

Article

## Effects of Additives on the Morphology and Performance of PPTA/PVDF *in Situ* Blend UF Membrane

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**Abstract:** Poly(*p*-phenylene terephthalamide) (PPTA), a high-performance polymer with high modulus and good hydrophilicity, is often used as a reinforced material. However, due to its high crystallinity, micro-phase separation often occurs in the blends. In this paper, PPTA/poly(vinylidene fluoride) (PVDF) compatible blend solution was synthesized by *in situ* polycondensation. Blend ultra-filtration membrane was prepared through the immersion phase inversion process. In order to obtain desired pore structure, the effects of different additives including hydrophilic polymer (polyethylene glycol (PEG)), inorganic salt (lithium chloride (LiCl)) and the surfactant (Tween-80) on the morphology and performance of PPTA/PVDF blend membranes were studied. The membrane formation process was investigated through ternary phase diagram (thermodynamics) and viscosities (kinetics) analysis. It was found that, with the increasing of LiCl content, a porous membrane structure with long finger-like pores was formed due to the accelerated demixing process which resulted in the increase of porosity and pore diameter as well as the enhancement of water flux and the decline of PEG rejection. When Tween content increased to over 3 wt%, dynamic viscosity became the main factor resulting in a decreased phase separation rate. The transfer of PEG and LiCl molecules onto membrane surface increased the surface hydrophilicity. The effect of Tween content on membrane hydrophilicity was also correlated with the compatibility of blend components.

**Keywords:** poly(*p*-phenylene terephthalamide); poly(vinylidene fluoride); additive; membrane formation mechanism; morphology; separation performance

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## 1. Introduction

Due to its excellent chemical and mechanical properties, poly(vinylidene fluoride) (PVDF) ultrafiltration (UF) membrane has been widely used in water and wastewater treatment and bio-separation [1,2]. However, the strong hydrophobicity contributed to the flux decline and frequent back-flushing operation which will induce the deterioration of membrane mechanical strength and even membrane rupture. Therefore, it is very important to enhance the hydrophilicity and mechanical strength of PVDF membrane. Poly(*p*-phenylene terephthalamide) (PPTA), a high-performance polymer with high modulus and good hydrophilicity, is often used as a reinforced material. However, due to its high crystallinity, micro-phase separation often happens during the conventional blending process. In our previous study, PPTA/PVDF blend membrane with excellent hydrophilicity was successfully prepared by *in situ* polycondensation to overcome the phase separation [3].

During the immersion phase inversion process, thermodynamic and kinetic properties of the casting solution are the two important aspects which influence the morphology and properties of the final membranes. For the blend membranes, the blending ratio, polymer concentration and the selection of solvent and nonsolvent play a crucial role in influencing these two aspects. However, in order to obtain the desired membrane pore structure, the application of different additives is essential. Many researchers have attempted to explain the membrane-forming mechanism from the changes of kinetic and thermodynamic properties of casting solution during the phase inversion process when a suitable additive is introduced into the casting solution [4–7]. The incorporation of a small amount of hydrophilic polymers such as polyethylene glycol (PEG) or polyvinyl pyrrolidone (PVP) always have the trend to form macrovoids while the macrovoids would be suppressed at high content of additives [8,9]. Pagidi [10] added polymeric additives such as polyvinylpyrrolidone (PVP), polyetherimide (PEI), PEG and polyethersulfone (PES) in order to achieve both higher permeation flux and fouling resistance of polysulfone (Psf) membrane. The presence of PVP increased the instability and viscosity of casting solution which favored the instantaneous demixing and led to the formation of macrovoids in the membrane structure. Psf membranes with PVP as additives showed the highest pure water flux and the strongest anti-fouling resistance. In addition, the introduction of inorganic additives could accelerate the phase separation rate and contribute to a membrane structure with lots of interconnected pores. The resulted membrane exhibits excellent mechanical strength and thermal stability [11,12]. Ebert [13] investigated the influence of TiO<sub>2</sub> as inorganic filler in poly(vinylidene fluoride) (PVDF) and polyamideimide (PAI) membranes on the membrane compaction behavior. Results indicated that the addition of 40 wt% TiO<sub>2</sub> greatly enhanced the anti-compaction properties of PVDF membrane even though more finger-like pores were formed in the modified membrane. Amirilargani [14] has found that the addition of small amounts of hydrophilic surfactants such as Tween-80 would increase the formation of macrovoids and finger-like pores in the sub-layer of the polyethersulfone (PES)

membranes. In order to obtain desired membrane morphology, it is necessary to investigate the effect of additives on the morphology and performance of PPTA/PVDF blend membrane.

Our previous study [3] was a preliminary investigation on the preparation of PPTA/PVDF porous membrane which was mainly centered on the effect of different blending ratio of PPTA/PVDF on the rejection and water flux. In addition, the membrane formation mechanism was not explained. This paper aimed to explore the effect of different kinds of additives on the morphology and separation performance of PPTA/PVDF *in situ* blend membranes. Membrane formation mechanism was studied through the thermodynamic and kinetics properties of the casting solution. The correlations among the formation process, membrane morphology and performance were also investigated.

## 2. Experimental Section

### 2.1. Materials

Poly(vinylidene fluoride) (PVDF, FR-904,  $\eta_{inh} = 1.6$  dL/g) powder was supplied by Shanghai 3F New Materials Co. Ltd., China. *P*-phenylene diamine (PPD,  $\geq 99\%$ ), terephthaloyl dichloride (TPC,  $\geq 99\%$ ), *N*-methyl-2-pyrrolidone (NMP,  $\geq 99\%$ ) and anhydrous LiCl ( $\geq 99\%$ ) were obtained from Aladdin Co. Ltd., Shanghai, China. Polyethylene glycol (PEG,  $M_w = 20,000$  and  $100,000$ ) and Tween-80 were provided from Tianjin Kemiou Chemical Reagent Co. Ltd., China. LiCl powder was calcined at  $400$  °C prior to be used.

### 2.2. The Synthesis of PVDF/PPTA Blend Casting Solution

PVDF and LiCl (2 wt%) powders were dissolved in NMP at  $60$  °C. A certain amount of *p*-phenylene diamine (PPD) was added into the solution at ambient temperature, and then terephthaloyl chloride (TPC) powder (TPC/PPD 1.01/1, molar ratio) was poured into the system at  $5$  °C under rigorous stirring for 1 h. Then the temperature was increased to  $65$  °C. Additives with different compositions including 6 wt% PEG-20,000, 6 wt% LiCl, 4 wt% PEG-20,000 + 2 wt% LiCl and 4 wt% PEG-20,000 + 1 wt% LiCl + 1 wt% Tween-80 were introduced into the solution. Two hours later, *in situ* polycondensation was completed and the reaction solution was degassed for 12 h at room temperature. Polymer concentration and blending ratio of PPTA/PVDF were fixed at 18 wt% and 20/80, respectively. The casting solution above was used to investigate the thermodynamic properties.

In addition, additives composed of PEG-20,000 (0–8 wt%), LiCl (0–5 wt%) and PEG-20,000 (4 wt%) + LiCl (1 wt%) + Tween-80 (0–4 wt%) were also introduced into blend solution to investigate the effect of additive content on membrane formation process. The viscosity of casting solution was measured by oscillatory rheological testing on a controlled-strain RVDV-II+P Digital Viscometer (Brookfield engineering laboratories, Middleboro, MA, USA) at  $25$  °C.

### 2.3. The Preparation of PVDF/PPTA Blend Membrane

The resulted casting solution was cast onto cleaned glass plates at ambient temperature using a stainless steel casting knife with a gap distance of  $250$   $\mu\text{m}$ . Then, the plates were immersed immediately in deionized water. Nascent membrane was washed with deionized water several times and then stored in 5 wt% NaHSO<sub>3</sub> aqueous solution.

#### 2.4. Ternary Phase Diagram of PPTA-PVDF/NMP/Water System

The ternary phase diagrams of different casting solution were obtained through cloud point titration measurements as reported in previous literature [15–17]. The cloud point data were measured through titration method by adding water slowly into the polymer dope under vigorous agitation at 25 °C. The cloud point was obtained when local precipitation emerged and the solution would not turn homogeneous again. If not, continue to add water slowly into the polymer dope under vigorous agitation. As we know, the gel is usually metastable and its formation generally undergoes imperceptible changes after a long time. In order to avoid potential sources of reduced reproducibility, the time after adding water was extended to 4 h to well observe whether gel was formed or not under a microscope. The compositions at the cloud point were calculated by weight. Each cloud point of casting solutions was measured for three times and calculated average. A series of demarcation points (liquid-liquid demixing or gelatin) is obtained. The demarcation boundary can be reached by connecting the demarcation points. Gelatin value ( $G_v$ ) was the weight ratio of nonsolvent in casting solution at the cloud point and was obtained as follows:

$$G_v = \frac{m_{ns}}{m_c + m_{ns}} \times 100\% \quad (1)$$

where  $m_{ns}$  and  $m_c$  were the weight of nonsolvent and initial casting solution, respectively.

#### 2.5. Characterization of Membrane Morphology and Parameter

The morphology and parameter of blend membranes with different additives including PEG-20,000 (0–8 wt%), LiCl (0–5 wt%) and PEG-20,000 (4 wt%) + LiCl (1 wt%) + Tween-80 (0–4 wt%) respectively, were investigated.

##### 2.5.1. Field Emission Scanning Electron Microscopy (FESEM)

Surface and cross-section morphologies of membranes were observed through the field emission scanning electron microscope (FESEM, Hitachi, S-4800, Tokyo, Japan). Membrane samples were freeze-fractured and coated with gold before FESEM examination.

##### 2.5.2. Porosity and the Mean Pore Size

Membrane porosity ( $\varepsilon$ ) was calculated by the ratio of pore volume to geometrical volume of the membranes [18]:

$$\varepsilon = \frac{(W_w - W_d)\rho}{SL} \quad (2)$$

where  $W_w$  and  $W_d$  were the weight of wet membranes (g) and dried membranes (g), respectively.  $S$ ,  $L$ , and  $\rho$  were the membrane area ( $\text{cm}^2$ ), average thickness (cm) and pure water density ( $\text{g cm}^{-3}$ ).

The average effective through-pore size of blend membranes was measured by means of a capillary Flow Porometer CFP 1500 AEXL (Porous materials Inc., Ithaca, NY, USA) as described before [19].

Membrane pore size was very difficult to accurately determine for its complicated pattern. Average pore size in present work was investigated by filtration velocity method. The volume of permeate water was obtained using an ultrafiltration cell connected to a compressed nitrogen gas flow. The transmembrane pressure was regulated to 0.1 MPa in case of excessively deformation of pore structure, the permeate water was collected once gas pressure reached stable. Average pore size was calculated following the revised Guerout-Elford-Ferry Equation [20]:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q_T}{\varepsilon \times A \times \Delta P}} \quad (3)$$

where  $\varepsilon$  was membrane porosity (%),  $\eta$  the water viscosity (Pa·s),  $l$  the membrane thickness (m),  $Q_T$  the permeate water per unit time ( $\text{m}^3 \cdot \text{h}^{-1}$ ),  $\Delta P$  the operational pressure (Pa) and  $A$  the effective membrane area ( $\text{m}^2$ ).

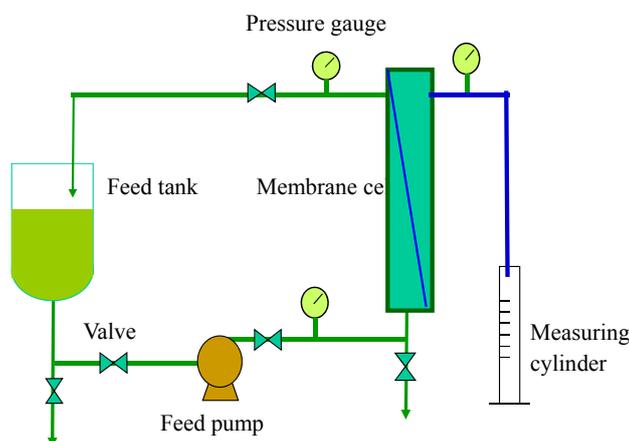
## 2.6. Characterization of Membrane Performance

The performance of blend membranes with different additives including PEG-20,000 (0–8 wt%), LiCl (0–5 wt%) and PEG-20,000 (4 wt%)+LiCl (1 wt%)+Tween-80 (0–4 wt%) respectively, were investigated.

### 2.6.1. Permeation Flux (F) and PEG Rejection (R)

The permeation tests of membranes were carried out in a cross-flow filtration cell at 25 °C with an effective membrane area of 33.2  $\text{cm}^2$  as illustrated in Scheme 1.

**Scheme 1.** Schematic diagram of the cross-flow filtration unit.



Membranes were initially pre-compacted at 0.20 MPa to get a steady flux. Then, water flux was measured at 0.10 MPa and calculated by the following equation [21]:

$$F = \frac{V}{At} \quad (4)$$

where  $F$  was the water permeate flux ( $\text{L} \cdot \text{m}^{-2} \text{h}^{-1}$ );  $V$  was the water permeation volume (L);  $A$  and  $t$  were the effective membrane area ( $\text{m}^2$ ) and filtration time (h), respectively.

The PEG concentrations in the feed and the permeate solutions were measured by a UV-Vis spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co. Ltd., Beijing, China) at a wavelength of 510 nm, respectively. The rejection ( $R$ ) is calculated as:

$$R = 1 - \frac{C_p}{C_f} \quad (5)$$

where  $C_p$  and  $C_f$  were PEG concentrations in the permeate and feed solutions, respectively.

### 2.6.2. Water Contact Angle Measurement (WCA)

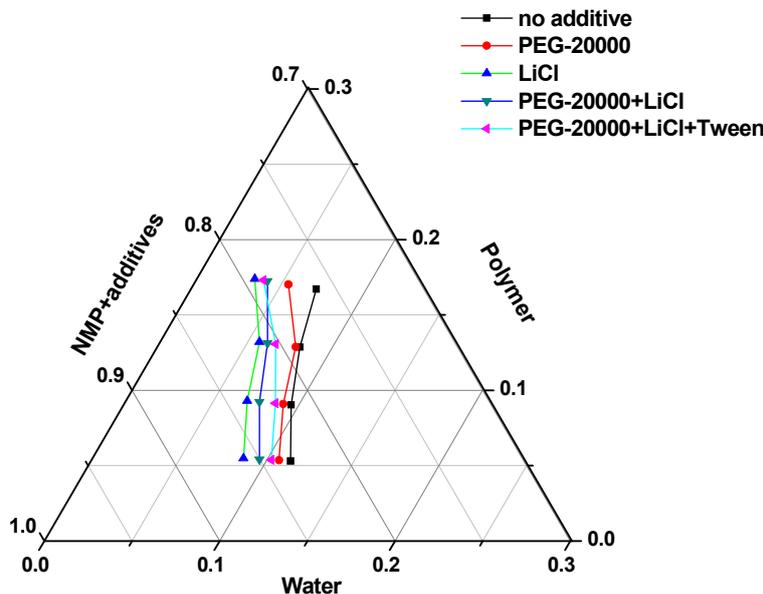
Water contact angle (WCA) of membrane surface was determined on a Kruss Instrument (CM3250-DS3210, Munich, Germany) at ambient temperature.

## 3. Results and Discussion

### 3.1. Thermodynamics of Membrane Formation

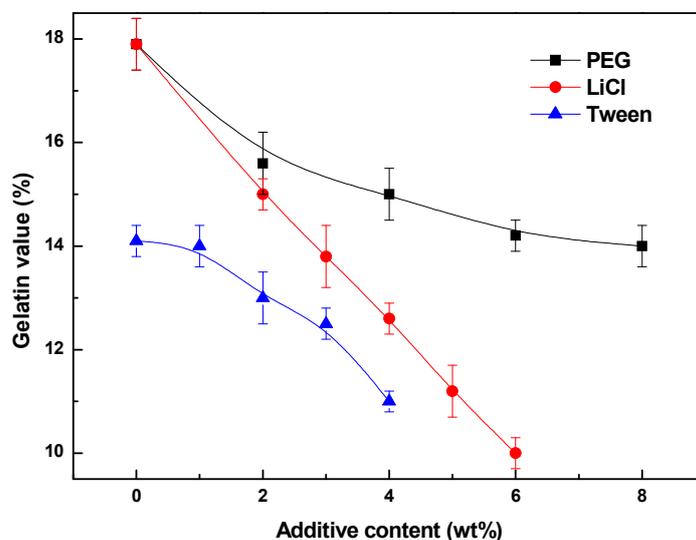
The distance between the the isothermal cloud point curve and the solvent axis reflects the extent of thermodynamic stability of the casting solution. Figure 1 showed the effect of different additives on ternary phase diagram of PPTA-PVDF/NMP/water system. It could be seen that upon the nonsolvent diffusion into the casting solution, the introduction of additives into the solution broke the system thermodynamic equilibrium and the system tended to be unstable. Since PVDF is a crystalline polymer, only the gelatin was firstly observed during the measurement process of the cloud point. The similar phenomenon was also obtained in other literatures [22,23]. Thus, the obtained data reveal gelation equilibrium of the PPTA-PVDF/NMP/water with different additives. When LiCl was added, the gel equilibrium line was closer to the solvent axis which indicated that the gel was more prone to be induced than using the other two kinds of additives. Some researchers attributed this to the strong polarity of LiCl which initiated the PVDF crystallization in casting solution [24]. And thereby the phase separation was induced at lower nonsolvent concentration. Additionally, the position of the gel equilibrium line of compound additive (PEG + LiCl) was between the lines of PEG and LiCl and was more approached the line of LiCl. This indicated that LiCl played a very important role on the thermodynamic stability of the casting solution. The addition of a small amount of LiCl would break the system thermodynamic equilibrium. While using compound additive (PEG + LiCl + Tween), the thermodynamic property of the casting solution was more stable than that of compound additive PEG + LiCl. This was because that with the introduction of the hydrophilic surfactant (Tween) the compatibility between polymer and inorganic additives was improved and the meta-stable structure of the casting solution was well adjusted. Moreover, the surfactant could form micelles with the solvent which were not easy to congregate into big micelles [14]. As a result, the solvent and nonsolvent exchange rate became more consistent as well as improving the thermodynamic stability of the casting solution. These favored the formation of small and uniform pores.

**Figure 1.** Ternary phase diagram of poly(*p*-phenylene terephthalamide) (PPTA)-poly(vinylidene fluoride) (PVDF)/*N*-methyl-2-pyrrolidone (NMP)/additives/water system at 30 °C.



The effects of additive contents on the thermodynamic properties of membrane casting solution were further studied through the variations of gelatin value as shown in Figure 2. It could be seen that with the increasing of the additive content, all the gelatin values of different casting solution were reduced, indicating that the nonsolvent capacity gradually decreased with the introduction of the additive. Moreover, the gelatin value declined more significantly with the increasing of LiCl content than that of the other additives. When the Tween content was below 3 wt%, the gelatin value decreased slowly and then it was followed by a quick decline when the Tween content continued to increase over 4 wt%. It indicated that the effect of Tween concentration on the thermodynamic properties of casting solution became apparently only when Tween content was higher than 3 wt%.

**Figure 2.** Effect of additive content on gelatin value at 30 °C.



### 3.2. Kinetics of Membrane Formation

The effects of different additives on the dynamic viscosity of casting solution were listed in Table 1. It could be found that the influence of LiCl content on the viscosity was the most significant and the viscosity value was much larger than that of using PEG and Tween as additives. This was due to the interaction between the electron donating groups  $\text{Li}^+$  and PVDF segments, and the interaction also existed between PVDF and NMP molecules. It facilitated the formation of an interconnected network structure composed polymer-additive-solvent. This network structure gradually developed with the increasing of LiCl content. Consequently, the viscosity significantly increased [25].

As for the polymer additive PEG, when the PEG content was low, the additive and polymer could be fully extended in the solvent resulting in a low viscosity. However, when PEG content increased over 6 wt%, the polymers compatibility became poor resulting in the emergence of local PVDF crystallize and the formation of the gel. Consequently, the solution viscosity increased greatly.

The effects of the surfactant (Tween) on the membrane formation process were explained from the two aspects below. On the one hand, the addition of fewer Tween could form small micelles with polymer additive, inorganic additive and solvent. Large micelles were suppressed due to surface tension of Tween, which increased the casting solution viscosity. The phase separation rate would be decreased and the solvent-nonsolvent exchange rate was more consistent with lots of uniform small pores. While adding large amounts of Tween, the small micelles composed of surfactant-polymer-solvent-additive would be destroyed, large molecules would be entangled resulting in the higher solution viscosity. The solvent and nonsolvent diffusion rate will be blocked.

**Table 1.** The dynamic viscosity of the solution dope with different additives.

<b>Additive Content (wt%)</b>	<b>0</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
Dynamic viscosity (Pa·s) of the dope with LiCl	15.1	–	29.6	54.3	91.6	218.4	–	–	–
Dynamic viscosity (Pa·s) of the dope with PEG	15.1	–	20.1	–	43.2	–	65.6	–	121.0
Dynamic viscosity (Pa·s) of the dope with Tween	45.1	55.6	60.2	76.5	89.1	–	–	–	–

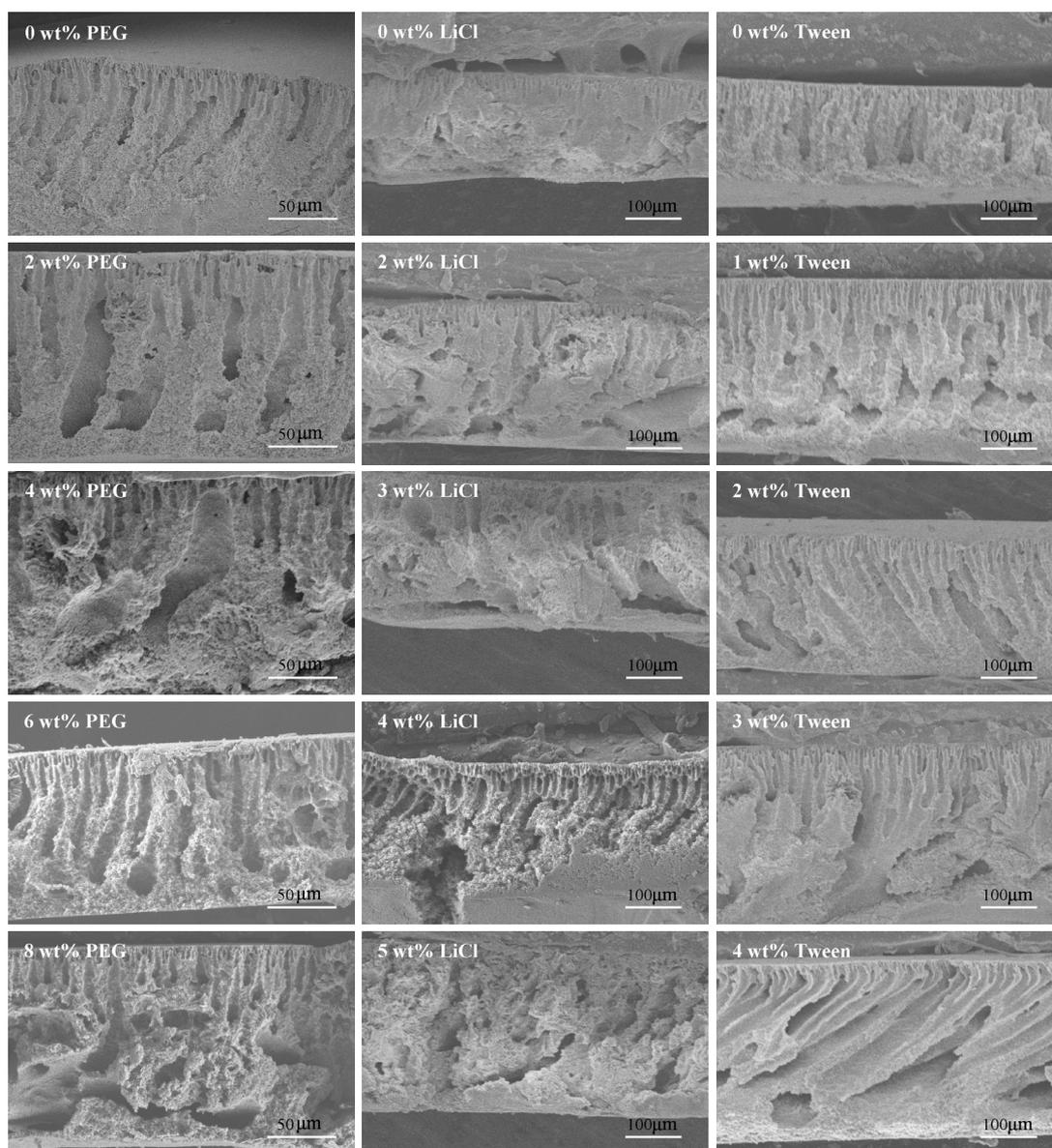
The higher viscosity and more stable thermodynamic properties would induce delayed phase separation or contribute to the decrease of instantaneous phase separation rate. The final membrane exhibited sponge-like pore or short finger-like pore structure. In contrast, instantaneous phase separation would occur, the resulted membranes showed the typical finger-like pore structure. However, during the actual membrane formation process, both of the kinetic and thermodynamic factors should be considered. The final membrane morphology was determined by the dominant factor.

### 3.3. Effects of Additives on Membrane Morphology

Figure 3 showed the FESEM photos of different blend membranes using PEG, LiCl and PEG (4 wt%) + LiCl (1 wt%) + Tween as additives, respectively. It could be seen that membranes without additives exhibited short finger-like pores. With the addition of PEG or LiCl, the finger-like

pores became long and gradually extended next to the bottom when PEG and LiCl contents were 6 wt% and 4 wt%, respectively. However, with the further increasing of PEG, the finger-like pores became short with lots of closed macrovoids in the sub-layer. The long finger-like pores were destroyed with lots of collapsed pores in the cross section. As Figures 5 and 6 showed, both of the average pore size and porosity initially increased and then significantly decreased with the increasing of PEG content.

**Figure 3.** The effects of additive content on the morphology of PPTA/PVDF blend membranes ( $\times 350$ ).



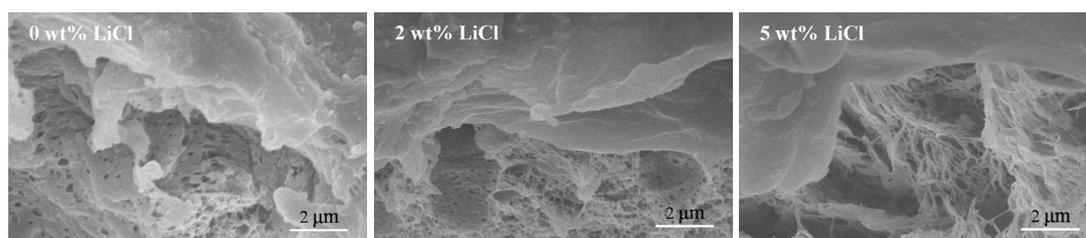
From the above analysis of thermodynamic and kinetic properties of casting solution, solution viscosity increased slowly with the increasing of PEG content from 0 to 6 wt% while the thermodynamic stability gradually deteriorated. Obviously, the latter at this stage played the leading role in the membrane formation process. However, when the PEG content further increased to 8 wt%, the gelatin values lightly decreased, which implied that the thermodynamic stability of the

casting solution deteriorated slightly. Therefore, significant increasing of the solution viscosity led to the delayed phase separation when the casting solution was immersed into the coagulation bath.

The addition of LiCl seriously broke the thermodynamic equilibrium of PPTA-PVDF/NMP/H<sub>2</sub>O system and the gelatin value rapidly decreased. In addition, the addition of LiCl made the dynamic viscosity of casting solution increase rapidly. As shown in FESEM pictures, the main influence of LiCl on the membrane formation process was ascribed from the thermodynamics. With the introduction of LiCl, thermodynamic properties of the system gradually became unstable and hence quickened the phase separation rate, resulting in the presence of macropores stacking phenomenon in the cross sectional pictures of PPTA/PVDF blend membranes (5 wt% LiCl). The accelerated phase separation contributed to a bigger pore size and a higher porosity, as shown in Figure 5 and 6, respectively.

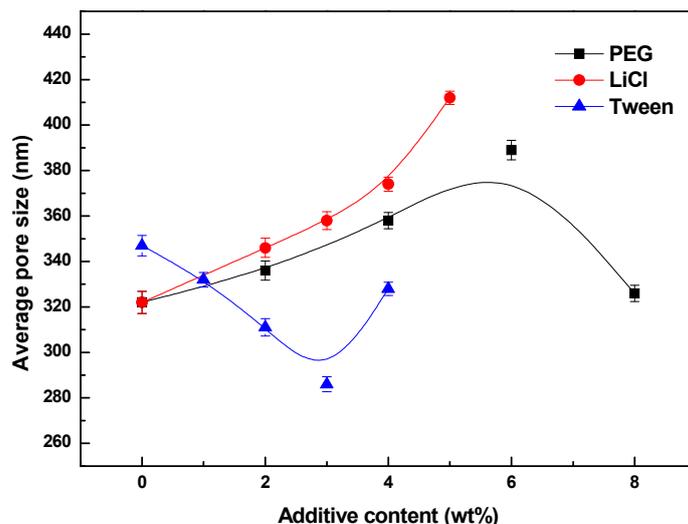
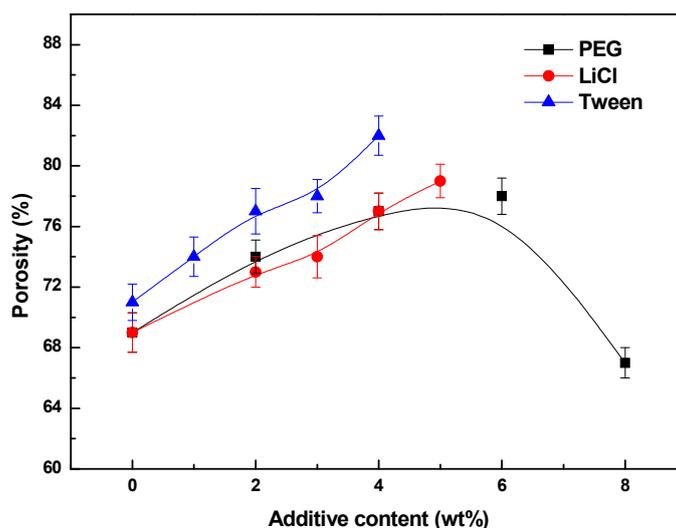
In addition, the salvation action among inorganic additives, solvents and polymers could link up big pores and form a network structure with lots of sponge-like pores [26], as shown in Figure 4. It could be clearly seen that with the addition of LiCl the number of through pores can be effectively increased, resulting in a high porosity and an increased water flux, as shown in Figures 5 and 7, respectively.

**Figure 4.** The effect of LiCl content on the top skin morphology of PVDF/PPTA blend membranes ( $\times 10,000$ ).



As Figure 3 showed, all blend membranes with Tween as the additive exhibited the typical finger-like pore structure. However, the pore size measurements in Figure 5 suggested that with the increasing of Tween content from 0 wt% to 5 wt%, the average pore size firstly decreased gradually and then increased suddenly. Blend membrane with 3 wt% Tween had the smallest pore dimension about 286 nm. In addition, it could be seen in Figure 6 that the porosity kept increasing with the addition of Tween.

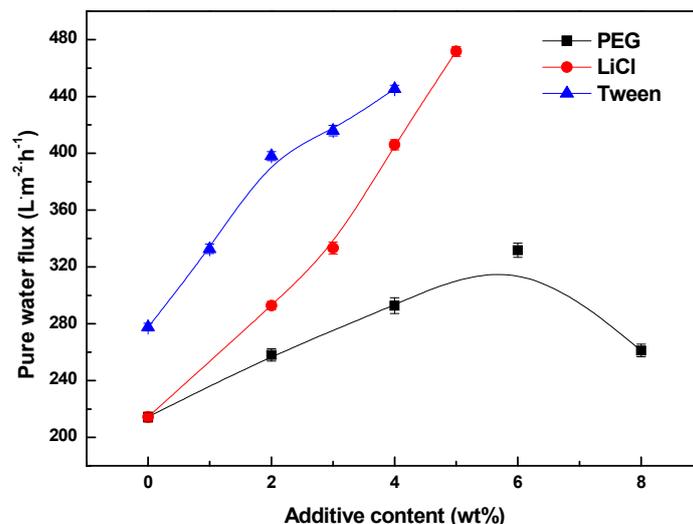
From the results of thermodynamics analysis, gelatin value decreased slightly from 18 wt% to 16.5 wt% with the increasing of Tween content from 0 wt% to 3 wt%. These results indicated that thermodynamic properties of casting solution remained basically unchanged when Tween content was below 3wt%. Therefore, dynamic viscosity became the main influencing factor during membrane formation process. Solution viscosity increased with the increasing of Tween content resulting in the slow down of the phase separation rate and a reduction of the membrane surface pore size. The addition of surfactant rendered the system thermodynamic stability while the inorganic additives could be uniformly dispersed in the polymer matrix so that the final pore distribution was more evenly. Although the dynamic viscosity continued to increase when Tween content increased to 4 wt%, a large number of surfactants induced a poor thermodynamic compatibility between different components of casting solution which accelerated the demixing process and thereby resulted in an increase of membrane surface pore size.

**Figure 5.** The variations of membrane average pore size with different additive content.**Figure 6.** The variations of membrane porosity with different additive content.

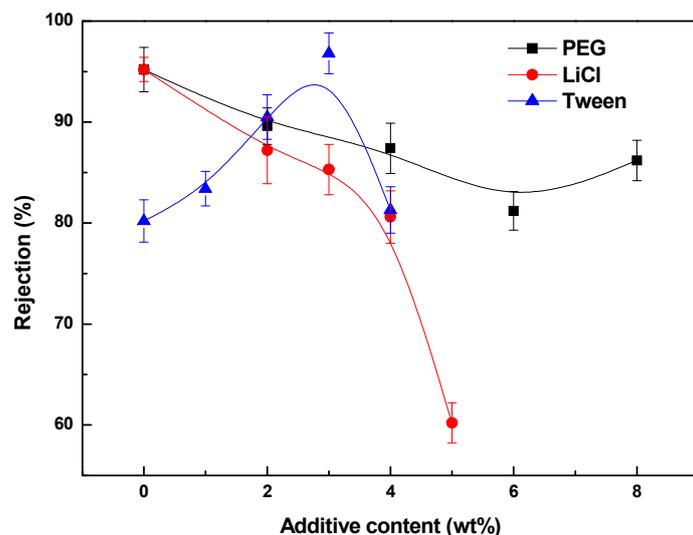
### 3.4. Effects of Additives on Membrane Performance

Changes of membrane structure will cause the variations of separation performance. Figures 7 and 8 showed the effects of different additive contents on the pure water flux and the PEG-100,000 rejection of different blend membranes. It could be seen that with the introduction of the additive PEG, the water flux of blend membranes increased slowly at first and then decreased rapidly, while the PEG-100,000 rejection showed the opposite trend. This was because both of the larger membrane pore and higher porosity caused the enhancement of the flux. However, the former would also decrease the rejection. As Figure 5 and 6 showed, with the increasing of PEG content from 0 to 6 wt%, the surface pore size and porosity of blend membranes gradually increased which caused the initial increasing of water flux and the decline of PEG rejection. When the PEG content increased to 8 wt%, the delay phase separation resulted in the smaller pore size and lower porosity. Consequently, the water flux decreased while the PEG rejection significantly increased.

**Figure 7.** The variations of the pure water flux with different additive contents.



**Figure 8.** The variations of the PEG-100,000 rejection with different additive contents.

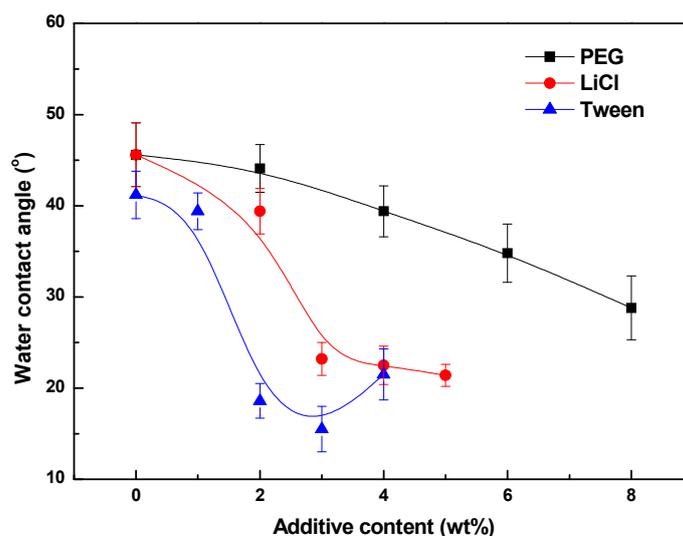


As can be seen in Figure 8, with the addition of LiCl, the water flux of blend membranes gradually increased, while the PEG rejection decreased quickly. This was because that the surface pore size gradually increased and more macrovoids emerged resulting in the improvement of membrane porosity. As the Tween content increased from 0 to 3 wt%, both of membrane water flux and rejection increased. It could be attributed to the decrease of membrane surface pore size. With the incorporation of the surfactant, more interconnected network pores were produced which resulted in the continuously increasing of membrane porosity and water flux. When Tween content increased to 4 wt%, the water flux continued to increase, while the PEG rejection gradually decreased. This was due to the presence of surface macropores during the instantaneous phase separation process.

Effects of different additive contents on the water contact angle of PPTA/PVDF blend membranes were shown in Figure 9. It could be seen that with the increasing of PEG concentration the WCA value continuously declined which indicated that the membrane surface hydrophilicity was gradually improved. The hydrophilicity differences are mainly determined by the presence of PPTA and the

structure of PPTA aggregation. Besides, the introduction of additives has also an important impact on the membrane surface hydrophilicity. During the membrane formation process, double diffusion between the solvent NMP and nonsolvent water molecules facilitated the transfer of hydrophilic PEG molecules onto nascent membrane surface which contributed to the hydrophilicity improvement. The addition of LiCl also promoted the hydrophilicity enhancement of blend membrane surface. This was because of the strong moisture absorption of LiCl. The number of free polar groups on the membrane surface increased with the increasing of LiCl content, and thus surface hydrophilicity was improved.

**Figure 9.** The variations of the water contact angle (WCA) with different additive contents.



The effects of Tween on the surface hydrophilicity of blend membranes could be considered from the two aspects as follows. On the one hand, Tween-80 with lots of hydroxyl groups could interact with water molecules. During the phase separation process, more and more surfactant molecules moved onto membrane surface with the increasing of Tween concentration resulting in the continuously improvement of surface hydrophilicity. On the other hand, it was found that the surface hydrophilicity was proportional to the compatibility between blending components [17]. Good compatibility could be obtained by the adding of small amount of Tween. However, when the Tween content increased to 4 wt%, the compatibility became poor. Consequently, the WCA value decreased initially and then gradually increased.

Through the comparison of the effects of the above three kinds of additives on the structure and separation performance of PPTA/PVDF blend membranes, it could be found that LiCl had the most significant influence on pore formation. The addition of PEG greatly affected the emergence of long finger-like pores while Tween had little effect on the formation of the finger-like pores Tween mainly influenced the membrane surface pores and its uniform distribution. These results were also consistent with the thermodynamic and kinetic variations of the casting solution within these three kinds of additives.

#### 4. Conclusions

The effects of different kinds of additives including hydrophilic polymers (PEG), inorganic salt (LiCl) and surfactants (Tween-80) on the morphology and performance of PPTA/PVDF blend

membranes were systematically investigated through the thermodynamic and kinetic analysis of membrane casting solution.

Thermodynamic phase diagrams indicated that the addition of PEG or LiCl both deteriorated the thermodynamic properties of casting solution, while the negative effect of LiCl was more significant. Tween acted as a thermodynamic stabilizer of the blend solution. Dynamic viscosity measurements suggested that the introduction of LiCl into the casting solution made the viscosity increase rapidly.

When PEG content varied in the range of 0–6 wt%, the thermodynamic properties of casting solution played a leading role on the pores formation. However, when PEG content increased over 6 wt%, the high dynamic viscosity suppressed the demixing rate resulting in the decrease of membrane surface pore size and the emergence of short finger-like pore structure. Therefore, the water flux slowly increased followed by a rapid decrease, while the PEG rejection of blend membrane showed the opposite trend. The effects of LiCl on the membrane-forming process were mainly ascribed from the thermodynamic factor which contributed to the continuous enlargement of membrane pores. Dynamic viscosity became the leading factor when a small amount of Tween was introduced. However, when Tween content was more than 4 wt%, the poor thermodynamic properties of casting solution dominated the phase separation process. The increase of porosity at low Tween content and the enlargement of average pore size at high content were responsible for the variations of water flux and PEG rejection of the blend membranes.

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### Author Contributions

Yu-Feng Zhang and Dong-Qing Liu coordinate and fund the entire investigation. Hong-Bin Li and Xiao-Feng Liu completes the experiments and characterization of the blend membranes. Wen-Ying Shi proposes some constructive explanations and suggestions about the analysis as well as the revisions of this manuscript.

### Conflicts of Interest

The authors declare no conflict of interest.

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