



## Research Paper

## Anionic/Non-ionic Surfactants in Aqueous Phase of Thin Film Composite Poly (Paraphenylene Terephthalamide) Nanofiltration Membranes

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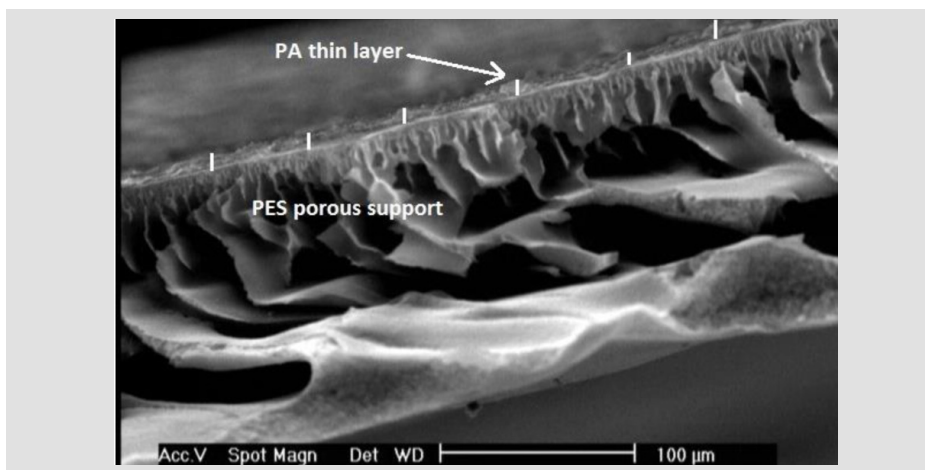
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### GRAPHICAL ABSTRACT



### HIGHLIGHTS

- Preparation of thin film composite nanofiltration membranes
- Different surfactants were used in aqueous phase
- The morphology and performance were changed in the presence of non-ionic surfactants

### ABSTRACT

In this work, the Interfacial polymerization (IP) technique was employed using terephthaloyl chloride (TPC) and p-phenylenediamine (PPD), as reactant monomers, to prepare poly(paraphenylene terephthalamide) thin film composite (TFC) nanofiltration on polyethersulphone (PES) support layer. The effects of six different anionic and non-ionic surfactants, in the aqueous phase on the morphology and performance of membranes were investigated. The performance of membranes was evaluated by the pure water flux (PWF) and the rejection of salt solutions. By addition of anionic surfactants, the morphology and performance were unaltered, while, in the presence of non-ionic surfactants, both morphology and performance were changed. Furthermore, the conditions for IP process were examined.

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## 1. Introduction

Nanofiltration (NF) is a membrane process with separation characteristics between the reverse osmosis (RO) and the ultrafiltration (UF) [1-3]. NF has various industrial applications such as wastewater reclamation; industrial

water production; water softening; and separation of compounds with different molecular weights in textile, pharmaceutical and biochemical industries [4-9]. A wide range of desirable properties was observed for the NF process, including high permeation flux, low operation pressure, and low

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maintenance cost in comparison with the RO [10, 11]. But, the NF may not completely eliminate all ions especially small one and monovalent ions in comparison with the RO.

Thin film composite (TFC) membranes are the most applicable NF membranes, which have the superior performance compared to membranes with asymmetric structure [11-14]. A TFC membrane is prepared by fabrication of an ultra-thin skin layer (active layer) on a porous support via the interfacial polymerization (IP). In this method, the skin layer is generally obtained by the reaction between two monomers i.e. a polyfunctional amine in the aqueous phase and a polyfunctional acid chloride in the organic solvent [15]. Since the water and the hydrocarbon solvents are immiscible, polymerization reaction takes place at the interface of the two liquids. This procedure was invented by Mogan in 1965 [16]. The commonly used monomers are aliphatic or aromatic diamine (amine monomer), such as piperazine (PIP), m-phenylenediamine (MPD) and p-phenylenediamine (PPD) [7, 17]; and acid chloride monomers, such as trimesoyl chloride (TMC), isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) [11, 17, 18].

In order to enhance the membrane performance, the support and the active layers should be optimized for their particular function. The support layer gives appropriate mechanical strength as well as low resistance to the permeate flow, while the active layer is the key component, which mainly controls separation properties of the proposed membrane [17]. In better words, separation performance of TFC membranes is performed by the active layer.

The presence of surfactants as additives in the aqueous/organic solution(s) can improve the structure of the film and the support layers [18]. Surfactants are capable to improve the IP by assisting with transfer the monomer from the aqueous phase into the organic layer [19]. This phenomenon enhances the properties of the prepared TFC on the support layer of the NF membrane [20]. The summary of the various surfactants and their effect on the TFC membranes for NF purpose and prepared via the IP technique is presented in Table 1 [20-24]. To the best of our knowledge in the open literature, the influence of TPC as the acid chloride monomer and the PPD as the amine monomer with respect to their lower price compared to TMC and PIP monomers has not yet been reported. Furthermore, there is no report for using the following six different surfactants, including sodium lauryl ether sulfate (SLES), triethanolamine lauryl ether sulfate (TEA-LES) and disodium laureth sulfosuccinate (DLS) as anionic ones as well as cocamide monoethanolamine (cocamide-MEA), polysorbate 20 and nonylphenol as non-ionic ones in TFC membranes in the open literature. So, in the present study, TFC nanofiltration membranes were prepared through the IP technique using PPD and TPC monomers on a PES layer. The performance of TFC membrane was optimized by varying a number of parameters, including the monomer concentration, polymerization reaction time and curing temperature. The effect of adding different ionic/nonionic surfactants in the aqueous phase during the IP step on improving separation properties and the permeation flux was also investigated. The relation between the separation performance and the used surfactants is discussed in details. Furthermore, the performance of the TFC NF membranes was characterized by evaluating their rejection for NaCl, MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions.

## 2. Experimental

### 2.1. Materials

Distilled water was used for all experiments in this study. PES (Ultrason E6020P, M<sub>w</sub>=58,000 g/mol) was supplied from BASF (Germany). Polyvinylpyrrolidone (PVP; 25,000 g/mol), dimethylacetamide (DMAc), PPD and TPC were supplied from Merck Company. SLES, TEA-LES and DLS as anionic surfactants as well as cocamide-MEA, polysorbate 20 and nonylphenol as non-ionic surfactants all were purchased from Sigma-Aldrich. The rejection performance was evaluated using NaCl, MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions (from Merck).

### 2.2. Preparation of PES membrane as support layer

The PES support membrane was prepared via the immersion precipitation phase inversion method using casting solutions involving 17 wt. % PES and 2 wt% PVP, as pore former, in the dimethylacetamide (DMAc), as solvent. The solution mixed with a mechanical stirrer, continuously, for 8 h at 400 rpm. Having a homogeneous solution, this dope kept at room temperature for elimination of the air bubbles for around 12 h.

A film applicator with the constant height of 150 μm was employed for casting the solution on a clean glass plate. This is a common thickness used

for the preparation of the support membrane. The casting process was carried out at ambient condition. Afterward, the glass plate was immediately immersed into the distilled water bath (10 °C) for 24 h in order to precipitate the polymer and form the support membrane. Finally, obtained samples were placed between two sheets of filter paper and were dried for 24 h at ambient temperature.

### 2.3. Preparation of TFC membranes

As mentioned earlier, the TFC layer was prepared by IP technique. The typical procedure used in this study is as follows. The PES support membrane was fixed on a glass plate. The PPD (0.1-0.3 wt. %) as the aqueous phase was poured on top layer of the support membrane and was then allowed to diffuse into the support pores at room temperature for 10 min. A soft rubber roller was used to eliminate tiny bubbles and remove excess solution from the soaked surface of the support membrane. Afterwards, the PPD layer on the PES support membrane was allowed to contact with the TPC (dissolved in the n-hexane solution (0.1-0.3 wt. %)) for about 1 to 6 min (for determining the best one), to occur the IP reaction. Then, the excess TPC solution was drained off. For completing the polymerization step, the TFC membrane was heated (50–90 °C) in an oven for about 4 min. Finally, the prepared TFC membranes washed several times by distilled water.

### 2.4. Characterization methods

#### 2.4.1. Performance of membranes

The pure water flux (PWF) and the salt rejection were tested in a dead-end cell at room temperature. Schematic diagram of the dead-end apparatus is shown in Figure 1. Pressurized nitrogen was applied to control the operating pressure. The test cell was equipped with a magnetic stirrer to mitigate the effects of concentration polarization on the membrane surface. Each membrane was initially pressurized with distilled water at 5 bar for 30 min, and then the pressure was reduced to 4 bar. The PWF (kg/m<sup>2</sup> h) was then calculated as follows:

$$PWF = \frac{Q}{A t} \quad (1)$$

where,  $Q$  is the permeated pure water (kg);  $A$  is the membrane area ( $11.53 \times 10^{-4}$  m<sup>2</sup>), and  $t$  is the operating time (h). The membranes selectivity was evaluated by examining the ion rejection for NaCl, MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions at 4 bar. The concentration of the feed was fixed at 2000 g/L. The ions concentration of the permeation and feed solutions were measured by a conductivity meter (JENWAY 4510, UK). The salt rejection (%) was calculated as follows:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where  $R$  is the percent of salt rejection;  $C_p$  is the concentrations of the permeation, and  $C_f$  is the feed concentration.

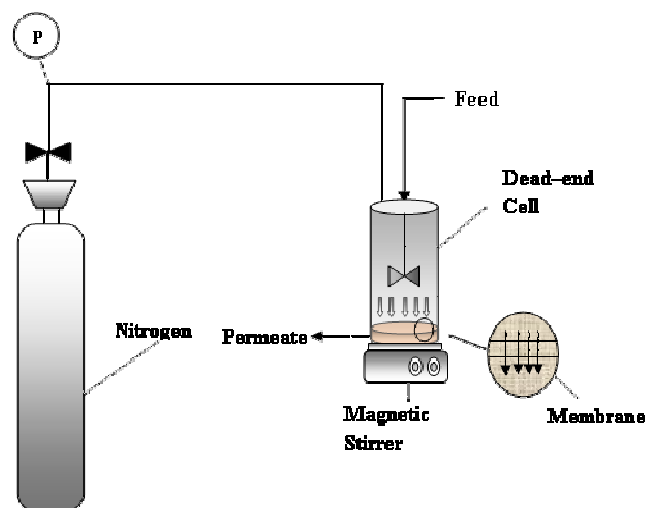


Fig. 1. The dead-end filtration set-up.

Table 1

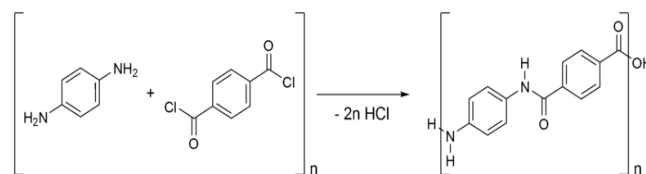
Review of various surfactants used in the TFC NF membranes prepared by interfacial polymerization technique.

Support	Monomers	Surfactants	Addition phase	Remarks	Ref.
PES/MF	PIP and TMC	TEAC, TBAB, CAS-TEA and BMMIC	Aqueous	- The results indicated that addition of four types of amine salts surfactants with different molecular structures, molecular weights and charges noticeably affected the membrane properties.	[20]
PES/UF	PIP and TMC	SDS, and Triton X-100	Organic	- The membranes containing CTAB and SDS indicated high permeations and superior rejections.	[21]
PES/UF	PIP and TMC	SDS, CTAB and Triton X-100	Aqueous	- CTAB showed no considerable changes in the PWF and salt rejection. - Addition of Triton X-100 changed the performance and morphology of skin layers. - No desirable changes were shown in the presence of SDS.	[22]
PES/MF	PIP and TMC	SLS	Aqueous	- At low concentration of SLS, the performance of membrane remained unaltered.	[23]
PS/UF	MPD and TMC	TEBAB, TMBAB and TEBAC	Aqueous	- Achieving 40% increase in the water flux upon 0.2 wt.% TEBAB added. - Addition of TMBAB and TEBAC played no role in improving interfacial properties.	[24]

#### 2.4.2. Membrane morphology and FTIR-ATR

The surface and the cross-section morphologies of membrane samples were observed using the scanning electron microscope (SEM) (Philips XL30E).

Chemical characterization of the poly(paraphenylene terephthalamide) thin layer membranes was studied by the Fourier transforms infrared (FT-IR, Equinox 55 Bruker) spectrometer with the attenuated total reflectance (ATR) spectroscopy. A sample of the membrane's thin layer cut and mounted in the ATR cell. For each sample, the IR spectra collected at the spectral resolution of  $4\text{ cm}^{-1}$  by accumulating 32 scans. The measured wave number range was  $4000\text{--}400\text{ cm}^{-1}$ .



Scheme 1. The mechanism of interfacial polymerization.

### 3. Result and discussion

#### 3.1. Characterization of thin layer on the PES support membrane

The poly(paraphenylene terephthalamide) thin layer on the support layer can be prepared by reacting the TPC and the PPD in aqueous and organic phases, respectively. Scheme 1 shows the mechanism of the IP reaction between the TPC and the PPD. As could be observed, the acyl chloride group of the TPC readily reacts with the amine groups of the PPD to form the amide group in the chemical structure of the TFC membrane.

ATR-IR analysis has employed to characterize the chemical structure of the membrane's skin layer. The ATR-IR indicates that the IP reaction is successfully completed (Figure 2). The peak at  $1572\text{ cm}^{-1}$  assigns to the C-N in poly (paraphenylene terephthalamide). The peak at  $1630\text{ cm}^{-1}$  appears the indicator of the C=O group band of an amide functional group. Moreover, the peak at  $3340\text{ cm}^{-1}$  assigns to the  $-\text{COOH}$  groups, which indicates that some amounts of TPC have not reacted with the PPD. However, they have been involved in the reaction with the water presented in the surrounding; and caused to form the carboxylic acid group. The amide groups also confirm formation of the thin layer on the PES support one.

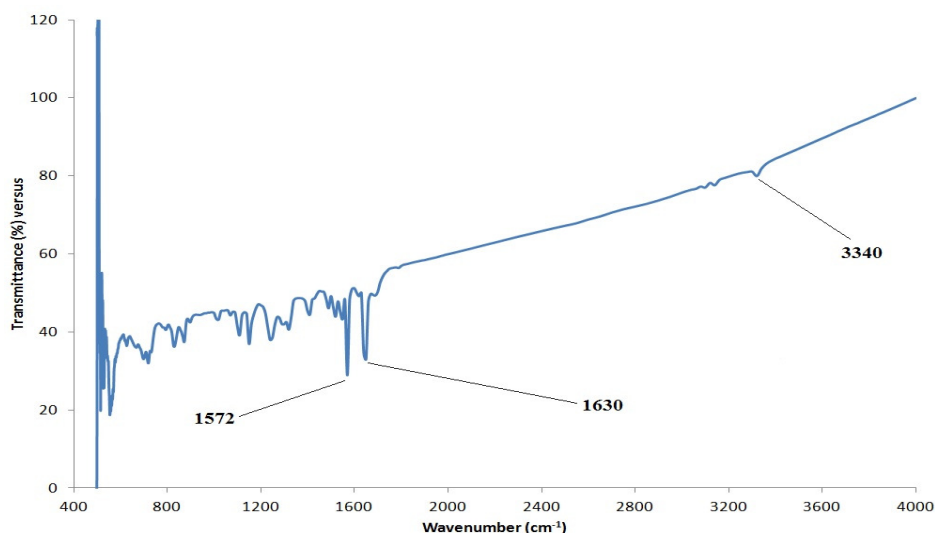


Fig. 2. ATR-IR spectrum of PA skin layer.

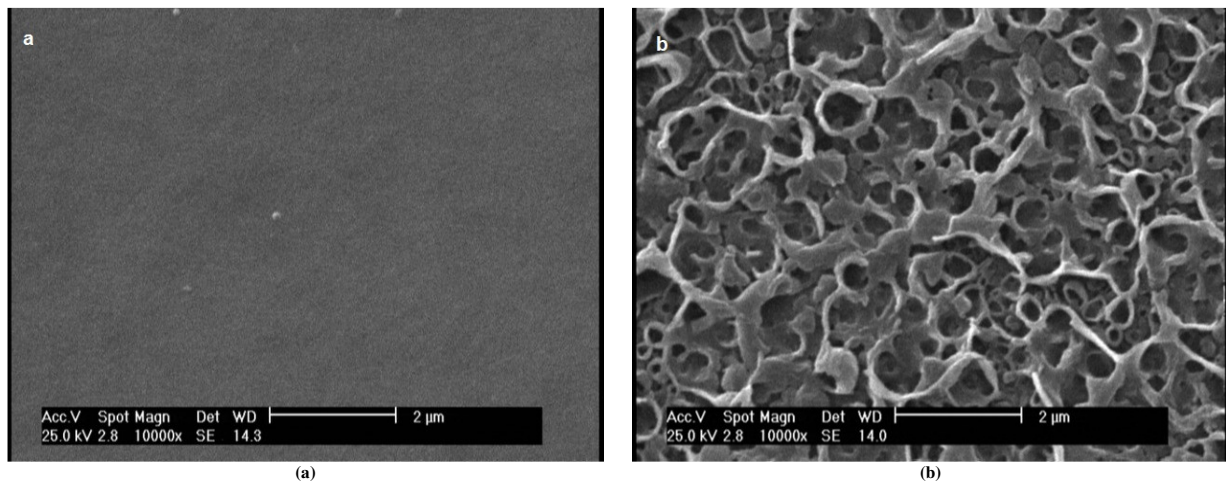


Fig. 3. Surface SEM micrographs of: (a) PES support surface and (b) PA skin layer surface.

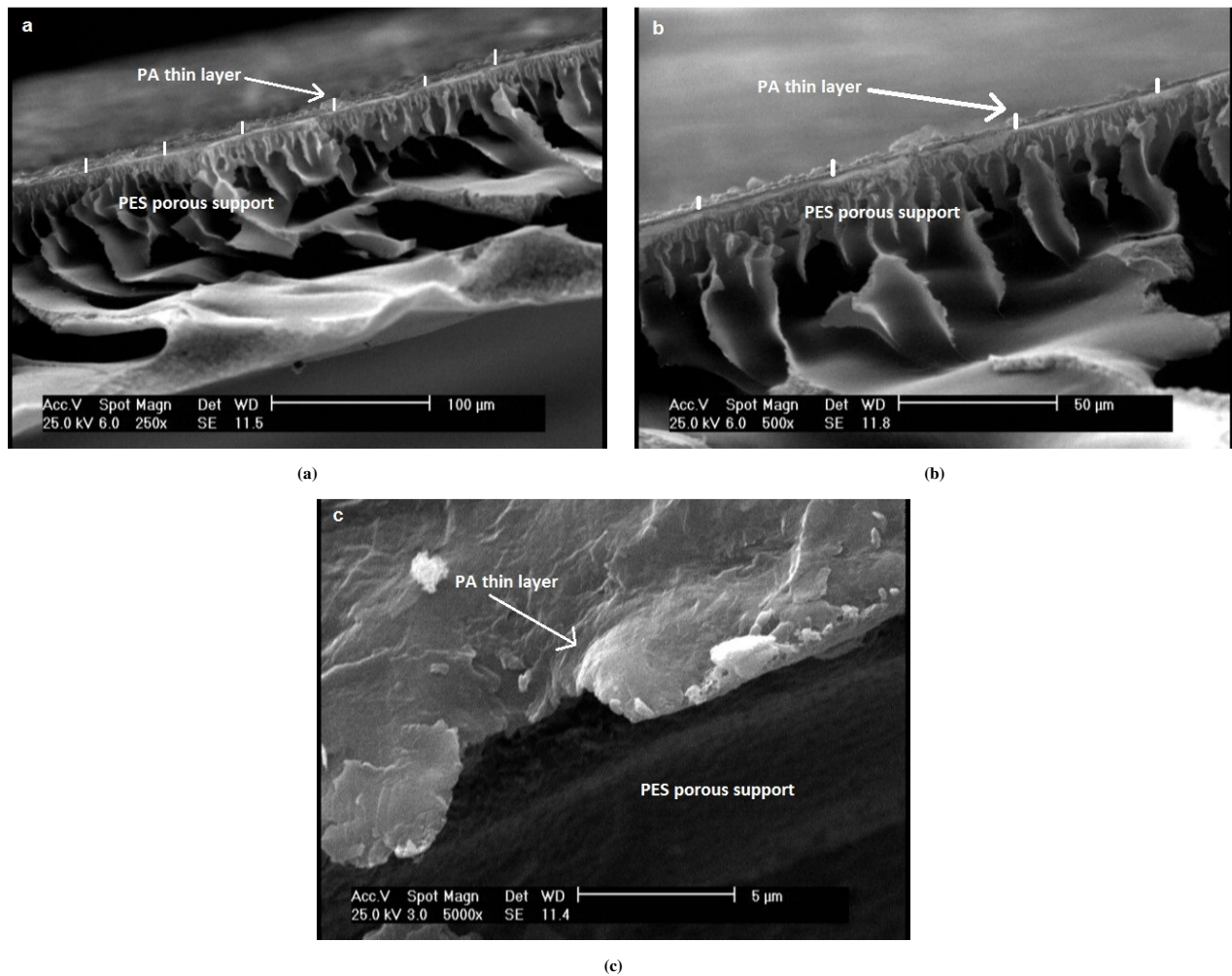


Fig. 4. Cross-section SEM micrographs of PA skin layer with the magnifications of (a) 250, (b) 500, and (c) 5000.

The surface morphology of the PES support and unmodified (without surfactants) poly(paraphenylene terephthalamide) thin layer are shown in Figure 3-a, which shows a flat and smooth surface. Figure 3-b shows a rough surface after the formation of poly(paraphenylene terephthalamide) on the PES support. Cross-sectional SEM micrographs of the skin layer are also shown in Figure 4. Formation of an upper thin layer on the PES membrane could be proven by these figures.

### 3.2. Effects of interfacial polymerization conditions on PWF and salt rejection

#### 3.2.1. Monomers concentrations

Effect of monomers' concentration on the salts rejection and PWF of membranes is shown in Table 2. In this case, other parameters remained constant (i.e. the immersion time in the aqueous phase was 10 min, the IP reaction time was 3 min and the curing temperature was 80 °C) and the



monomers concentration in the aqueous and organic solutions changed from 0.1 to 0.3 wt.%. For membranes containing the same PPD concentration, those ones had the higher TPC concentration, removed more solutes while resulted lower PWF. On the other hand, at constant TPC concentration, the membranes with 0.3 wt.% PPD showed the highest solutes rejection and the lowest PWF, as well. The membrane composed of 0.3 wt.% PPD and 0.3 wt.% TPC evaluated as the best sample in term of solutes rejection performance.

**Table 2**

Effect of monomers concentrations on the performance of the TFC membranes: the immersion time in the aqueous phase was 10 min; IP reaction time was 3 min and curing temperature was 80 °C.

PPD (%)	TPC (%)	PWF (kg/m <sup>2</sup> h)	Rejection (%)		
			NaCl	MgSO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>
0.1	0.1	32.2	3.2	21.0	25.5
0.2	0.1	30.0	7.2	38.1	42.7
0.3	0.1	26.8	12.1	50.1	57.3
0.1	0.2	31.8	4.6	27.3	31.6
0.2	0.2	29.0	9.3	40.0	46.9
0.3	0.2	26.0	16.7	55.5	59.1
0.1	0.3	31.2	9.1	31.0	35.7
0.2	0.3	28.1	10.8	45.8	53.6
0.3	0.3	25.1	20.1	58.8	63.2

The observed salts rejection and PWF behaviors of the membranes with monomers concentrations can be explained in terms of both the chemical and morphological changes that can take place during the formation of poly(paraphenylene terephthalamide) thin layer [2, 7]. These results indicate that both concentrations of PPD and TPC affect the membrane performance. In better words, at lower concentration of either PPD or TPC, the rate of polymerization is expected to be low due to the lack of required concentration of one of them at the IP sites. This phenomenon results in the formation of "thin and loose" poly (paraphenylene terephthalamide) layer which poorly rejects the salt while permeates more amount of water. In addition, as the results show, salts rejection increases and PWF decreases when the TPC concentration increases through the constant rate of increasing the PPD concentration. Solutions with higher concentrations of PPD lead to the formation of dense and compact membranes, so PWA decreased. Also, high concentrations of TPC strengthen the IP reactions and affect the membranes' structure and improve salts rejection, as well. The prevailing reactant in the IP is a monomer that has the lowest reaction activity. In this study, TPC is considered as the determinant IP reaction rate, because the reaction between the PPD and the TPC is much slower than that between the PPD and other monomers [25].

### 3.2.2. Interfacial polymerization reaction time

Table 3 shows the variation of salts rejection and the PWF values versus the IP reaction time between the TPC and the PPD in order to form poly(paraphenylene terephthalamide) thin layer. As could be observed, with increasing the IP reaction time, initially salts rejection increases whereas PWF decreases. According to Morgan [16], the IP between an acid chloride and diamine occurs on the organic side of the aqueous-organic interface. The IP is a diffusion-controlled reaction and exists in a self-limiting phenomenon [9]. Therefore, the IP reaction time plays an important role in determining the extent of polymerization. As a result, the top thin layer thickness of the TFC membrane increases with increasing the polymerization time. It will be stopped growing when the thickness of the thin layer is enough to prevent the diffusion of the monomer from one phase into another. Thus, for shorter reaction time, the extent of cross-linking is low and for this reason, the PWF of the membrane is high. After a certain period of reaction, the PWF almost remains constant because the thickness of the selective layer is almost constant. However, increasing in the TPC reaction time leads to improve the membrane surface layer which results in reduced PWF and increased salt rejections.

### 3.2.3. Curing temperature

Table 4 indicates the effect of curing temperature (from 50 to 90 °C) on the NaCl, MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> rejection and the PWF of membranes. Curing

temperature of the nascent poly(paraphenylene terephthalamide) thin layer membrane has a profound influence on the performance. Increasing curing temperature from 50 to 70 °C increases the NaCl, MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> rejection from 19, 56.22 and 59.63% to 20.41, 60.11 and 65.25%, respectively, and then almost levels off. However, the water flux was decreased continuously from 30.2 down to 21.8 kg/m<sup>2</sup>.h with increasing the curing temperature from 50 to 90 °C. From the molecular point of view, coupling a thermal energy leads to an increase in the translational motion of the macromolecules and also it allows functional groups to approach which leads to further reaction and compactness of the poly(paraphenylene terephthalamide) thin layer. The increase in curing temperature leads to increase in the salt rejection and decrease in water flux. This is because the nascent poly(paraphenylene terephthalamide) thin layer gel structure becomes more and more compact with the consequent decrease in the pore size and the porosity of the poly(paraphenylene terephthalamide) thin layer [7].

**Table 3**

Effect of IP reaction time on the performance of the TFC membranes: monomers concentrations were 0.3 %wt; immersion time in the aqueous phase was 10 min and curing temperature was 80 °C.

IP Reaction time (min)	PWF (kg/m <sup>2</sup> h)	Rejection (%)		
		NaCl	MgSO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>
1	29.1	16.8	54.1	56.3
2	27.5	18.8	56.3	60.1
3	25.1	20.1	58.8	63.2
4	24.2	20.6	60.4	65.7
5	23.8	20.7	60.5	65.9
6	23.3	20.7	60.8	66

**Table 4**

Effect of curing temperature on the performance of the TFC membranes: monomers concentrations were 0.3 %wt; immersion time in the aqueous phase was 10 min and IP reaction time was 4 min.

Curing temperature (°C)	PWF (kg/m <sup>2</sup> h)	Rejection (%)		
		NaCl	MgSO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>
50	30.8	19.0	56.2	59.6
60	28.1	20.0	58.7	63.1
70	24.5	20.4	60.1	65.2
80	24.2	20.6	60.4	65.7
90	24.0	20.8	60.6	65.7

### 3.3. Thin layer containing anionic/ non-ionic surfactants

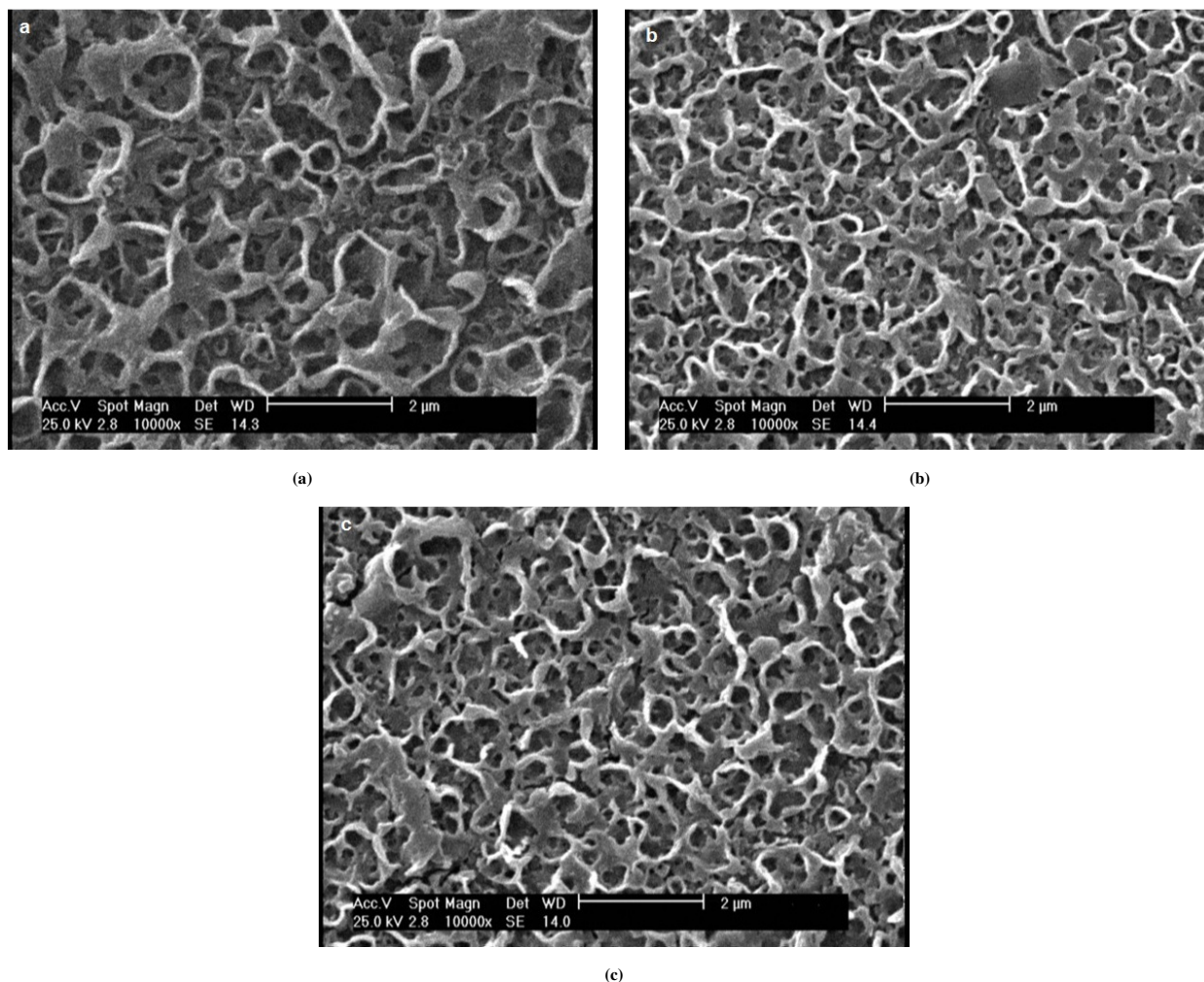
Surfactants constitute the most important group of detergent compounds, which is just a contraction of the phrase "surface active agent". They are amphiphilic. The term "amphiphile" indicates that one part of the molecule likes a certain solvent while the other part likes another solvent, and two solvents are immiscible. Usually one solvent is the water, and the water-loving part is called hydrophilic (i.e. head). The other part is hydrophobic (i.e. tail), which normally consists of a long alkyl chain. It does not like to be in water and prefers to be in an oily environment or air [26]. In this study, anionic and non-ionic surfactants were employed in the active layer of TFC NF membranes.

After obtaining the optimum parameters related to the monomers' concentration, the TPC reaction time and the curing temperature, experiments were carried out to investigate the effect of surfactants on the thin layer formation. The surfactants were used in the aqueous phase. The utilized conditions for the concentrations of both TPC and PPD were 0.3 wt.%; surfactants concentrations were 0.3 w/v. %; reaction time was 4 min and curing temperature was 70 °C. Table 5 shows compositions used for the preparation of thin layers on the support membrane samples.

It is worth quoting that, the highest salts rejection values has been reported in the literature when the surfactants concentration was about 0.3 w/v. %, therefore this value was considered in this study [21, 22].

**Table 5**  
Compositions of membrane thin layers.

Membrane	TPC (wt. %)	PPD (wt. %)	SLES (w/v %)	TEA-LES (w/v %)	DSLS (w/v %)	cocamide-MEA (w/v %)	polysorbate 20 (w/v %)	nonylphenol (w/v %)
L <sub>0</sub>	0.3	0.3	0	0	0	0	0	0
L <sub>1</sub>	0.3	0.3	0.3	0	0	0	0	0
L <sub>2</sub>	0.3	0.3	0	0.3	0	0	0	0
L <sub>3</sub>	0.3	0.3	0	0	0.3	0	0	0
L <sub>4</sub>	0.3	0.3	0	0	0	0.3	0	0
L <sub>5</sub>	0.3	0.3	0	0	0	0	0.3	0
L <sub>6</sub>	0.3	0.3	0	0	0	0	0	0.3



**Fig. 5.** Surface SEM micrographs of PA skin layer surface in the presence of anionic surfactants: (a) SLES, (b) TEA-LES, and (c) DSLS.

### 3.3.1. Membrane morphologies with anionic surfactants

Anionic surfactants contain a hydrophilic group, which carries a negative charge, such as a carboxylate, sulfonate or sulfate group. In this study, SLES, TEA-LES and DSLS were used as anionic surfactants. Figures 5a and b represent the surface micrographs of poly(paraphenylene terephthalamide) thin layer containing SLES and TEA-LES anionic surfactants, respectively. These figures indicate that by adding the SLES and the TEA-LES, no significant changes can be observed on morphology of the thin layer. Figure 5c indicates that DSLS anionic surfactant affects the porosity of thin layer. These phenomena can be explained by this fact that the chain length of linear molecular structure of the DSLS is longer than that of SLES and TEA-LES ones, and probably affect the surface of poly(paraphenylene terephthalamide) thin layer. However, the comparison between morphology of poly(paraphenylene terephthalamide) thin layer in the presence of anionic surfactants (L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub>) and the case without surfactant indicates that no

morphology of PA has greatly altered.

### 3.3.2. Membrane performance with anionic surfactants

Performance of membranes containing the anionic surfactants in the aqueous phase was investigated in the term of the PWF and salt rejection. The PWF of the proposed membranes is shown in Figure 6. The PWF increases from 24.5 kg/m<sup>2</sup>.h up to 25.7 and 27.1 kg/m<sup>2</sup>.h for the L<sub>1</sub> and the L<sub>3</sub> membranes, respectively. On the other hand, it decreases approximately down to 22 kg/m<sup>2</sup>.h for the L<sub>2</sub> membrane. The obtained results demonstrate that the poly(paraphenylene terephthalamide) thin layer of the membrane containing DSLS permeated the highest pure water compared to the other anionic surfactants.

The previous researches indicate that the interaction between the polymer and the surfactant depends on their molecular structure and the net charges, either on the surfactant or the polymer [27-29]. The effect of functional

groups and the chain length of the surfactant on the polymer–surfactant interaction has been studied [29]. The characteristic treatment of the applied polymer with the surfactant is similar to the surfactant micellization in the solution, and it takes place above a critical aggregation concentration (CAC) which is lower than that of the corresponding critical micellization concentration (CMC). Obviously, the hydrophobic characteristic of the polymer and the surfactant is responsible for the interaction [28]. The surfactant's alkali chains reach the hydrocarbonic structure of the polymer, and they connect to the polymer matrix. Nevertheless, the hydrophilic and polar segments freely leave [21]. SLES, TEA-LES and DSLS have a linear alkyl ether chain in their structure. Probably, due to the surfactants' concentration, SLES and DSLS can form a PA-surfactant complex during the IP process. Therefore, due to formation of this complex, the repulsion between the chains increased and leads to a slight increase in the free volume and the PWF. However, by addition of TEA-LES probably, ether groups in the linear alkyl chains of TEA-LES can form an attraction and binding force between poly(paraphenylene terephthalamide) chain functional groups. The interaction between the alkyl ether and the poly(paraphenylene terephthalamide) chains decreases the free volume of poly(paraphenylene terephthalamide) chains, resulting in the PWF reduction [21, 22].

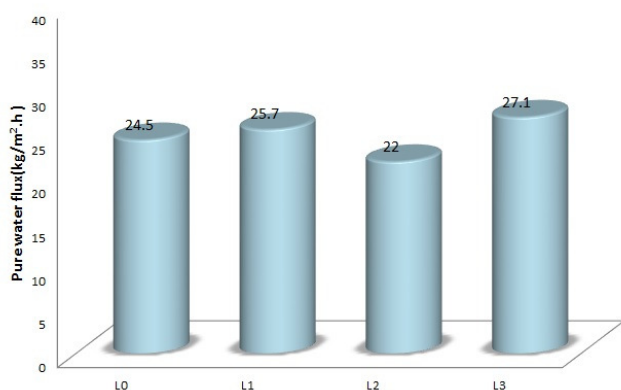


Fig. 6. Effect of anionic surfactant on PWF.

Figure 7 shows the effect of anionic surfactants on the salts' rejection. The NaCl, MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> rejection performance for the L<sub>1</sub> membrane is around 18.8, 66.4 and 69.5%, respectively. The rejection of salts for the L<sub>2</sub> is 20.8, 64.3 and 68%, respectively. Moreover, the rejection of salty solutions using L<sub>3</sub> membrane is around 20.9, 61.8 and 67.5%, respectively.

Comparing the three anionic surfactants, regardless of the type of anionic surfactants, the rejection value for MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> is increased. But, this increasing trend is not significant (see Figure 7). Nevertheless, SLES shows the highest MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> rejection, while DSLS shows the lowest rejection for the proposed salts. However, different result could be observed for the NaCl rejection as shown in Figure 7. As can be seen in this figure, by adding the TEA-LES and DSLS surfactants in aqueous phase, the NaCl rejection is remained constant, approximately. But in the presence of SLES, the NaCl rejection is decreased (see Figure 7).

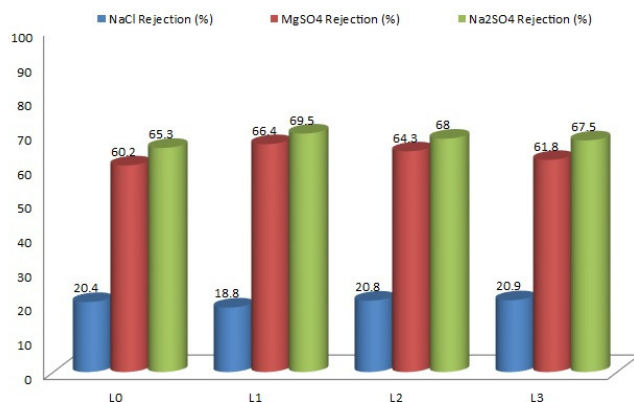


Fig. 7. Effect of anionic surfactant on the rejection of salts.

The separation mechanism of the NF membranes is affected by the surface charge, the ion diffusion coefficient, the ion size and its charge [21,22,30]. For these membranes and the L<sub>0</sub> one, the same order of rejection of salts is observed as follows: Na<sub>2</sub>SO<sub>4</sub>> MgSO<sub>4</sub>> NaCl. It is clear that the rejection for bivalent anions such as the SO<sub>4</sub><sup>2-</sup> is higher than that other electronegative ions such as the Cl<sup>-</sup>. However, the cations rejection (e.g. Mg<sup>2+</sup> and Na<sup>+</sup>) is in the reverse order. In another word, the rejection rate for the Mg<sup>2+</sup> is lower than the Na<sup>+</sup>. These results demonstrate that the TFC membranes used were all negatively charged. Therefore, the membrane with more negative charge rejects more Na<sub>2</sub>SO<sub>4</sub> and less NaCl. It is worth quoting that, the trend is exactly opposite of the membrane with less negative charge. Accordingly, the increase in surface charge is expected due to the negative charge of the applied anionic surfactants. It can be concluded that in the presence of SLES, the poly(paraphenylene terephthalamide) thin layer has the highest negative surface charge compared to other anionic surfactants.

### 3.3.3. Membrane morphologies with non-ionic surfactants

Non-ionic surfactants are active molecules that have no electric charge. The hydrophilic part drives their water solubility from highly polar groups as polyethylene oxide or sugars. Figure 8a shows the surface images of poly(paraphenylene terephthalamide) thin layers containing cocamide-MEA surfactant (L<sub>4</sub> membrane). This figure indicates that by adding the cocamide-MEA, the poly(paraphenylene terephthalamide) thin layer morphology is slightly changed to a compressed thin layer. Figure 8b shows the top surface SEM image of poly(paraphenylene terephthalamide) thin layer prepared with the polysorbate 20 (L<sub>5</sub> membrane) in the aqueous phase. As could be observed, the denser polyamide thin film (see Figure 8b) is formed on the surface of the PES support. Furthermore, Figure 8 represents the surface images of poly(paraphenylene terephthalamide) thin layer containing nonylphenol (i.e. L<sub>6</sub> membrane) which exhibits a dense, smooth and compressed skin layer. As a result, the non-ionic surfactant can clearly influence the poly(paraphenylene terephthalamide) thin layer and changes the morphology of the thin layer.

### 3.3.4 Membrane performance with non-ionic surfactants

Effect of non-ionic surfactants on the PWF is shown in Figure 9. The PWF decreased down to ~19.8, 18.2 and 17.5 kg/m<sup>2</sup>·h for L<sub>4</sub>, L<sub>5</sub> and L<sub>6</sub> membranes, respectively. The results showed that the highest PWF is obtained in the presence of cocamide-MEA.

It is supposed that the surfactants assist the monomer in the aqueous phase to move into the organic phase [17, 20]. With addition of surfactants to the aqueous phase, its surface tension can be diminished. Thus, PPD diffusion across the interface towards the organic phase can be influenced. As a result, the development in IP takes place and consequently, improves the property of TFC membrane, and eventually a dense layer is formed. This phenomenon causes more diffusion of reactant monomers towards the interface layer, leading to form a compressed poly(paraphenylene terephthalamide) thin layer. Therefore, L<sub>6</sub> has the lowest PWA due to formation of dense and smooth layer in the presence of nonylphenol.

The effect of non-ionic surfactants on the salt rejection of prepared membranes is shown in Figure 10. The results indicated that the NaCl, MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> rejection for membranes is increased by adding of non-ionic surfactants. The L<sub>6</sub> membrane (modified by nonylphenol surfactant) exhibited the highest rejection for MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> salts. As could be observed in this figure, the salts rejection by PA thin layer comprising cocamide-MEA is in the order of Na<sub>2</sub>SO<sub>4</sub>> MgSO<sub>4</sub>> NaCl. But the salts' rejection for other membranes follows the order of MgSO<sub>4</sub>> Na<sub>2</sub>SO<sub>4</sub>> NaCl. The ions' rejection capability is affected by two important factors for charged membranes, including the Donnan exclusion and the mobility of ions across the membrane [21, 22].

The membranes' performance is dependent on the ion charge, diffusion coefficient, and the size of ions. The mobility of ions across the membrane plays an important role in their rejection capability. The diffusion coefficient and effective size of ions determine the ion mobility. Due to the formation of a denser polyamide layer in the presence of polysorbate 20 and nonylphenol, the Donnan exclusion would be less effective. Therefore, ion diffusion can be well-defined as the dominant separation mechanism, resulting in low difference between rejection values. Hydration radius for Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, and Cl<sup>-</sup> are 0.429, 0.38, 0.365 and 0.347 nm, respectively [21]. The Mg<sup>2+</sup> ion has largest hydration radius compared to others, resulting in low mobility and diffusion, as well. Therefore, the Mg<sup>2+</sup> rejection is increased by adding polysorbate 20 and nonylphenol in comparison with adding the cocamide-MEA in the aqueous phase.



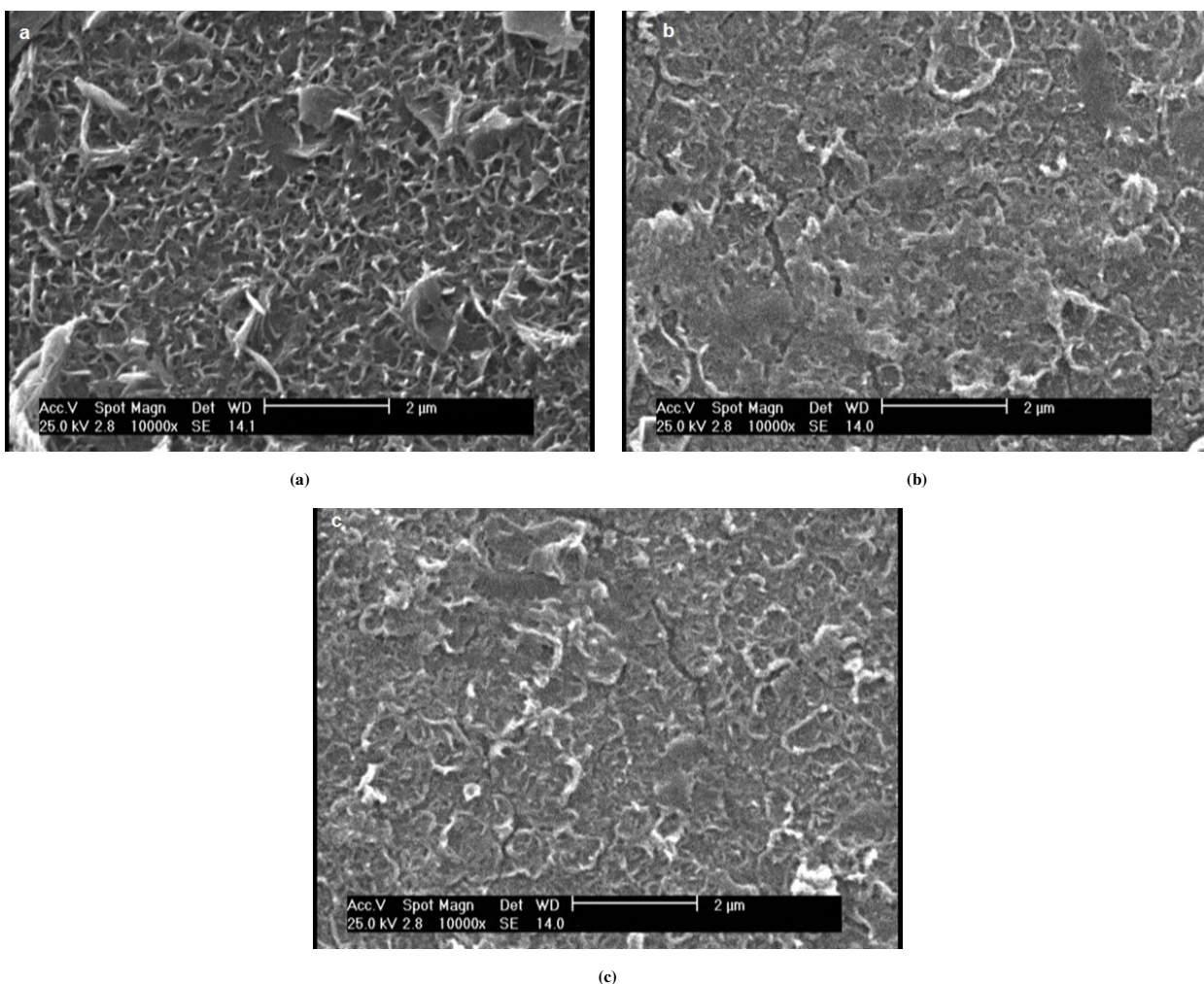


Fig. 8. Surface SEM micrographs of PA skin layer surface in the presence non-ionic surfactants: (a) cocamide-MEA, (b) polysorbate 20, (c) nonylphenol.

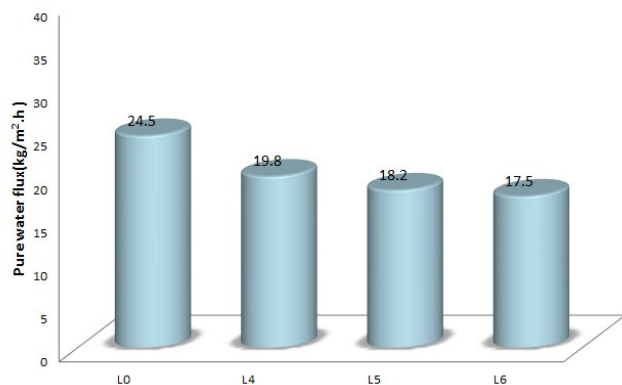


Fig. 9. Effect of non-ionic surfactant on PWF.

#### 4. Conclusions

In this study, the effect of surfactants in aqueous phase on the morphology and the performance of TFC membranes was investigated. Results indicated that the optimum condition for preparing the poly(paraphenylene terephthalamide) NF membrane was 0.3 wt% PPD in the aqueous phase, 0.3 wt% TPC in the organic phase. The best IP reaction time and the curing temperature were 4 min and 70 °C, respectively. The results exhibited that by adding anionic surfactants, no significant change in the morphology, the rejection of salts and the PWF was observed. Furthermore, membranes containing the SLES had the highest rejection for Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> salts compared to the other anionic surfactants. Also, the poly(paraphenylene terephthalamide) thin layer containing the DSLS had the

highest PWF among the anionic surfactants. In the presence of non-ionic surfactant, the morphology and the performance have changed. The salt rejection has increased, and the PWF has decreased. By adding the nonylphenol, a densest layer has formed, and the highest salts rejection has been obtained among the anionic/non-ionic surfactants. It should be noted that by adding the nonylphenol, salts' rejection (including NaCl, MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>) has increased from 20.4, 60.2 and 65.3% to 26.0, 81.8 and 77.2%, respectively. Finally, by introducing the anionic/non-ionic surfactants, the performance of the poly (paraphenylene terephthalamide) thin layer is superior compared to the membrane without surfactant. However, the non-ionic surfactants showed better effects on the performance than that of the ionic-surfactants.

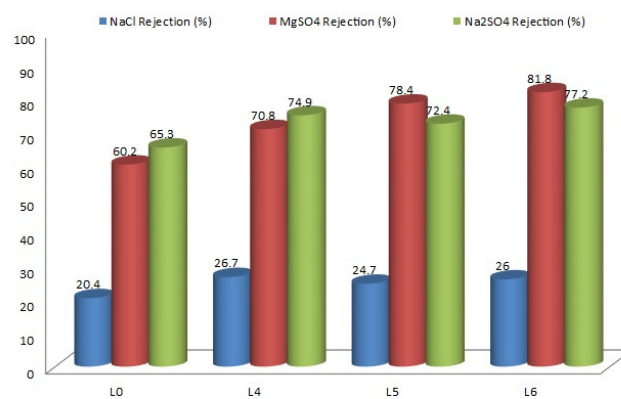


Fig. 10. Effect of non-ionic surfactant on the rejection of salts.



## 5. Nomenclatures

A	Membrane area
ATR	Attenuated total reflectance
CTAB	1-Butyl-3-methylimidazolium chloride
CAS-TEA	Camphorsulfonic acid triethylamine
BMMIC	Cetyltrimethylammonium bromide
C <sub>f</sub>	Concentrations of the feed solutions
C <sub>p</sub>	Concentrations of the permeation
Cocamide-MEA	Cocamide mono ethanol amine
DMAC	Dimethylacetamide
DSLS	Disodium laureth sulfosuccinate
IP	Interfacial polymerization
IPC	Isophthaloyl chloride
MPD	m-Phenylenediamine
NF	Nanofiltration
PIP	Piperazine
PES	Polyethersulfone
PS	Polysulfone
PPD	P-Phenylenediamine
PWF	Pure water flux
PVP	Polyvinylpyrrolidone
Q	Quantity of permeated pure water flux
R	Percent of salt rejection
SDS	Sodium dodecyl sulphate
SLES	Sodium lauryl ether sulfate
SLS	Sodium lauryl sulfate
T	Operation time
TBAB	Tetrabutylammonium bromide
TEAC	Tetraethylammonium chloride
TEA-LES	Triethanolamine lauryl ether sulfate
TEBAB	Triethyl benzyl ammonium bromide
TEBAC	Triethyl benzyl ammoniumchloride
TFC	Thin film composite
TMBAB	Trimethyl benzyl ammonium bromide
TMC	Trimesoyl chloride
TPC	Terephthaloyl chloride

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