Improvements in permeation and fouling resistance of PVC ultrafiltration membranes via addition of Tetronic-1107 and Triton X-100 as two non-ionic and hydrophilic surfactants

Hesamoddin Rabiee, S. Mojtaba Seyedi, Hossein Rabiei and Negar Alvandifar

ABSTRACT

Two non-ionic and hydrophilic surfactant additives, Tetronic-1107 and Triton X-100, were added to poly(vinyl chloride)/NMP polymeric solution to prepare ultrafiltration membranes via immersion precipitation. Surfactants at three different weight percentages up to 6 wt% were added, and the fabricated membranes were characterized and their performance for water treatment in the presence of bovine serum albumin (BSA) as a foulant was assessed. The scanning electron microscopy images indicated remarkable changes in morphology due to higher thermodynamic instability after surfactant addition. The membranes are more porous with more macro-voids in the sub-layer. Plus, the membranes become more hydrophilic. Water flux increases for the modified membranes by nearly two times and the ability of membranes for flux recovery increases from 66% to over 83%. BSA rejection reduces slightly with the addition of surfactants, however this parameter is still almost over 90% for the membranes with the highest amount of surfactants.

Key words | antifouling membranes, poly(vinyl chloride), Tetronic-1107, Triton X-100, ultrafiltration

LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>ε</td>
<td>Membrane porosity (%)</td>
</tr>
<tr>
<td>ωw</td>
<td>Weight of the wet membrane (g)</td>
</tr>
<tr>
<td>ωd</td>
<td>Weight of the dry membrane (g)</td>
</tr>
<tr>
<td>A</td>
<td>Membrane effective area (cm²)</td>
</tr>
<tr>
<td>δ</td>
<td>Membrane thickness (cm)</td>
</tr>
<tr>
<td>ρw</td>
<td>Water density (0.998 g/cm³)</td>
</tr>
<tr>
<td>rm</td>
<td>Mean pore radius (nm)</td>
</tr>
<tr>
<td>η</td>
<td>Viscosity of water (8.9 × 10⁻⁴ Pa.s)</td>
</tr>
<tr>
<td>Q</td>
<td>Volume of the permeated pure water per unit time (m³/s)</td>
</tr>
<tr>
<td>ΔP</td>
<td>Operation pressure (MPa)</td>
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<tr>
<td>J</td>
<td>Flux of solution (kg/m² h)</td>
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<tr>
<td>M</td>
<td>Mass of permeated water (kg)</td>
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<tr>
<td>Δt</td>
<td>Permeation time (h)</td>
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<tr>
<td>Jw,1</td>
<td>Water flux (l/m² h)</td>
</tr>
<tr>
<td>Jw,2</td>
<td>Flux of cleaned membrane (l/m² h)</td>
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<tr>
<td>FRR</td>
<td>Flux recovery ratio (%)</td>
</tr>
<tr>
<td>R</td>
<td>BSA rejection (%)</td>
</tr>
<tr>
<td>CF</td>
<td>Ion/BSA concentration in feed (ppm)</td>
</tr>
<tr>
<td>CP</td>
<td>Ion/BSA concentration in permeate (ppm)</td>
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INTRODUCTION

Nowadays, membrane processes are one of the most practical methods of separation for different applications such as: gas separation (Baker & Low 2014; Rabiee et al. 2014a), oil and natural gas separation (Baker & Lokhandwala 2008; Rabiee et al. 2015a), water treatment (Curcio et al. 2015; Deowan et al. 2015) and in the food and pharmaceutical industries (Daufin et al. 2001; Ionics Inc. 2004; Cheryan 2013), mainly because of the low operation cost and reduced footprint (Noble & Agrawal 2005). Modification of membranes’ structure and properties to improve their performance for various applications such as waste/water...
treatment, has been studied over recent decades. Ultrafiltration membranes prepared using the phase separation method have been widely researched, and different methods of modification have been applied to enhance their antifouling properties and water flux. During the phase inversion process and membrane formation, the solvent of the casting polymeric solution film is exchanged with non-solvent in the coagulation bath, and membranes are fabricated (Eirich & Strathmann 1973). Numerous parameters in this method have an influence on membrane morphology and its performance, such as temperature of the coagulation bath, type and concentration of polymer used, type and concentration of additives and type of solvent and non-solvent (Chaturvedia et al. 2001; Sadrzadeh & Bhattacharjee 2013).

The thermodynamics and kinetics of the polymeric solution affect the membranes’ morphology and performance. Thermodynamic instability is related to instantaneous demixing and the interactions between the solvent, non-solvent and additives (Strathmann et al. 1975). The more the polymeric solution is thermodynamically unstable, the faster phase inversion and demixing occur (Rahimpour et al. 2007). Addition of different additives to the polymeric solution leads to changes in the viscosity of the solution; therefore, the kinetics of the polymeric solution are influenced, and this causes the morphology and performance of the membranes to change (Yong et al. 1991).

As addition of different materials with unique characteristics influence the properties of membranes and can be used to modify their morphology and separation performance, several attempts have been carried out to modify the structure and performance of membranes, such as: addition of hydrophilic additives (Chakrabarty et al. 2008a, 2008b; Davood Abadi Farahani et al. 2015), incorporation of nanoparticles in membranes (Maximous et al. 2009, 2010; Huang et al. 2012; Shen et al. 2012; Rabiee et al. 2014b, 2015b) and preparation of membranes from blending polymeric systems (Xiuli et al. 1998; Musale et al. 1999; Reddy & Patel 2008; Shu et al. 2011; Amirilargani et al. 2012). The properties of membranes are a trade-off between thermodynamic enhancement and kinetic hindrance during the phase inversion process (Lee et al. 2005).

Polymers such as poly(ethersulfone) (PES) (Barth et al. 2000; Chaturvedia et al. 2001; Idris et al. 2007; Amirilargani et al. 2010), polysulfone (PSF) (Tsai et al. 2002; Chakrabarty et al. 2008a), poly(vinylidene fluoride) (PVDF) (Zuo et al. 2008; Pezeshk et al. 2012), polyacrylonitrile (PAN) (Kim et al. 2002; Yang & Liu 2003; Wan et al. 2006), poly(vinyl chloride) (PVC) (Mei et al. 2011; Davood Abadi Farahani et al. 2015) and cellulose acetate (CA) (Saljoughi & Mohammadi 2009) have been widely used for membrane preparation via phase inversion. PVC seems to be a great choice due to its high mechanical and chemical resistance (to acids, halogens or oxidants), low cost, acceptable stability at high temperatures and solubility in different industrial solvents. However, for hydrophobic polymers like PVC, fouling during ultrafiltration is very considerable; therefore different attempts have been made to deal with this problem. Addition of nano TiO2 particles has led to remarkable changes in morphology and performance of the membranes (Rabiee et al. 2014b). TiO2 addition also resulted in an increase in flux recovery ratio (FRR) and foulant rejection properties of the membranes. Another method is the addition of a hydrophilic polymer like poly(vinyl butyral) to the membrane structure, which ultimately will result in higher surface hydrophilicity and, consequently, improved antifouling (Peng & Sui 2006). Other commonly used additives like polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) have been studied and an increase in the rate of phase inversion after the addition has been reported (Mei et al. 2011; Davood Abadi Farahani et al. 2015).

Addition of surfactants to the polymeric solution leads to modification of the morphology and performance of the membranes due to changes in the rate of solvent-nonsolvent exchange and membrane formation, and they are being used to enhance performance of the membranes (Kingma 2015). Tween surfactants are among the most commonly used materials, and addition of Tween-20 and Tween-80 to PES membranes was investigated by Amirilargani et al. (2010). They reported increases in water flux and porosity of the membranes with the addition of a small amount of Tween (Saljoughi et al. 2009; Amirilargani et al. 2010). Tween-20 has been also used as a pore-former for PVDF membranes, and it resulted in enhancement of the water flux and membranes with higher porosity (Chang et al. 2014). Tetronic-1107, another hydrophilic surfactant, was added to modify PSF membranes, and it led to a continuous increase in water flux and more hydrophilic surface (Mousavi et al. 2013). The effects of Triton X-100 addition on PES membranes were studied by Rahimpour et al. (2007), and they observed formation of large finger-like pores in the sub-layer of the membranes and higher porosity. As a result, the water flux more than doubled with 2 wt% Triton X-100 addition, compared to the membranes without Triton X-100 (Rahimpour et al. 2007). Recently, the effects of Brij-58 addition on PES nanofiltration membranes were studied, and an increase in water flux from 30 L/m2h to over 70 L/m2h after 6 wt% Brij 58 addition was reported. In addition, membranes became more efficient at rejecting amoxicillin and ceftriaxone (Omidvar et al. 2015).
of ionic and non-ionic surfactants to CA nanofiltration membranes also resulted in membranes with higher porosity and a thinner skin layer, which were more efficient in rejecting solutes in comparison to the neat CA membrane (Ghaemi et al. 2012a, 2012b).

Based on the results published in the literature, addition of Tetronic-1107 and Triton X-100, along with other hydrophilic surfactants, to ultrafiltration membranes has had a remarkable effect on water flux and FRR, but there has been no investigation into their addition to PVC membranes (Amirilargani et al. 2013; Mousavi et al. 2013; Namaghi & Mousavi 2014; Jalaei salmani 2016). Addition of Tetronic-1107 to PSF led to an increase in the thickness and surface pore size of the membranes and higher water flux (Mousavi et al. 2013). Also, Triton X-100 was added to dairy wastewater to investigate its effect in micellar-enhanced ultrafiltration (Namaghi & Mousavi 2014; Jalaei salmani 2016), and the results show that this surfactant can adsorb foulants of the feed and be subsequently rejected by PAN UF membranes. Therefore, its environmental properties are suitable and it can prevent contaminants passing through when used in the structure of a UF membrane.

In addition, as PVC is a very suitable choice for membrane preparation, new methods to improve its performance should be studied. Therefore, in the current study, the effects of Tetronic-1107 and Triton X-100 as hydrophilic and non-ionic surfactants on the morphology and performance of the prepared membranes were investigated. Furthermore, mean pore size and porosity, hydrophilicity of the surface of the membranes, and water and Bovine serum albumin (BSA) flux were measured, and the fouling resistance of the membranes was calculated. The membranes showed an increase in porosity and a significant increase in water flux along with an increased ability to recover their water permeation after foulant flux.

**EXPERIMENTAL**

**Materials**

PVC was supplied by Arvand Petrochemical Co., Iran in the form of a fine powder. Tetronic-1107 (ethylenediamine tetraakis (propoxylate-block-ethoxylate) tetrol, HLB = 24), CAS # = 26316-40-5, and Triton X-100 (polyethylene glycoltert-octylphenyl ether), CAS # = 9002-93-1, were used as the surfactant additives (supplied by Aldrich) and their chemical structures are shown in Figure 1. The solvent, N-methyl-2-pyrrolidone (NMP), and PEG with a molecular weight of 1,000 Da were also purchased from Merck. BSA was used as a foulant and was bought from Sigma.

**Membrane preparation**

The flat sheet asymmetric membranes were prepared with the phase inversion method using NMP and water as the solvent and non-solvent. First, PVC was dissolved in NMP by stirring for about 24 h to have a 16 wt% PVC homogenous solution. Then 5 wt% PEG 1,000 Da as the invariable additive was added to the solution. Subsequently, surfactants were added to the solution at three different percentages based on the literature from 2 to 6 wt% (Mousavi et al. 2013; Chang et al. 2017). When a homogenous solution was obtained, it was put in an ultrasonic bath to obtain a bubble-free solution before casting. Then the solution was cast using a film applicator with 150 μm clearance gap on a glass plate substrate. Immediately afterwards, the film was put into the coagulation bath at room temperature, and the solvent-nonsolvent exchange started. The samples were held there for at least 30 min and then put in a fresh bath to complete phase inversion and remove any residual solvent from the membranes’ structure. The samples were finally put between two sheets of filter paper for drying. The composition of the casting solution is presented in Table 1.

**MEMBRANE CHARACTERIZATION**

**Scanning electron microscopy**

Scanning electron microscopy (SEM) images were obtained using VEGA\TESCAN SEM (Czech Republic) to study the morphology of a cross-section of the fabricated membranes. For this purpose, membranes were fractured in liquid nitrogen.
and were coated with gold. SEM images were taken under very high vacuum conditions, operating at 20 kV. The images are taken at two different magnifications, 50 μm and 10 μm.

Contact angle

Hydrophilicity of the membranes was evaluated via measurement of the static water contact angle using an OCA20 (Dataphysics Instruments, Germany). First, the samples were air dried and then deionized water droplets were put upon the membrane surface. After that, the contact angle between membrane and water was measured. The test was carried out at 25 °C and the average of five samples is reported here.

Porosity and pore size

Membrane porosity (Equation (1)) and mean pore size (Equation (2)) were measured according to their dry-wet weight (Shi et al. 2012; Vatanpour et al. 2012; Zhang et al. 2013):

$$\varepsilon(\%) = \frac{w_w - w_d}{\rho_w A \delta_0} \times 100$$ (1)

where $w_w$ and $w_d$ are weights of the wet and dry membranes, respectively, $\delta_0$ is the membrane thickness (cm), $\rho_w$ is the density of pure water (0.998 g/cm³) and $A$ is the membrane area (cm²). It should be noted that the surface of the samples were dried carefully and then the wet membranes were vacuum dried at 60 °C for 24 h and were measured for the dry-wet weight. The mean pore radius ($r_m$) of the membranes was also measured by the Guerout-Elford-Ferry equation, as follows (Hamid et al. 2011; Vatanpour et al. 2012; Zhang et al. 2013):

$$r_m = \sqrt{\frac{(2.7 - 1.29\varepsilon) \times 8\eta Q}{\varepsilon A \Delta P}}$$ (2)

where $Q$ is the measured flux (m³/s), $\eta$ is the water viscosity (8.9 × 10⁻⁴ Pa.s) and $\Delta P$ is the operation pressure (2 bar).

Permeation experiment

The evaluations of pure water flux (PWF) and protein rejection were carried out using a dead-end membrane set-up, such as the one used in our previous article (Rabiee et al. 2014b), with a membrane effective area of around 19.6 cm². In the first step, the membranes were pretreated and compacted at the high-pressure difference of 3 bar for 30 min. Then, the PWF tests were conducted at an operation pressure of 2 bar. The permeates were collected and weighed over a given period, using Equation (3):

$$J = \frac{M}{A \Delta t}$$ (3)

where $J$, $\Delta t$, $M$ and $A$ are flux, permeation time, mass of permeated water and membrane effective area, respectively.

Antifouling properties

For the analysis of the membrane fouling resistance, after 90 min pure water flux and washing the feed tank, the permeation of 500 ppm BSA was measured to study membrane rejection and antifouling properties. For this purpose, the membranes are first put in distilled water for 1 h for washing and finally the pure water flux was measured for another 90 min to obtain the recovery ratio (FRR) of the membranes using Equation (4):

$$FRR(\%) = \left(\frac{J_{water,2}}{J_{water,1}}\right) \times 100$$ (4)

where $J_{water,2}$ and $J_{water,1}$ are the flux of pure water after and before the BSA flux, respectively.

In order to evaluate the BSA concentration, UV absorbance of the permeate was measured at 280 nm. The percentage of BSA rejections ($R$) was evaluated by Equation (5), where $C_p$ (ppm) and $C_F$ (ppm) were the BSA concentrations in the permeate and feed solutions, respectively. As the BSA concentration in the permeate, compared to the feed, is very low, using Equation (5) is an appropriate way to calculate the rejection of the BSA.

$$R(\%) = \left(1 - \frac{C_p}{C_F}\right) \times 100$$ (5)

Table 1 | Composition of the casting solution

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PVC (wt%)</th>
<th>Tetronic-1107 (wt%)</th>
<th>Triton X-100 (wt%)</th>
<th>PEG 1,000 Da (wt%)</th>
<th>NMP (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>M1</td>
<td>16</td>
<td>2</td>
<td>0</td>
<td>4</td>
<td>78</td>
</tr>
<tr>
<td>M2</td>
<td>16</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>76</td>
</tr>
<tr>
<td>M3</td>
<td>16</td>
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<td>0</td>
<td>4</td>
<td>74</td>
</tr>
<tr>
<td>M4</td>
<td>16</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>78</td>
</tr>
<tr>
<td>M5</td>
<td>16</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>76</td>
</tr>
<tr>
<td>M6</td>
<td>16</td>
<td>0</td>
<td>6</td>
<td>4</td>
<td>74</td>
</tr>
</tbody>
</table>
RESULT AND DISCUSSION

Morphology of the membranes

The morphology of the membranes after surfactant addition was studied by taking cross-sectional SEM images, as shown in Figures 2 and 3, and remarkable changes can be seen. The membranes have a typical asymmetric structure containing finger-like pores and macro-voids in the sub-layer with a rather dense top layer. As the surfactant composition in the polymeric solution increases, the sub-layer becomes more porous and the structure containing fully developed finger-like pores is replaced by one with more macro-voids. The porosity of the fabricated membranes in phase inversion is directly related to changes in the rate of solvent-non-solvent exchange during immersion precipitation, and as the rate of non-solvent entering the casting film becomes higher than that of the solvent leaving the film; more porous membranes will be fabricated (Strathmann et al. 1975; Strathmann & Kock 1977).

Figure 2 | The cross-sectional morphology of the membranes with Tetronic-1107 at different concentrations: (a) 0 wt%, (b) 2 wt%, (c) 4 wt%, (d) 6 wt%.
Two parameters have an influence on the morphology of the fabricated membranes via immersion precipitation, thermodynamic instability and the kinetics of the polymeric solution (Strathmann & Kock 1977). The thermodynamic instability of the polymeric solution is related to the interaction between solvent, nonsolvent, polymer and additives. The addition of different compounds like surfactants has an effect on the interaction (Madaeni et al. 2013). As the surfactants used are highly soluble in water, they tend to leach out of the casting film when it is put in the coagulation bath. Therefore, the rate of solvent-nonsolvent exchange, or in other words the velocity of membrane preparation increases, and the membranes are formed significantly faster (Zeman & Tkacik 1988; Sadrzadeh & Bhattacharjee 2013).

It is well-known that the miscibility between the additive and the coagulant is of great importance in the formation of macro-voids (Chakrabarty et al. 2008a; Sadrzadeh & Bhattacharjee 2013). Hence, the addition of a hydrophilic surfactant with high water miscibility leads to faster leaching of solvent from the membranes’ structure.

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**Figure 3** | The cross-sectional morphology of the membranes with Triton X-100 at different concentrations: (a) 0 wt%, (b) 2 wt%, (c) 4 wt%, (d) 6 wt%.
and the casting solution becomes thermodynamically more unstable. It can be said that once the casting solution is in contact with water, the generation of nucleated droplets of the polymer lean phase in the casting polymer solution starts and these nuclei lead to formation of macro-voids (Smolders et al. 1992). Thereby, instantaneous demixing occurs and it results in membranes with higher porosity. The addition of surfactants leads to greater thicknesses for the fabricated membranes, as presented in Figure 4. This increase in thickness can be attributed to higher porosity of the membranes after surfactant addition (Saljoughi et al. 2009; Sadrzadeh & Bhattacharjee 2013).

In addition to the thermodynamics of the polymeric solution, the kinetics of the phase inversion has an important effect and this is related to the viscosity of the casting solution (Zhang et al. 2010). An increase in solution viscosity was visually evident, although it was not measured numerically, because as shown in Table 1, for the casting solution of modified membranes surfactant is added instead of NMP while other components are constant. Therefore, as the
surfants are rather more viscous liquids compared to NMP, viscosity increases, hence, diffusion from the casting film to the non-solvent bath is hindered, and, consequently, exchange rate and instantaneous demixing is delayed and membranes with denser structures are fabricated (Yong et al. 1991; Sadrzadeh & Bhattacharjee 2013).

**Effect of surfactant addition on thickness of the membranes**

Figure 4(a) shows the effect of Tetronic-1107 and Triton X-100 addition on the thickness of the prepared membranes. The thickness of the prepared membranes increases as more surfactant is added to the casting solution and becomes 123 μm for the membrane fabricated from the casting solution with 6 wt% surfactant. Once the casting solution has entered the coagulation bath for membrane preparation, phase inversion and solvent-nonsolvent exchange starts and the original thickness of the casting film reduces (Nechifor & Popescu 1990). Therefore, the concentration of polymer increases. NMP and water are naturally highly miscible and when the casting film enters the nonsolvent bath, mutual diffusion of water-NMP at occurs at several points, and nuclei of the polymer-poor phase are formed. Polymer concentration at this polymer-poor phase (which is the interface of pores and macro-voids) increases until it reaches the solidification point at which the polymer content is high enough to form a solid phase (Sadrzadeh & Bhattacharjee 2013; Rabiee et al. 2014b). In this process, for the systems with instantaneous demixing, the velocity of membrane formation and solidification is greater and, as a result, thicker membranes are fabricated (Mousavi et al. 2013). It was visually observed that the membranes were formed faster after surfactant addition and more precise results are reported in a similar study (Chang et al. 2014). With the addition of highly water-miscible additives such as Tetronic-1107 and Triton X-100 surfactants, the system will have more thermodynamic instability (Wang et al. 2006; Liu et al. 2012), hence, the diffusion rate increases and it results in greater thickness of the prepared membranes.

**Effect of surfactant addition on pore size and porosity of the membranes**

The porosity of the membranes was calculated by using Equation (1) and the results are shown in Figure 4(b). The figure shows that surfactant addition leads to a continual increase in overall porosity of the membranes. The main reason for this observation is the presence of more and larger macro-voids in the membranes’ structure, as seen in the SEM images, and it was also seen that the thickness of the membranes increases with more surfactant addition in a constant polymer concentration, which means higher porosity (Saljoughi et al. 2009; Chang et al. 2014). The porosity of the membranes increases from 65% for the bare PVC membrane to 82% and 76% for the membranes containing 6 wt% Tetronic-1107 and Triton X-100, respectively.

Another factor that was calculated for the membranes was their pore size using Equation (2). As can be seen from Figure 4(b), this parameter reduces for the membranes as more surfactant is added to the casting solution. As discussed earlier, addition of hydrophilic surfactants to the casting solution results in a higher thermodynamic instability of the solution and, therefore, the membranes are formed more quickly, and are thicker and more porous. As the formation of membranes becomes faster, the concentration of polymer at the interface of pores and macro-voids increases more quickly and once solidification point is reached they do not extend (Strathmann et al. 1975; Strathmann & Kock 1977; Chakrabarty et al. 2008a). Hence, the pore size of the membranes becomes smaller in this situation (Shin et al. 2005; Amirlargani et al. 2010). This can also be seen from the SEM images of prepared membranes with higher magnification near the top layer, as shown in Figure 5, where an increase in the number of pores is evident (near the skin layer), and it can be concluded that surface porosity has increased. In addition, a reduction in the thickness of the top layer is observed, which is mainly because of instantaneous demixing and a faster solvent-nonsolvent exchange rate, as discussed above (Ghaemi et al. 2012a, 2012b; Chang et al. 2014).

**Effect of surfactant addition on surface hydrophilicity of the membranes**

Contact angle measurement is a commonly used method to evaluate changes in the surface hydrophilicity of the membranes. Results of this test show that as more surfactant is added to the membranes’ structure, the contact angle reduces continuously, which means the membranes become less hydrophobic, as indicated in Figure 4(c). Hydrophobicity is directly related to fouling of the membranes which is a common issue in filtration processes. As PVC is quite highly hydrophobic, several methods have been considered to deal with this problem like blending PVC with another hydrophilic polymer (Liu et al. 2012), addition of nanoparticles (Rabiee et al. 2014b), etc.
Here, the contact angle reduces from 71° for the bare PVC membrane to around 56.5° and 51° for PVC/6 wt% Triton X-100 and PVC/6 wt% Tetronic 1107, respectively. The reduction for the membranes with Tetronic-1107 is greater than that for the ones with Triton X-100, which means PVC/Tetronic-1107 membranes become more hydrophilic. Also, as seen before for PVC/Tetronic-1107 membranes, the increase in porosity and thickness, and reduction in mean pore size is greater than that for PVC/Triton X-100 membranes. It can be concluded that the membranes containing Tetronic-1107 make the thermodynamics of the casting solution more unstable, therefore membranes are fabricated faster with higher hydrophilic properties. This can also be attributed to the hydrophilic-lipophilic balance (HLB), which is an empirical expression for the relationship of the hydrophilic and hydrophobic fractions of a surfactant. The HLB for Tetronic-1107 and Triton X-100, based on the information provided by the producer or scientific papers (Slinde & Flatmark 1976; Mousavi et al. 2015), is 24 and 13.5, respectively. Hence, Tetronic-1107 is more hydrophilic than Triton X-100 and the addition of an additive which is miscible with a non-solvent results in having more porous membranes (Sadrzadeh & Bhattacharjee 2015). The results are also in accordance with the observations made in the high magnification SEM images of the membranes: (a) without surfactant; (b) 6 wt% Tetronic-1107; (c) 6 wt% Triton X-100.

Figure 5 | High magnification SEM images of the membranes: (a) without surfactant; (b) 6 wt% Tetronic-1107; (c) 6 wt% Triton X-100.
with the water flux and flux recovery ratio data that are introduced in the following sections.

**Effect of surfactant addition on water/BSA flux and BSA rejection of the membranes**

The effect of Tetronic-1107 and Triton X-100 addition on the flux of water and BSA was investigated using a dead-end cell ultrafiltration system, operating at 2 bar. The results are shown in Figure 6(a), and, as seen, surfactant addition results in a continuous increase of water and BSA permeation. For example, water flux rises from 189 kg/m² h for the bare PVC membrane to 324 kg/m² h for PVC/6 wt% Triton X-100 and 342 kg/m² h for PVC/6 wt% Tetronic-1107 membranes. The main reason for this observation is due to a greater hydrophilic surface after surfactant addition and changes in the morphology of the membranes (Ghaemi et al. 2012a; Mousavi et al.)

![Figure 6](https://iwaponline.com/wst/article-pdf/74/6/1469/459017/wst074061469.pdf)
Hydrophilicity is directly related to contact angle, as mentioned earlier. The membranes with a greater hydrophilic surface are more capable of passing water, and they attract water molecules more easily; therefore, water diffusion and penetration through these membranes are greater than through those with a more hydrophobic surface (Amirilargani et al. 2010). In addition, as observed in Figures 2 and 3, after surfactant addition membranes become more porous with a thinner skin layer, which resists permeation (Chang et al. 2014). Hence, the membranes are more permeable due to their structures. In Figure 6(a), the water and BSA fluxes for PVC/Tetronic-1107 membranes are greater than those for PVC/Triton X-100 membranes and consistent results in this regard were obtained for their characteristic properties.

Figure 7 | Pure water and BSA flux of the membranes with and without surfactant in three 90 min sections: first pure water flux, second the BSA flux and third water flux again after washing the membranes for 30 min with pure water.
In addition to having a high water flux, membranes with acceptable performance should be able to reject foulants and show desirable selectivity to pass molecules. BSA was used as the foulant in this work and its rejection properties for the prepared membranes are shown in Figure 6(b). As the membranes become more hydrophilic after surfactant addition, they adsorb BSA molecules less, and it means a higher BSA rejection (Rabiee et al. 2014b), however, the formation of more macro-voids means a reduction in BSA rejection (Rahimpour et al. 2007; Amirilargani et al. 2010). Hence, these two parameters neutralize their effect and, overall, a slight decrease in BSA rejection is observed (Zhang et al. 2012; Chang et al. 2014). The membranes still have a BSA rejection of almost 90% and, for example, for PVC/Tetronic-1107 membranes, it reduces from 96% to 89% with 6 wt% addition.

**Fouling resistance properties of the membranes**

Generally, the membranes which possess high antifouling properties are appropriate for use in ultrafiltration processes. Especially polymers like PVC, which is rather vulnerable due to its natural hydrophobicity. When these membranes are in contact with feeds containing foulants, like the ones in dairy and food-processing (Daufin et al. 2001; Ionics Inc. 2004) or milk concentration (Madaeni & Rahimpour 2009), they tend to adsorb these compounds, and thereby their water flux and separation efficiency will be influenced. Hence, it is important for the membranes to recover their water permeation and, in order to assess this ability, the water flux before and after BSA permeation is measured and compared in Figure 7. Water flux is measured at 2 bar for 90 min, then permeation of solution containing 500 ppm BSA is assessed, and after that the membranes are washed, and water flux is measured again. The FRR can be calculated using these data and Equation (4). Water flux becomes almost constant as time goes on.

Addition of Tetronic-1107 and Triton X-100 results in a greater FRR for the membranes as shown in Figure 6(c), which means surfactant addition has led to having membranes with a better ability to recover their water flux. The main reason behind this phenomenon is enhancement in wettability or hydrophilicity of the membranes after modification with surfactants (Mousavi et al. 2013; Chang et al. 2014). The FRR increases from nearly 66% for the bare PVC membrane to 83% and 86% for PVC/6 wt% Triton X-100 and PVC/6 wt% Tetronic-1107 membranes, respectively. The difference between improvement of the FRR for PVC/Triton X-100 and PVC/Tetronic-1107 membranes is consistent with a reduction in contact angle data, which was higher for the latter (Saljoughi et al. 2009; Amirilargani et al. 2010).

**CONCLUSION**

In this research, the effect of Tetronic-1107 and Triton X-100 addition as two non-ionic and hydrophilic surfactants on the morphology and performance of PVC UF membranes was studied. The percentage of surfactants varied up to 6 wt%, while the amount of PVC and PEG was constant. There was a remarkable increase in water flux from almost 186 kg/m² h to 324 kg/m² h and 342 kg/m² h for the membranes fabricated from casting solutions containing 6 wt% Triton X-100 and Tetronic-1107, respectively. In addition, the membranes have more fouling resistance ability and the FRR increased from 66% to over 83% and 86% for PVC/6 wt% Triton X-100 and PVC/6 wt% Tetronic-1107 membranes. Addition of surfactants leads to having fewer hydrophobic membranes with higher porosity and more macro-voids, which are the main reasons for improved water flux and FRR.

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**REFERENCES**


Ionics Inc. 2004 Membrane technology benefits the food processing industry. Filtration & Separation 41 (8), 32–33.


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