

# Role of organic additives in the preparation of polyetherimide membranes for solvent resistant nanofiltration

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## Abstract

The incorporation of non-solvent organic additives in the casting solution has emerged as a significant technique in membrane fabrication. This approach enables the manipulation of membrane morphology and facilitates the preparation of high-performance membranes. Our work focusing on investigating the impact of various organic additives on the development of integrally skinned polyetherimide asymmetric nanofiltration membranes, which has not been explored in solvent resistant nanofiltration (SRNF). The additives investigated in this study can be classified into three categories: hydrophilic monomers, hydrophilic polymer and surfactant additives. The effect of these organic additives on PEI membrane performance was evaluated by separating methylene blue (MB, molecular weight 374 Da) from ethanol solution, and membrane morphology was characterized by scanning electron microscope (SEM).

**Keywords:** polyetherimide; organic additives; phase inversion; solvent resistant nanofiltration

## 1. Introduction

Asymmetric membranes have been widely utilized in various applications such as osmosis, microfiltration and nanofiltration <sup>1</sup>. These membranes consist of a thin top layer that acts as a selective barrier film, and a porous sublayer with macrovoids, pores, and micropores, which provide mechanical strength <sup>2</sup>. The preparation of these membranes typically involves a phase inversion process. It is well-established that the membrane morphology and structure are influenced by kinetic parameters, such as the rate of solvent/non-solvent exchange (usually water and low molecular alcohol). In addition, thermodynamic parameters including phase diagrams, polymer/solvent interactions, solvent/non-solvent interactions, the coagulation bath, and interfacial stability play a significant role in the membrane formation mechanism. Hence, careful selection of materials such as polymers, solvents, and non-solvents is crucial for the preparation of asymmetric membranes.

One commonly employed approach to modify the phase inversion process and improve process flexibility is the addition of a third component to the casting solution, which typically comprises a polymer and a solvent. This allows for the production of versatile membranes. Conventional additives consisting of polymers <sup>3-5</sup>, inorganic salts <sup>6</sup> and surfactants <sup>7, 8, 9</sup>, are frequently used for this purpose. Consequently, the incorporated additives in casting solution can affect membrane morphology and performance. However, this results in a highly complex thermodynamic/kinetic situation that is challenging to analyze and predict. The influence of these additives on membrane structure and performance largely depends on the non-solvent power of the additives, their concentration in the casting solution, and the specific

polymer/solvent system. Non-solvent additives can improve the hydrophilicity of the membrane, enhance pore formation, and create a spongy membrane structure by preventing the formation of finger-like macrovoids. The effect of non-solvent additives on macrovoid formation depends on their concentration in the casting solution. At low concentrations, they induce the formation of macrovoids. However, beyond a certain limit, a large number of stable polymer-lean nuclei are induced, inhibiting further growth of nuclei and macrovoid formation. This effect is reinforced by the decreased osmotic pressure difference near the non-solvent front during immersion in the coagulation bath<sup>10</sup>. Overall, the incorporation of non-solvent additives offers a convenient and effective way to develop high-performance membranes.

Numerous research studies have explored the role of non-solvent additives in the membrane preparation process<sup>11, 12, 13</sup>. Hydrophilic monomers have been used as additives in the casting solution to improve membrane performance. In-Chul et al.<sup>14</sup> reported that increasing the content of acetic acid in the casting solution resulted in lower coagulant value and higher viscosity due to a highly entangled solution conformation. This led to a decrease in flux and an increase in solute rejection. Another study by Ahmad<sup>15</sup> explored the effects of acrylic acid and 2-hydroxyethylmethacrylate on the morphology and performance of PES membranes. Their findings indicated that these additives had two primary effects on membrane formation: increasing the hydrophilicity of the membranes and altering the surface and sublayer morphology. In terms of polymer additives, particularly hydrophilic polymers like PVP<sup>4, 16</sup> and PEG<sup>5, 17, 18</sup>, have also been widely used as pore-forming agents in the casting solution. The concentration and molecular weight of these additives determine the structure of the resulting membrane<sup>19, 20</sup>. They affect the viscosity and hydrophilicity of the casting solution, as well as the interactions between the polymer, solvent, and non-solvent, thereby influencing the thermodynamics and kinetics of the phase inversion process. The addition of polymer additives destabilizes the polymer solution and promotes the diffusion of solvent out of the polymer chains in the coagulation bath. During phase inversion, it is assumed that the polymer additives are dissolved by water, creating micropores in their original locations. The presence of pore-forming agents increases the porosity of the membrane and prevents the formation of macrovoids, leading to higher flux and lower rejection<sup>17, 20</sup>. However, some studies have shown that the permeability of the membrane improves only up to a certain point with the addition of polymer additives. Beyond that point, the viscosity of the casting solution increases, slowing down the diffusion exchange rate of solvent and non-solvent during phase inversion<sup>13</sup>. In some cases, polymer additives have been found to act as pore-reducing agents rather than pore-forming agents<sup>5</sup>. In addition to hydrophilic non-solvent agents, the incorporation of surfactants shows a profound impact on membrane structure as they affect the interfacial properties between the coagulant and the polymer solution. Tsai et al.<sup>21, 22</sup> investigated the influence of sorbitan monoleate (Span 80) on polysulfone membranes and found that its addition into the casting solution suppressed the formation of macrovoids in asymmetric polysulfone membranes. Overall, the incorporation of non-solvent organic additives in the casting solution has proven to be an important technique in membrane preparation, allowing for the control of membrane morphology and the development of high-performance membranes.

However, despite being a competitive polymer, there is a scarcity of research focusing on the

influence of additives on the performance of PEI SRNF membranes. In our study, we aim to assess the effect of several non-solvent organic additives on the performance and morphology of PEI-based SRNF membranes. Three categories of organic additives, including hydrophilic monomers (acetic acid, acrylic acid, and acrylamide), hydrophilic polymers (PVP-K30, PEG-200, PEG-400) and surfactants (Tween and SDS) will be investigated in detail.

## 2. Experimental

### 2.1. Chemicals and materials

PEI (Ultem1000, General Electric) was used as the membrane material. The polymer was dried for 4 h at 150 °C prior to preparing casting solution. Dimethylacetamide (DMAc, AR grade, Tianjin Fuchen Chemicals, China) was used as the solvent. De-ionized water was used as coagulation media. Solution of methylene blue (MB, MW 374 Da, Beijing Chemicals) in ethanol was employed for testing membrane performance in organic solvent. PVP-K30 (AR, Guangdong Xilong Chemicals), PEG-200 (AR, Guangdong Xilong Chemicals), PEG-400 (AR, Guangdong Xilong Chemicals), Tween 20 (Sigma), Tween 40 (Sigma), Tween 60 (Sigma), Tween 80 (Sigma), SDS (Guangdong Xilong Chemical), acetic acid (Beijing Chemicals), acrylic acid (Beijing Chemicals) and acrylamide (Beijing Chemicals) were used as the additives. The other reagents used in our experiment include ethanol (EtOH, AR, Beijing Chemicals), isopropyl alcohol (IPA, AR, Beijing Chemicals), 1,6-Hexanediamine (HAD, AR, Sinopharm Chemicals), and de-ionized H<sub>2</sub>O. All chemicals were used without further purification.

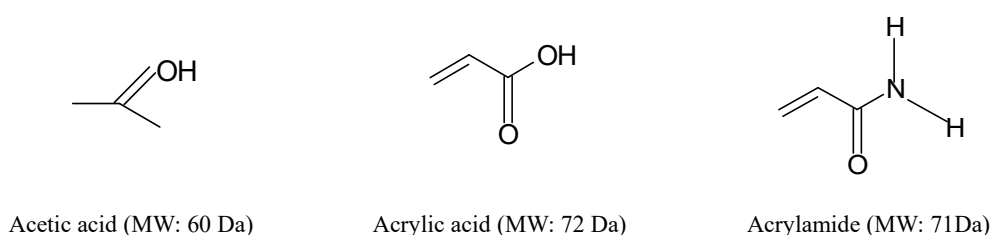


Illustration 1. The chemical structure of three hydrophilic monomers.

### 2.2. Membrane preparation

#### 2.2.1. preparation of casting solution

PEI (UT-1000) was dissolved at 50 °C with stirring in solvent (DMAc). After complete polymer dissolution, the casting solutions were kept at room temperature for 24 h to disengage air bubbles before membrane casting.

#### 2.2.2. Membrane casting and post-treatment

The homogeneous PEI (23 wt.%) dope solutions were used to casting 200 μm thick viscous film on a clear and smooth glass plate by an adjustable casting knife (Sheen 1117/150) on an automatic film applicator (Sheen 1137) with a speed of 3.0 m min<sup>-1</sup>. After casting, an evaporation period of 30 s was allowed before immersion into a de-ionized water coagulation bath for 10 min at room temperature, after which membranes were kept in de-ionized H<sub>2</sub>O for 24 h to remove all solvent.

Before a nascent membrane was used, all membranes were post-treated by a chemical crosslink method: (1) the membrane were immersed in IPA solvent exchange bath for 1 h; (2) the membranes were transferred from IPA to the crosslinking solution (10 wt% HAD in IPA) for 15 h. After that, the membranes were immersed in IPA to remove residual crosslinking solution in membrane pores; (3) the membranes were immersed in a conditioning solution (mixtures of poly (ethylene glycol) 400/IPA (60/40 wt%)) for overnight. Then, the membranes were removed from the conditioning solution and air dried to remove residual solvent from pores.

## 2.3. Characterization of the membranes

### 2.3.1. Filtration experiments

Before filtration, membranes were soaked in ethanol for at least 24 h. Filtration was carried out in a dead-end filtration cell (Sterlitech, HP4750) at a given pressure (100 psi or 200 psi) with a pressurized nitrogen cylinder. The effective surface area of the membrane was 0.00146 m<sup>2</sup> and 250 mL ethanol solution of MB at 35 µmol/L was charged in the cell. The solution was magnetically stirred at 200 rpm and the cell was immersed in a 35 °C water bath. After 30 min filtration, permeate samples were collected for flux and rejection measurements. Solvent flux (J) was determined by measuring volume of permeate (V) per unit area (A) per unit time (t) according to the following equation:

$$J = \frac{\Delta V}{A \cdot \Delta t} \quad (1)$$

Rejection rates (%) of dye solutes were calculated by:

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

where C<sub>p</sub> and C<sub>f</sub> denote the dye concentrations of permeates and feed solution, respectively. Concentrations of methylene blue in the permeate samples were analyzed by Shimadzu UV 2450-vis spectrophotometer at 652 nm. For each type of membrane, 3 coupons were cut and tested and the results were average values of these three measurements. Unless otherwise specified, filtration experiment was operated as following conditions: 35µmol/l MB in EtOH, 100 psi, 200 r/min, 35°C.

### 2.3.2. Membrane morphology

Scanning electron microscope (SEM, HITACH, S-4700) was used to obtain SEM images of cross-section of the prepared membranes. After membrane preparation, the membrane was dried in air and the samples were snapped in liquid nitrogen. Then, the membrane samples were mounted onto SEM stubs and coated with a thin gold layer. The SEM operating conditions were 12 mm working distance and 20 kV acceleration voltages.

## 3. Results and discussion

### 3.1 Effect of hydrophilic monomer additives

Fig. 1 shows the effect of hydrophilic monomer concentration in the casting solution on the ethanol flux and MB rejection of the prepared membrane. We found that the membrane flux reaches its maximum at a concentration of 1 wt% hydrophilic monomer and subsequently decreases. In contrast, the rejection exhibits an opposite trend, with the minimum value observed at an additive concentration of 1 wt%. The formation of phase inversion membranes



is controlled by two main factors: thermodynamics and kinetics, which are interconnected during the solidification of the cast film. Thermodynamics is associated with the phase equilibrium between the components in the system, while kinetics is related to the mutual diffusivities between them. When hydrophilic monomers are added to the casting solution, it increases the thermodynamic instability, promoting phase separation. However, it also leads to an increase in solution viscosity, which hinders the kinetics of phase separation. If the viscosity effect becomes significant or the diffusion delay outweighs the thermodynamic instability, the exchange rate between the solvent and nonsolvent is reduced. This ultimately results in a lower porosity of the sublayer in the formed membranes. With the incorporation of a small amount of hydrophilic monomer, the stronger affinity between hydrophilic monomers and the coagulant promotes instantaneous demixing of the membrane. This directly affects the formation of macrovoids in the membranes, as observed when compare membrane prepared using hydrophilic monomer additives with neat PEI membrane (Fig. 2A1-C1 and the picture in the upper right corner of Fig. 2A1). We found that the addition of a few hydrophilic monomers promotes the formation of membranes with increased macrovoids, leading to higher flux and decreased rejection. However, as more hydrophilic monomers are added, the viscosity of the casting solution increases, slowing down the exchange rate of solvent and non-solvent during phase inversion. Subsequently, the gradual reduction in macrovoids results in the top layer of the membrane becoming denser and thicker, ultimately forming a sponge-like structure (Fig. 2A4-C4).

Interestingly, it was also found that the effect of different hydrophilic monomers on membrane performance varies. For the case of 1 wt% hydrophilic monomer in the casting solution, the incorporation of acrylamide result in a higher flux than the incorporation of other two additives. This may be correlated with their distinct hydrophilic characteristic. From illustration 1, we can see that the molecular weight of these three hydrophilic monomers is close to each other. However, the hydrophilicity of the hydroxyl group (-OH) is stronger than that of the amino group (-NH<sub>2</sub>). In terms of hydrophilicity, these monomers can be ranked in the following order: acetic acid > acrylic acid > acrylamide. This means that acrylamide has a lower affinity for water. As a result, a casting solution containing acrylamide will undergo slower liquid-liquid demixing during phase inversion compared to a casting solution containing acetic acid or acrylic acid. Consequently, the incorporation of acrylamide leads to the formation of a denser membrane. As anticipated, it is apparent that the membrane structure obtained through the addition of acrylamide in the casting solution exhibits a denser structure with fewer finger-like macrovoids compared to the membranes prepared using acetic acid and acrylic acid as additives. This observation holds true across all additive concentrations tested (Fig. 2). However, with an acrylamide content of 1 wt% in the casting solution, the resulting membrane exhibits a dense structure, while also maintaining a high permeability. This could be attributed to the presence of larger finger-like pore sizes in the sublayer of the membrane, which contributes to its overall flux capacity. These data suggest that hydrophilic monomers facilitate for improving membrane flux at a lower addition concentration by forming more macrovoids. The development of sponge-like structures in membranes results from the higher addition concentration of hydrophilic monomers contributing to the decreased flux but increased rejection.

### 3.2. Effect of hydrophilic polymer additives

Next, we investigated the effects of three hydrophilic polymer additives on the membrane performance. It is shown that the ethanol flux reaches its peak value at a polymer additive dosage of 2 wt%. Subsequently, as the concentration of the polymer additive continues to increase, the flux progressively declines. In contrast, the rejection of membranes increases with increasing polymer concentration (Fig. 3). This result is consistent with S.A. Al Malek's report<sup>13</sup>. Previous research<sup>4, 12</sup> has assumed that the pore-forming agent is dissolved by water during the phase inversion process, and their original locations become micropores. Therefore, larger pores are expected with higher molecular weights of polymer additives. In our study, PVP-K30 has the highest molecular weight among three polymer additives. As anticipated, we observed a higher flux in membrane prepared with addition of PVP-K30 when compared with that of PEG-200 and PEG-400. It is evident that the macrovoids decrease and the pores become more interconnected with an increasing concentration of additives (Fig. 4). These results also indicate that the polymer concentration plays a crucial role in determining the final membrane thickness. With maximum PEG-200 or PEG-400 concentration, membranes exhibit a minimum membrane thickness compared to lower PEG concentrations. This can be explained by the slow exchange rate between the solvent and non-solvent during delayed demixing. The prolonged exchange process allows for a more uniform distribution, resulting in a uniform sponge-like membrane.

Notably, when the additive concentration reaches 8 wt%, we observed a distinct transformation in the membrane sublayer structure. The membranes containing PEG-200 or PEG-400 exhibit a fully sponge-like structure, whereas membranes with PVP still retain few macrovoids instead of a completely sponge-like structure. This distinct can be attributed to the variation in molecular weight between the additives. The smaller molecule weight of PEG-200 and PEG-400 enable them to act as a pore-forming agent, effectively reducing the formation of macrovoids. Conversely, the larger molecule weight of PVP-K30 contributes to the persistence of some macrovoids formed during its dissolution. This variation in membrane morphology highlights the influence of additive properties on the resulting membrane structure. Furthermore, we examined the microstructure of typical sponge-like and macrovoid features in membrane which was prepared with addition of PVP-K30. It is observed that there is no significant difference in the sponge-like structure among these membranes (Fig. 5A1-C1). However, there is a noticeable difference in the interconnectivity of the macrovoid structures. When the PVP dosage is 1 wt%, a well-organized and abundant microstructure of overlapped pores can be observed (Fig. 5A2). As the PVP-K30 dosage increases to 2 wt%, there is a shift towards larger-sized and more highly cross-linked pore structures (Fig. 5B2), which correlates with the observed increase in membrane flux. Moreover, with further increases in PVP-K30 content, both the size and quantity of the micro-pores noticeably decrease (Fig. 5C2). It is known that such a structure hinders the filtration of solutions, resulting in a decline in membrane flux. Taken together, these results suggest that the incorporation of a pore-forming agent facilitates the formation of macrovoids structures within the membrane in a specific range of addition, consequently enhancing the membrane's flux. Nonetheless, excessive addition of the agent leads to a decline in the membrane's flux while improving its retention capacity. Additionally, the molecular weight of pore-forming agent plays an important role in shaping microstructure

of membrane macrovoids.

### 3.3. Effect of surfactant additives

Another option for controlling the membrane formation process is introducing the surfactants additive in the casting solution, which has a significant impact on the structure of membranes by affecting the interfacial properties between the coagulant and the polymer solution<sup>8,21</sup>. When a hydrophilic coagulant, typically water, is used, hydrophilic surfactants can enhance the formation of macrovoids, whereas hydrophobic surfactants cannot. Conversely, when a hydrophobic coagulant is used, hydrophobic surfactants are more effective in altering the membrane structure than hydrophilic surfactants. Therefore, the miscibility between the added surfactants and the coagulant is crucial in the macrovoid formation process. In Lin's study<sup>23</sup>, it was found that the addition of appropriate surfactants can enhance the affinity between the solvent and the coagulant, leading to a shift from delayed demixing to instantaneous demixing. This shift promotes the formation of macrovoids. Tsai et al.<sup>21, 22, 24</sup> investigated the effects of Span-80 on PSF membranes and found that the introduction of Span-80 in the casting solution can suppress the formation of macrovoids. A study by A. Rahimpour<sup>9</sup> indicated that adding a small amount of SDS, an anionic surfactant, to the casting solution can induce the formation of macrovoids. Therefore, surfactants can play a crucial role in controlling the membrane structure by influencing the demixing process and promoting or inhibiting the formation of macrovoids and finger-like pores in the sublayer, depending on their hydrophilic or hydrophobic nature and their compatibility with the coagulant<sup>25</sup>.

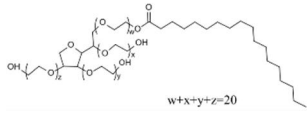
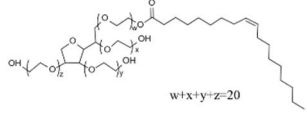
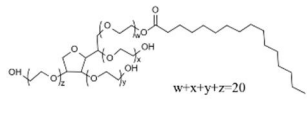
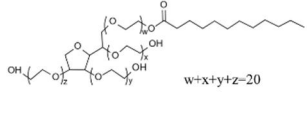
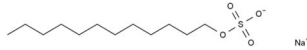
#### 3.3.1. Effect of Tween surfactants

The impact of Tween surfactants on membrane performance is demonstrated in Fig. 6 and the detailed information about these surfactants is listed in Table 1. Upon correlating the filtration results of membranes prepared using four different Tween surfactants at the same additive concentration with their corresponding HLB values, a clear trend emerged. It was observed that the membrane flux decreases as the HLB value of the surfactant increases, while rejection increases. Generally, for a hydrophilic coagulant, hydrophilic surfactants can enhance the formation of macrovoids by facilitating the affinity between the solvent and coagulant. This suggests that a higher HLB value surfactant may result in a stronger affinity between the solvent and coagulant, leading to faster demixing of the membrane and the induction of more macrovoids. In our study, we observed significant changes in the SEM images of the membrane cross-section with the increase of HLB value of the surfactant (Fig. 7A1-D1). The addition of surfactants with higher HLB values, such as Tween 20, promotes the formation of larger finger-like macrovoids in the sublayer of the membrane, while simultaneously reducing the porosity of the top layer. It is shown that the enlarged top layer morphology of the membrane exhibits a reduction in pore size when Tween 20 was used as an additive, while no significant differences in pore size were observed among the other membranes (Fig. 7A2-D2). Furthermore, a comparison between membranes prepared with Tween 20 and Tween 60 revealed that the former exhibits a thicker top layer with increased pore connectivity. This thicker top layer and its lower porosity are responsible for lower flux but higher retention. Most surfactants contain a hydrophobic alkali and a hydrophilic ionic group (polar group) in their structure. When these surfactant molecules enter an aqueous medium, the hydrophilic group tends to associate with

the water phase, while the hydrophobic group tends to move away from water. As a result, many surfactant molecules accumulate at the interface between the coagulant and the polymer solution. Surfactants with higher HLB values exhibit a stronger propensity to accumulate at the solvent/non-solvent exchange interface. The accumulation of surfactant molecules hinders the rate of exchange between the solvent and non-solvent (Fig. 8). Consequently, membranes with a denser top layer structure are obtained with an increase in the HLB value of the surfactant added to the casting solution. Therefore, membrane flux decreases with increasing HLB values of surfactants, while rejection increases.

**Table 1**

Detailed information about surfactants in experiments.

Surfactant	Chemical formula	HLB value	Structure
Tween 60	$C_{64}H_{126}O_{26}$	14.5	
Tween 80	$C_{64}H_{124}O_{26}$	15	
Tween 40	$C_{62}H_{122}O_{26}$	15.6	
Tween 20	$C_{58}H_{114}O_{26}$	16.7	
SDS	$C_{12}H_{25}SO_3Na$	40	

Taken together, our experimental findings establish a correlation between Tween surfactant impact on membrane performance and their HLB values. The presence of surfactants not only affects the formation of sublayer's finger-like macrovoids but also influences the porosity of the top layer. Surfactants with higher HLB values facilitate the formation of larger finger-like macrovoids in the sublayer and the induction of a thicker top layer, leading to decreased flux and increased rejection. Thus, the HLB value of the surfactant significantly affects its ability to modify the morphology and performance of the membrane.

### 3.3.2. Effect of sodium dodecyl sulfate (SDS) surfactant

In addition to the non-ionic Tween surfactants, we also investigated the impact of the anionic surfactant SDS on membrane performance and structure. It is shown that the ethanol flux displays a rising trend with increasing SDS concentration in the casting solution. The flux reaches its peak at an SDS addition of 1.5 wt% and then gradually decreases (Fig. 9). This observation aligns with the findings reported by A. Rahimpour<sup>9</sup>. In specific, the peak flux is nearly 10 times higher for the membrane prepared with the addition of SDS compared to membranes without SDS. On the other hand, MB rejection decreases as the SDS concentration increases. The data reveals that the addition of 0.5 wt% SDS leads to a 26% decrease in rejection.

The SEM images showing the membrane's cross-section and top layer, demonstrate that incorporating a small amount of SDS into the casting solution induces macrovoids formation in the membrane's sublayer, especially at 1.5 wt% of SDS, can be responsible for the higher flux. Moreover, the images of the membrane's top layer indicate that a more interconnected and sticky structure was observed with increasing SDS content in the casting solution, especially at 2 wt% and 2.5 wt% of SDS (Fig. 10).

The exist of SDS surfactant in the casting solution can potentially impact the membrane formation process in two ways: (1) a decrease in the rate of solvent evaporation, and (2) a reduction in the interaction between polymer chains resulting from the formation of a polymer-surfactant complex. SDS, being amphiphilic with a hydrophilic head and hydrophobic tail, forms a layer of SDS molecules on the surface of the casting film due to the hydrophilic nature of DMAC solvent. Consequently, reducing the rate of solvent evaporation and resulting in slower growth of the highly concentrated polymer in the casting solution. Additionally, for casting solutions containing 2 wt% and 2.5 wt% SDS, the SDS molecules and polymer are likely to form a micelle-like complex in the solution, while the excess free hydrophilic groups of SDS repel each other in the casting solution. The formation of this complex reduces the interaction between the polymer chains. During the membrane formation process, the repulsive forces between SDS molecules corrupt the pore and leave defects in the membrane structure (Fig. 8). Both of these phenomena result in a delayed demixing of the casting solution during the phase separation process when SDS is present. This delay, in turn, creates a more conducive environment for the formation of finger-like pores in the sublayer. While the growth of the top layer, which primarily determines membrane rejection, is hindered. As a result, the membrane flux decreases with higher SDS concentration in the casting solution. And a declined rejection was observed with the increase of SDS content in the casting solution. Thess data suggest that the incorporation of SDS in the casting solution facilitates improving membrane flux, but impairs their retention performance.

#### 4. Conclusions

This study examined the influence of three organic additives, specifically hydrophilic monomers, hydrophilic polymers, and surfactants, on membrane performance and morphology. The results of our experiment indicate that hydrophilic monomers can enhance membrane flux at a lower addition concentration by creating more macrovoids. The development of sponge-like structures in membranes results from the further addition of hydrophilic monomers contributing to the decreased flux but increased rejection. In terms of hydrophilic polymers with a pore-forming function, it shows that the incorporation of additives facilitates the formation of macrovoids structures within the membrane in a specific range of addition. Specifically, PVP-K30 maintains the ability to generate few macrovoids structures in the sublayer of the membrane, even with the addition of higher content in the casting solution, owing to its higher molecular weight. Regarding the surfactants effect, our results indicate a correlation between the impact of Tween surfactants on membrane performance and their HLB values. The membrane flux decreases with increasing HLB values of surfactants, while rejection increases. However, the incorporation of SDS in the casting solution facilitates improving membrane flux, but impairs their retention performance.

**Conflict of interest statement**

The authors declare that there are no conflicts of interests.

**Data availability and reproducibility statement**

The numerical data from Figures 1, 3, 6 and 9 are tabulated in Tables S1–S4. Error bars (where shown) in Figures 1, 3, 6 and 9 show the spread of data observed in triplicate measurements, where independent samples were tested for each measurement.

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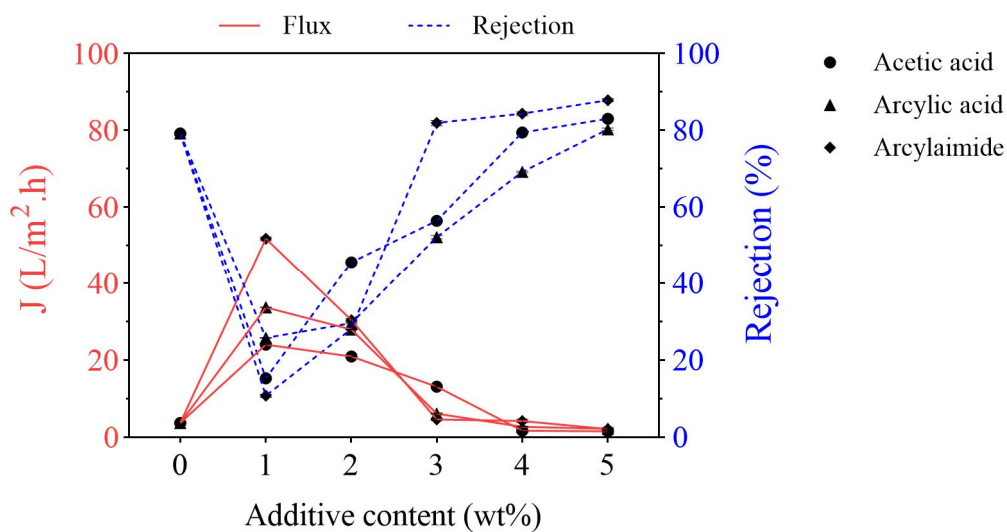


Fig. 1. Influence of three hydrophilic monomer additives on the EtOH flux and MB rejection of PEI membranes.

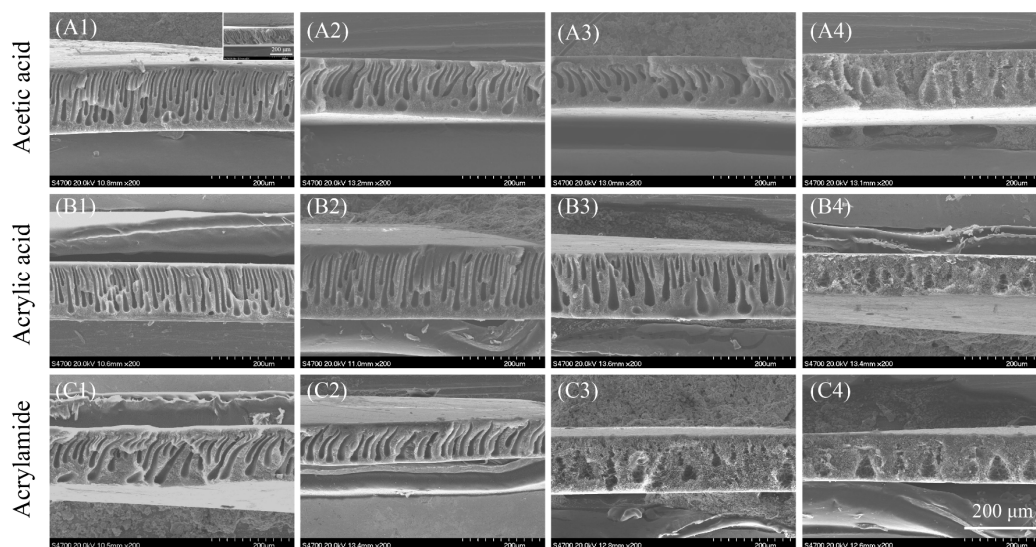


Fig. 2. Influence of the three hydrophilic monomers additives on the morphology of PEI membranes. The content of additives is: (A1-C1) 1 wt%; (A2-C2) 2 wt%; (A3-C3) 3 wt%; (A4-C4) 4 wt%. The picture in the upper right corner of A1 is neat PEI membrane without any additives.

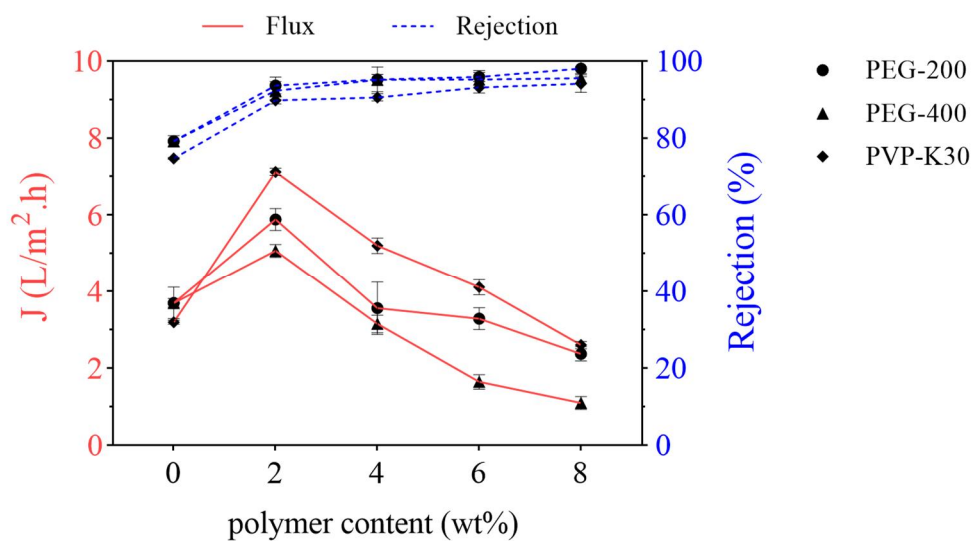


Fig. 3. Influence of three hydrophilic polymeric additives on the EtOH flux and MB rejection of PEI membranes. Filtration experiment was conducted under pressure of 200 psi.

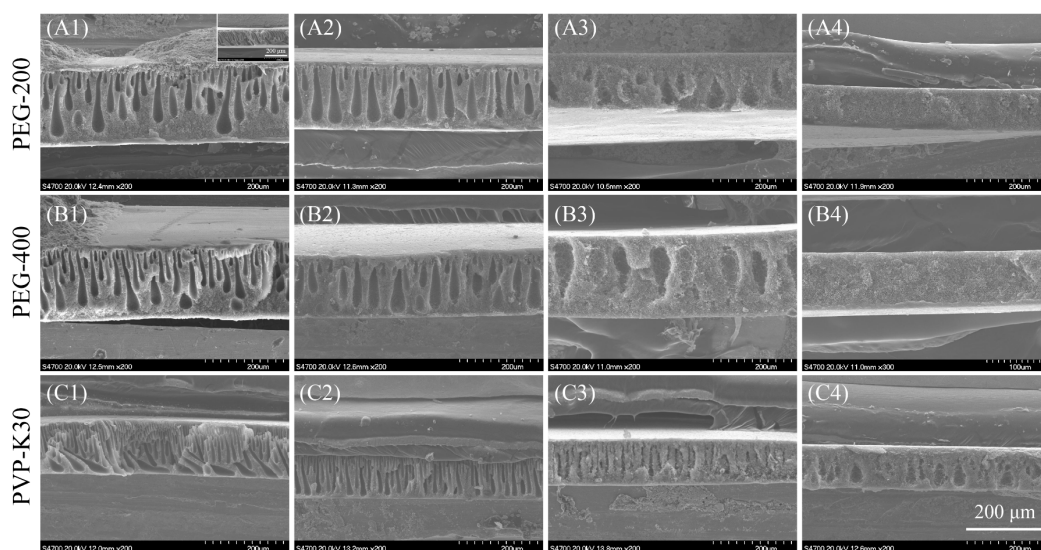


Fig. 4. Influence of the three hydrophilic polymeric additives on the morphology of PEI membranes. The content of additives is: (A1-C1) 1 wt%; (A2-C2) 2 wt%; (A3-C3) 4 wt%; (A4-C4) 8 wt%. The picture in the upper right corner of A1 is PEI membrane without any additives.

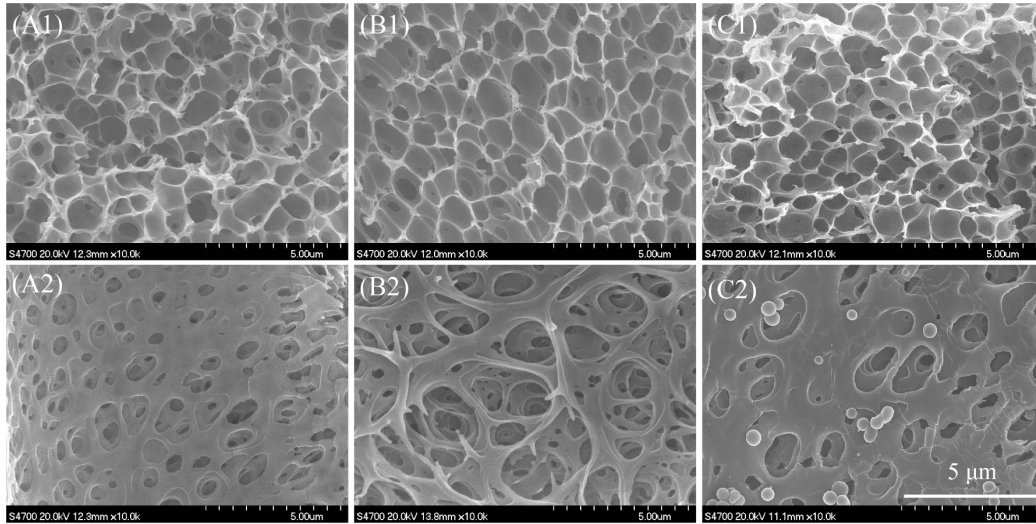


Fig. 5. The microstructure of sponge-like and macrovoids structure in PEI-based membranes when adding 1 wt% (A1 and A2), 2 wt% (B1 and B2) and 4 wt% (C1 and C2) PVP-K30 in casting solution. A1-C1 are sponge-like structure; A2-C2 are macrovoids structure.

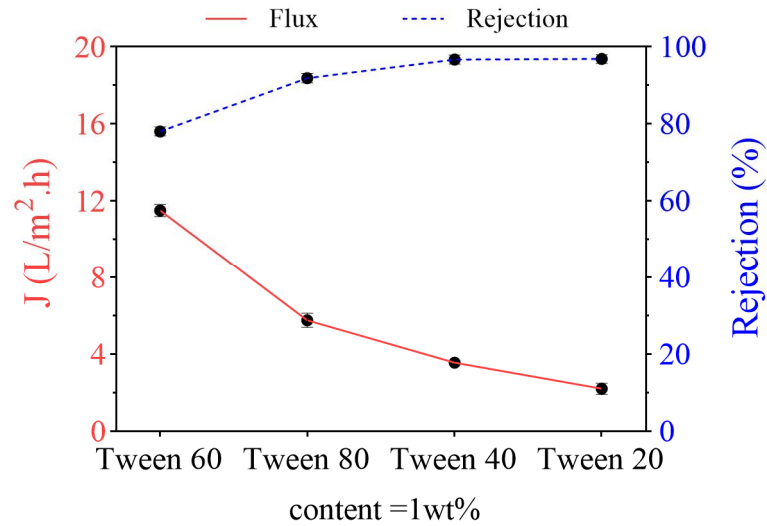


Fig. 6. Influence of the four Tween surfactants on the EtOH flux and MB rejection of PEI membranes. The content of surfactant is 1 wt%.

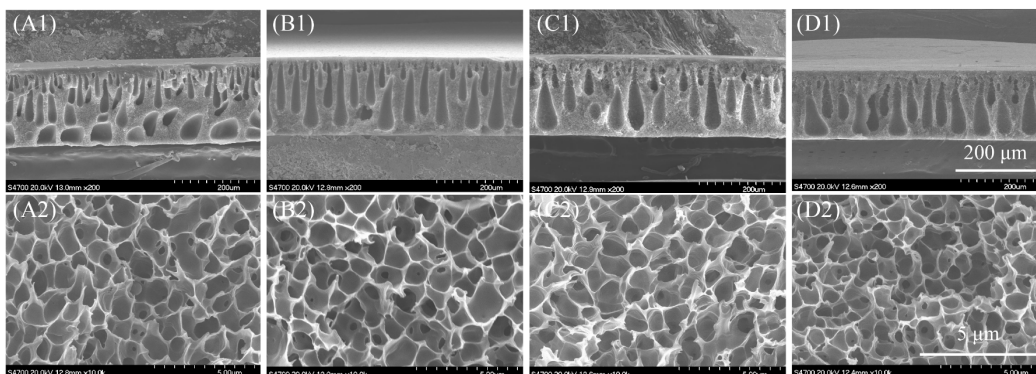


Fig. 7. Influence of the Tween surfactant additives (1 wt%) on the morphology of PEI membranes. A1 and A2: Tween



60; B1 and B2: Tween 80; C1 and C2: Tween 40; D1 and D2: Tween 20. (A1-D1) are the cross-section structures; (A2-D2) are the top layer structures.

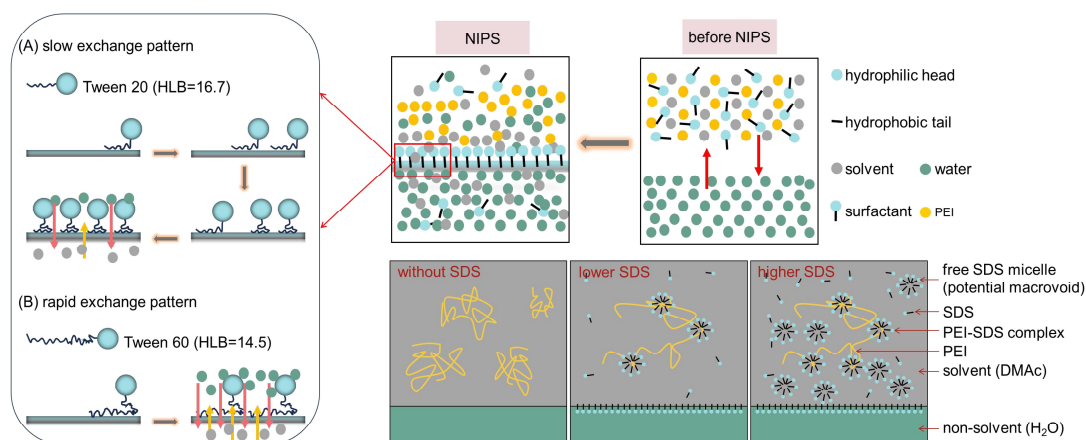


Fig. 8. Effect of the tween or SDS additives on the phase separation process.

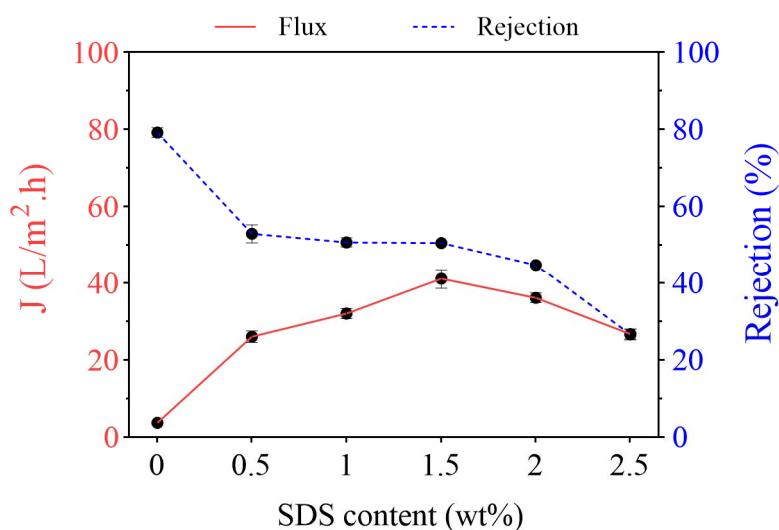


Fig. 9. Influence of SDS surfactant additive on the EtOH flux and MB rejection of PEI membranes.

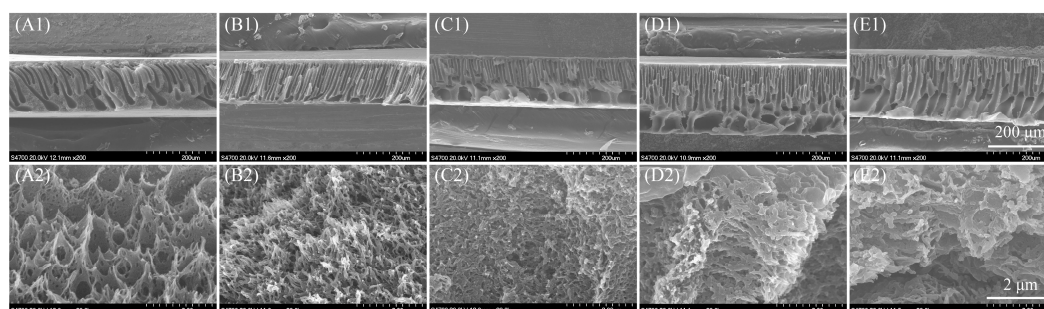


Fig. 10. Influence of the SDS surfactant additives on the morphology of PEI membranes: (A1-A2) 0 wt%, (B1-B2) 0.5 wt%, (C1-C2) 1.5 wt%, (D1-D2) 2.0 wt%, (E1-E2) 2.5 wt%. (A1-E1) are the cross-section structures; (A2-E2) are the top layer structures.

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