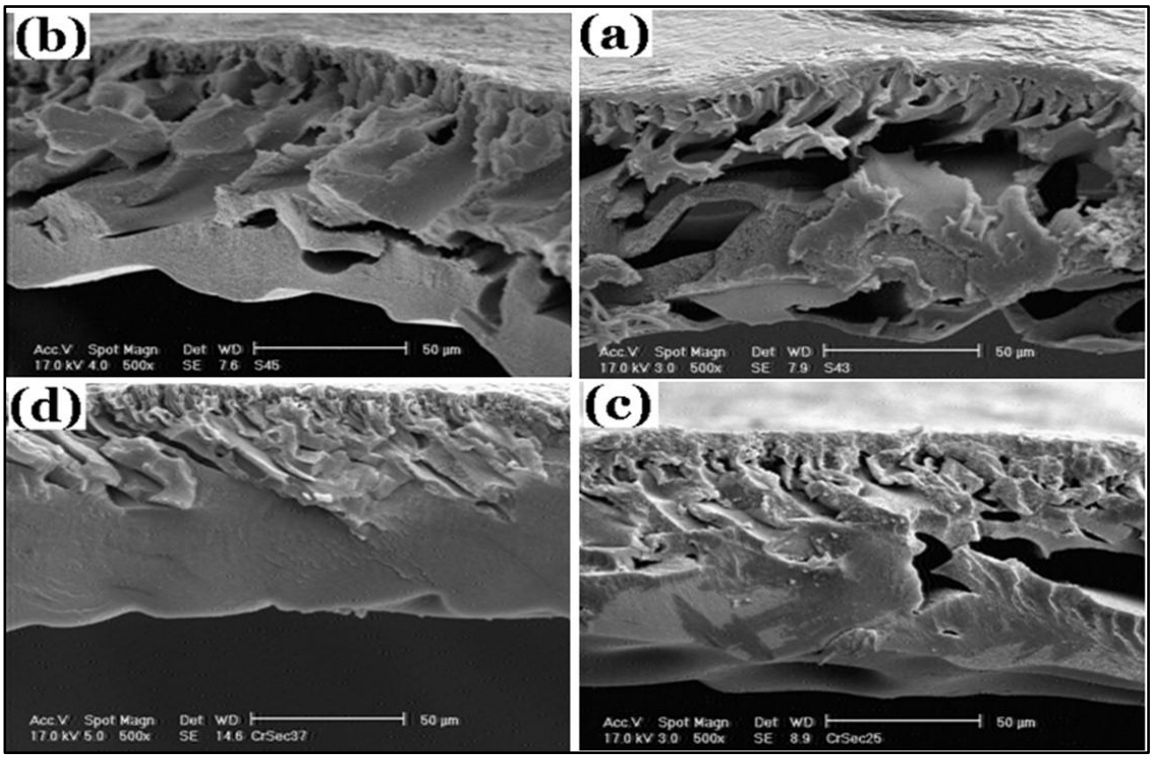

Fig. 5. (a, b, c, d) The effect of varying the concentration of PAN and IGEPAL on the cross-sectional images of PAN membranes (magnification=500×).

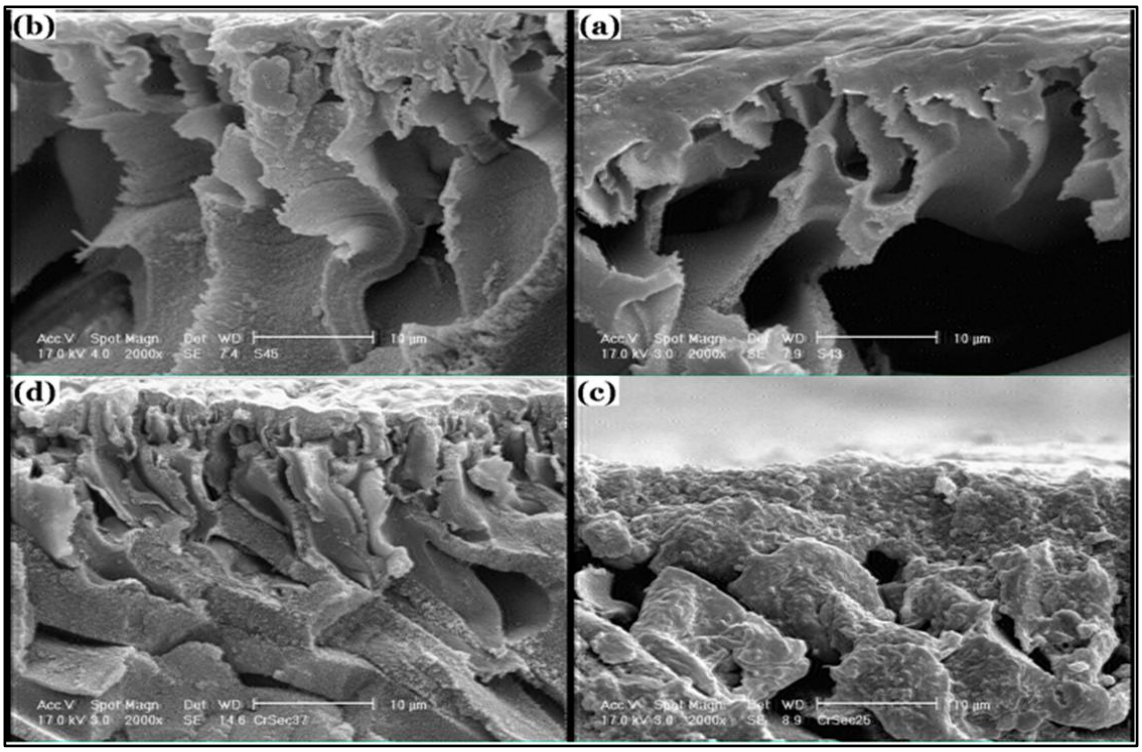

Fig. 6. (a, b, c, d)The effect of varying the concentration of PAN and IGEPAL on the cross-sectional images of PAN membranes (magnification=2000×).

The obtained results which are presented in Figure 7, show the largest, smallest and average values of the calculated membranes thicknesses for all samples.

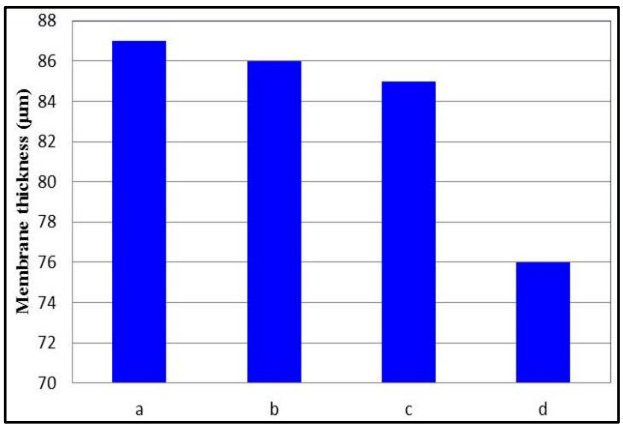

Fig. 7. Thickness of the prepared membranes (a) 8 wt% of PAN and 4 wt% of IGEPAL, (b) 10 wt% of PAN and 4 wt% of IGEPAL, (c) 12 wt% of PAN and 4 wt% of IGEPAL, and (d) 12 wt% of PAN.

Details of membrane formation mechanism have explained by Saljoughi *et al.* [9-15]. When the cast film is immersed into the coagulation bath (water), precipitation starts and the cast film thickness gradually decreases. This results in increasing the polymer concentration in the cast film. Simultaneously, miscibility between the solvent (NMP) and the non-solvent (water) causes that in several points of the film top layer and the bottom layer, diffusional flow of the solvent and the non-solvent takes place and consequently nuclei of the polymer-poor phase are formed. In fact, the low affinity between the PAN chains and water molecules at the points which water molecules diffuse results in the repulsion of PAN chains and consequently the formation of nuclei of a polymer-poor phase. Ultimately, growth of these nuclei continues until the polymer concentration at the pores or the macrovoids/solution interface becomes so high that solidification occurs. If the system exhibits instantaneous demixing, solidification occurs quickly after immersion of the cast film into the coagulation bath and this inhibits the precipitation process. This result in increasing the membrane thickness and porosity because when the polymer content is constant and simultaneously the membrane thickness increases, total volume of a certain content of the polymer increases and this has a direct relationship with the membrane porosity. Acceleration of demixing has a direct relationship with the thermodynamic instability and the mutual diffusivities between the components in the system during solidification of the casting solution [9-15]. Increasing in IGEPAL concentration, as hydrophilic surfactant additive (which has high miscibility with the coagulant), results in more thermodynamic instability and rather mutual diffusivities between the components in the coagulation bath during solidification of the casting solution and this result in increasing thickness of the prepared membranes and the number and size of macrovoids in their sub-layers [9-15]. In addition, the presence of PAN with its long chains in the casting solution hinders rapid exchange between the solvent and non-solvent during membrane formation in the coagulation bath. Therefore, decreasing the PAN concentration from 12 wt.% to 10 and to 8 wt.% results in an increase in the mutual diffusivities between the non-solvent (water) and the solvent (NMP) during the solidification of the casting solution in the coagulation bath. This results in instantaneous demixing and consequently the formation of a membrane with a more porous structure [9-15]. In other words, higher PAN concentration produces a highly viscous casting solution, which slows down the membrane formation process and creates a thicker skin layer and a compact sub-layer [16].

Contact angle of membranes

Contact angles were measured to evaluate the alteration in the hydrophilicity and surface properties of nanoporous PAN membranes after blending with the IGEPAL and variation in PAN concentration. The influence of variation in PAN concentration and addition of IGEPAL, as a hydrophilic surfactant, in the casting solution on contact angle of PAN surface membranes is shown in Figure 8. As shown in Figure 8, the highest contact angle (79°) for PAN membrane, and in other words the lowest hydrophilicity, is obtained without the addition of IGEPAL. When IGEPAL is added to the casting solution, the contact angle of membrane is decreased. It means that, a more hydrophilic surface is produced by increase of IGEPAL in the casting solution.

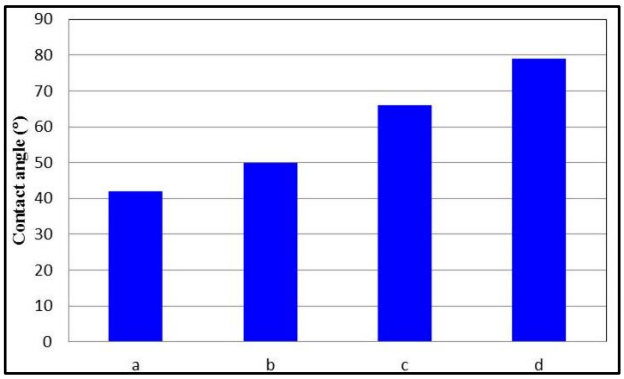

Fig. 8. Contact angle of the prepared membranes (a) 8 wt% of PAN and 4 wt% of IGEPAL, (b) 10 wt% of PAN and 4 wt% of IGEPAL, (c) 12 wt% of PAN and 4 wt% of IGEPAL, and (d) 12 wt% of PAN.

Also, according to Figure 8, the increase in PAN concentration from 8 to 12 wt.% results in higher contact angle and therefore lower membrane hydrophilicity. It should be noted that the quantity of the residual IGEPAL, that has a direct relationship with the membrane hydrophilicity, determines the wettability of the PAN membranes. The amount of the residual IGEPAL highly depends on IGEPAL/PAN ratio in casting solution. At lower ratio, fewer IGEPAL membrane structure remains. It is clear that the reduction of residual IGEPAL in the membrane structure results in higher contact angle and as a result preparation of the membrane with lower hydrophilicity. In addition, a noticeable increase in the porosity, particularly in the top layer and in the surface porosity, is only observed after varying the PAN concentrations as described above (see Figures 6, 7 and 8). The surface morphology affects the contact angle of water drops. It seems that a high porosity of the membrane top layer or the presence of large pores on the membrane surface can intensify the wettability of the prepared membranes [9].

Permeation properties of the PAN membranes

Permeation experiments were carried out to study the permeability of the PAN membranes. Table 4 depicts the pure water fluxes of membranes prepared from different concentrations of PAN and IGEPAL. As observed, the PWF of the PAN membranes are increased by the presence of the IGEPAL additive in the casting solution and by reducing the PAN concentration. The results can be explained with respect to the cross sectional SEM images (Figures 5 and 6) and alteration in the hydrophilicity of membranes (Figure 8). As mentioned before, these changes in the preparation parameters result in greater formation of macrovoids (i.e., a more porous structure), and consequently reduce the main resistance to feed permeation. Well as, hydrophilicity of the PAN membranes is increased by addition of IGEPAL to the casting solution and by reducing the PAN concentration. At the same time, the improved hydrophilicity can attract the water molecules inside the membrane matrix and help them to pass through the structure and therefore enhance the permeability [16]. This effects result in the formation of membranes with higher PWF.

Table 4. Effect of PAN and IGEPAL concentrations on the PWF of the prepared membranes.

Concentration of PAN (wt. %)	Concentration of IGEPAL (wt. %)	PWF (L/m2h)
8	4	524
10	4	405
12	4	332
12	0	183

CONCLUSIONS

The nano-porous polyacrylonitrile (PAN) membranes with high hydrophilic surfaces were prepared by addition of IGEPAL as an additive in the PAN casting solution. To prepare membrane, phase inversion induced by immersion precipitation technique was used. The morphological studies by SEM and AFM showed that the higher concentration of PAN results in formation of a membrane with a dense top and sub-layer with small pores on the surface. The membranes thickness and pure water flux of the PAN membranes are increased by the presence of the IGEPAL additive in the casting solution and by reducing the PAN concentration. After blending with the IGEPAL and variation in PAN concentration, to evaluate the alteration in the hydrophilicity and surface properties of nano-porous PAN membranes, contact angles were measured. The contact angle indicated a decrease in contact angle of PAN membrane surface with addition of IGEPAL and decrease PAN concentration. This demonstrated that a more

hydrophilic was produced. Finally, to study the permeability of the PAN membranes, permeation experiments were carried out. By presence of the IGEPAL additive in the casting solution and reducing the PAN concentration, results indicate increase in the PWF of the PAN membranes.

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