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Thermodynamic Stability of Polysulfone/Zinc Salt Membrane

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Abstract

In some applications, membrane thermodynamic stability may pose an important issue. Thermal instability may lead to membrane degradation, performance loss, or changes in membrane characteristics over time. This study focused on determining the thermodynamic stability of polysulfone (PSf) membrane and characterizing the membrane based on morphology. The membrane was created through a phase inversion method, using PSf as the base polymer, N-methyl-2-pyrrolidone (NMP) as the solvent, and zinc nitrate, zinc chloride, and zinc acetate as nonsolvent additives in varying concentrations. To determine the precipitation curve on a ternary phase diagram, cloud point measurements were conducted. The relationship between PSf concentration and the time required for the membrane to undergo phase separation was established. The results revealed a gradual increase in the precipitation rate as the PSf concentration rose. The findings indicate that higher PSf concentrations lead to greater stability of the dope solution. A recommendation to achieve better results on the thermodynamic stability aspect would be to increase the polymer to zinc salt ratio.

1. Introduction

Water is a resource that humans are becoming more and more dependent on due to the rapid rise in demand in both industry and daily life. As a result, wastewater treatment must be developed to expand the selection of clean water for use in daily life. Thanks to their ideal properties, such as high mechanical strength, stabillity, and simplicity of modification, polysulfone (PSf) membranes are frequently employed in the industry, notably for wastewater treatment. [1]

Membrane thermodynamic stability is a crucial consideration in certain applications. It can impact the durability and performance of membranes over time, often resulting in degradation or changes in their properties. One common concern is the occurrence of demixing or phase separation, where the membrane develops separate regions with varying polymer concentrations. This can negatively affect performance and selectivity. To address this, optimizing the polymer-solvent system becomes essential. Increasing thermodynamic stability can be achieved by adjusting polymer content, solvent composition, or introducing additives.

The primary objectives of this research were to fabricate a polysulfone/zinc salt membrane using the phase inversion method, to assess its thermodynamic stability, and to characterize its morphology using a scanning electron microscope (SEM). These objectives aimed to explore the potential of zinc salt additives in enhancing membrane performance and stability.

The study involved the use of zinc chloride, zinc nitrate, and zinc acetate as non-solvent additives in the fabrication process. Thermodynamic stability was evaluated in terms of the stability of the membrane dope solution. However, the availability and reliability of data were limited due to the scarcity of previous studies on this topic, which affected the accuracy of data analysis. Additionally, the research was conducted under strict time constraints, limiting the duration for data collection and analysis.

2. Materials and Methods

The procedure involves several steps starting with the sample preparation, quality inspection for the dope, and membrane characterization.

2.1 Materials

There are three types of material used in this study. The materials will include:

i. Polysulfone (PSf) was used as the main polymer material due to PSf having high mechanical strength, high chemical, and thermal stability in addition to excellent film forming ability.
ii. N-methyl-2-pyrrolidone (NMP) was used as the solvent.
iii. Zinc chloride ($ZnCl_2$), zinc nitrate ($Zn(NO_3)_2$) and zinc acetate ($Zn(CH_3CO_2)_2$) were used as non-solvent additives.

2.2 Preparation of Dope Solution

Figure 1 portrays the dope preparation equipment setup in membrane fabrication. 1g of $ZnCl_2$ was added in a beaker with a mechanical stirrer at a rate of 300 rpm in 60 °C under continuous stirring with 50g of NMP solvent. 1g PSf was progressively added while stirring continuously. The PSf solution was stored in a glass container at room temperature for at least 24 hours after being homogeneously dissolved in NMP for 4 hours. Based on the composition indicated in Table 1, the mixing process was repeated with varying PSf and zinc salt concentrations. The mixing process was repeated with varying PSf and zinc salt concentrations.

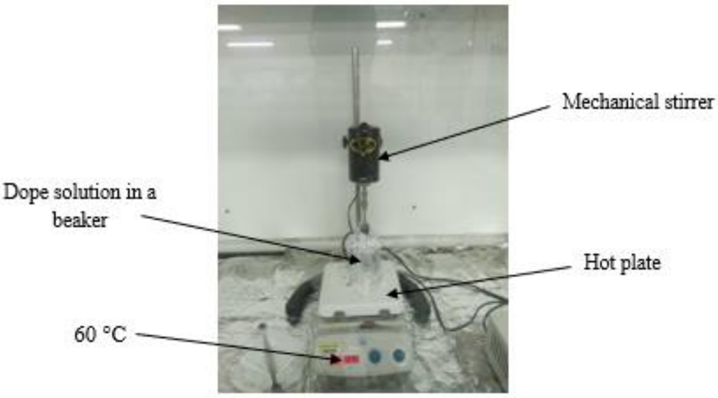


Fig. 1 *The experimental setup for dope solution preparation*

Table 1 *The composition of PSf/zinc salt membrane*

Sample	Mass of NMP (g)	Mass of PSf (g)	Mass of $ZnCl_2$ (g)	Mass of $Zn(NO_3)_2$ (g)	Mass of $Zn(CH_3CO_2)_2$ (g)
1	50	1	0	0	0
2		1	1	0	0
3		1	0	1	0
4		1	0	0	1
5		3	0	0	0
6		3	3	0	0
7		3	0	3	0
8		3	0	0	3
9		5	0	0	0
10		5	5	0	0
11		5	0	5	0
12		5	0	0	5

2.3 Solution Characterization via Ternary Phase Diagram

Solution characterization is a technique to determine optimal solution parameters before membrane formation. This study utilized cloud point determination to understand the phase behaviour of PSf solution systems. A ternary phase diagram was used to predict membrane morphology, while titration was performed to find the precipitation rate of the PSf solution in the non-solvent. Gradual addition of the non-solvent to the polymer dope solution allowed for determining the cloud point compositions based on weight.

2.4 Preparation of Flat Sheet Membrane

Phase inversion was used to prepare the PSf flat sheet membrane. On a glass plate, the dope solution was poured, and a metal ruler will be used to cast the material onto the glass plate. The glass plate with the cast film on it was transferred immediately into a distilled water bath at room temperature after the casting process. After a brief period, a thin polymeric layer ought to start to separate from the glass because of the phase inversion process. The flat sheet was then left to dry for roughly 48 hours at room temperature.

2.5 Characterization of Membrane

The SEM technique was utilized in this work to examine images of the surface morphology and cross section of the PSf membrane to observe its morphological structure. For this, a magnification of 750 with an accelerating voltage of 15.0 kV was used. Electronic console and an electron column make up a SEM instrument. The chosen membrane, which is approximately 1 cm x 5 cm in size, was first dried at room temperature. After a brief immersion in liquid nitrogen, the membrane was split into two pieces with a pair of forceps. To examine the cross-section morphology of the membrane, this process will make a clean incision of the membrane. The fracture area's cross-section surface morphology was then be analyzed. The membrane was coated with gold on the sputter coater device before moving on to the SEM equipment because they are made of non-conductive materials.

3. Results and Discussion

The dope solution with composition of PSf and zinc salt with the same ratio was tested through the cloud point test to find out the cloud point measurement. Scanning electron microscope (SEM) was used to observe the morphology to characterize the membrane. The characteristics of each sample are determined by the experiment's outcome. All experiments were carried out on samples in different parameters in terms of types of salt and concentration of polymer and non-solvents.

3.1 Isothermal Ternary Phase Diagram of PSf/NMP/Zinc Salt System

As can be seen from Figure 2, the cloud point diagrams significantly shifted towards the polymer–solvent axis. The overall trend for the precipitation rate for the system from highest to the lowest is PSf/$Zn(CH_3CO_2)_2$ > PSf/$Zn(NO_3)_2$ > PSf/$ZnCl_2$ > PSf solution which indicate that, at the isothermal thermodynamic equilibrium, less water is necessary to achieve phase-inversion. This additionally implies that the additions might improve thermodynamic liquid-liquid demixing, resulting in phase inversion promotion. Although the additives improved liquid-liquid demixing, the total solvent and non-solvent diffusion during phase-inversion can be influenced kinetically by the addition of additives due to the increase in solution viscosity.

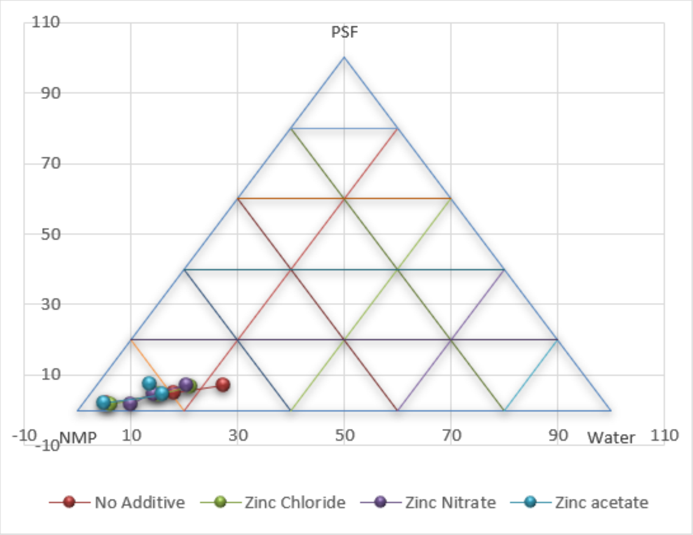


Fig. 2 *Overall ternary phase diagram of the experiment*

Based on Figure 3, [2] all the cloud point data were in the two-phase region and below the binodal curve. Since the cloud point is in a two-phase segment of a ternary phase diagram, it implies that phase separation occurs in the system at that temperature. The temperature at which a homogeneous solution turns turbid or cloudy due to the creation of a second phase is referred to as the cloud point. When the cloud point falls into a two-phase area, it indicates that the solution goes through liquid-liquid phase separation when cooled or heated at that temperature.

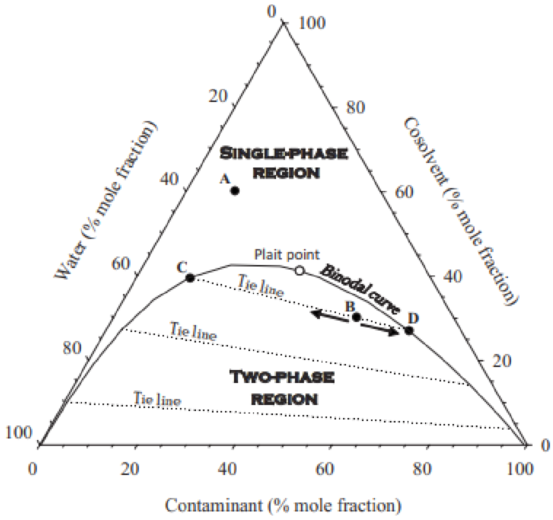


Fig. 3 *General ternary diagram for the polymer-solvent system (25 °C, 1 atm). [2]*

The system is thermodynamically unstable at that temperature if the cloud point is within the two-phase area of a ternary phase diagram. The inclination of a system to approach a state of lowest energy or free energy is referred to as thermodynamic stability. [3] The two-phase area in this scenario shows that the system may be separated into two different phases to obtain a lower free energy state. The system undergoes liquid-liquid phase separation at temperatures below the cloud point, resulting in the development of two coexisting liquid phases. The reduction of the system's free energy is the driving factor behind this phase separation.

The system can persist in a metastable condition even if it is thermodynamically unstable at the cloud point temperature. A situation in which a system is kinetically locked in a higher energy level but has not yet transitioned to the most stable state is referred to as metastability. [4] To achieve a thermodynamically stable condition, the system may need to be cooled or heated further to pass through the two-phase zone, permitting full phase separation into discrete phases.

3.2 Membrane Precipitation Rate

The graph in Figure 4 above displays the relationship between polysulfone (PSf) concentration and time taken for the membrane to undergo phase separation which was represented by the blue line. The graph shows a gradual increase in time taken for the precipitation to occur as PSf concentration increases. At a PSf concentration of 6%, there is a minimal increase in time, reaching a value of 22.68 s from 17.23 s at PSf concentration of 2%. However, at higher PSf concentrations of 10%, the time sharply increases until it reaches peak value of 48.88 s. The graph suggests a positive correlation between PSf concentration and time, indicating that higher PSf concentrations result in greater dope solution stability. The increase in time taken for precipitation to form with increasing PSf concentration can be attributed to improved polymer-solvent interactions, where the PSf concentration affects the interactions between the polymer chains and the solvent molecules. According to Nielen et al. [5], at higher PSf concentrations, the polymer chains are more closely packed, leading to increased intermolecular interactions. These interactions usually lead to an increase in viscosity thus can slow down the rate of phase separation by hindering the mobility and diffusion of the polymer chains within the solution.

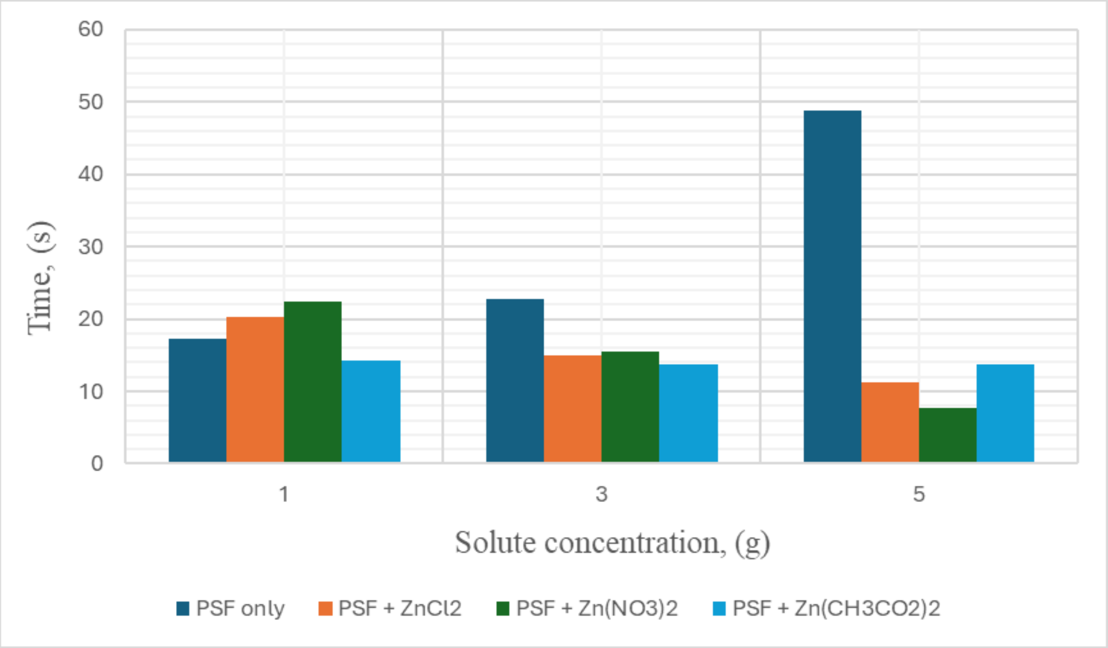


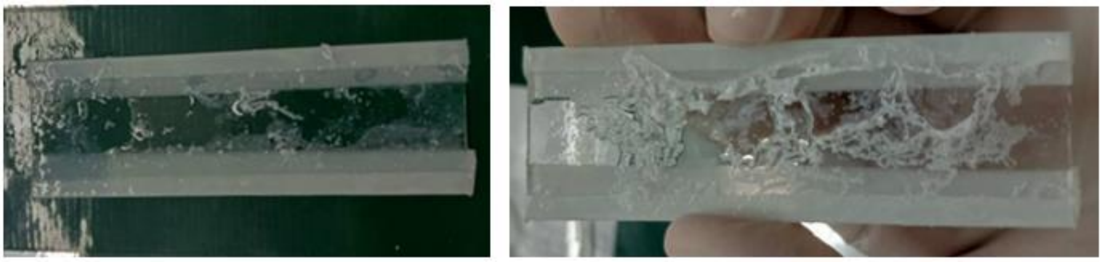
Fig. 4 *Graph of average time taken for phase separation against solute concentration in the solution*

Meanwhile, in the Figure 3.3, the effect of different additives such as zinc chloride, zinc nitrate and zinc acetate on the time taken for phase separation to occur was also recorded. Yet, different from the pure PSf only solution, the graph shows a gradual decrease in time taken for the precipitation to occur as additives concentration increases. Of the three different additives, zinc nitrate records the highest decrease in time followed by zinc chloride and lastly zinc acetate exhibits the least decrease in time compared to others. The decrease in time taken for precipitation to form with increasing additive concentration can be attributed to reduced viscosity of the solution due to addition of the zinc salt. Sue Ryeon Kim et al. [6], in past research also indicated that reduced viscosity of PSf/$ZnCl_2$/NMP solution decreased with polymer concentration until it reached certain concentration. Hence, it was concluded that the decrease in viscosity indirectly affects the rate of phase separation to be faster than without any additives.

3.3 Membrane Casting Process

The dope solution was cast onto a glass plate which then will be submerged in a water bath for the membrane to undergo phase inversion process. When a solution with PSf concentrations of 2% and 6% was used in the casting process, the membrane could not form properly. The attempts end up in the membrane breaking apart in the water bath as soon as it is submerged. This suggests that the polymer concentration is below the threshold required for membrane formation. Membrane formation requires a certain minimum polymer concentration to create a continuous polymeric matrix. A polymer concentration of 2% or 6% might be too low to generate the necessary polymer-polymer interactions and entanglements needed to form a cohesive membrane structure. With low polymer concentrations, the resulting polymeric network may lack the necessary strength and cohesion required for membrane formation. This can result in the formation of non-uniform films, defects, or a lack of continuity in the membrane structure.

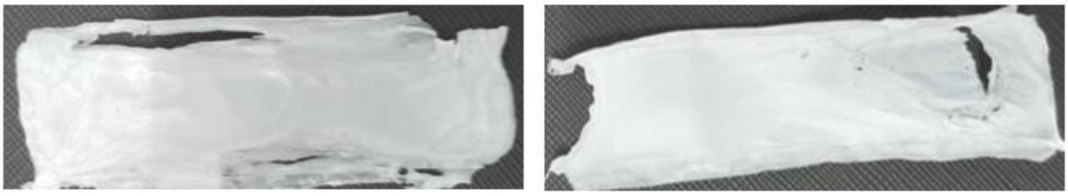
Apart from that, the viscosity of the casting solution also plays a crucial role in membrane formation. A low polymer concentration results in a lower solution viscosity, which can hinder the formation of a continuous membrane layer. Insufficient viscosity may lead to rapid solvent evaporation, preventing the polymer chains from organizing into a well-structured membrane. Membrane casting solutions may contain additives that aid in film formation, such as pore-forming agents or viscosity modifiers. If the concentration or selection of these additives is improper, it can impact the ability to form a membrane with desired properties. The presence of a non-solvent additive at an equal concentration to the polymer can induce phase separation during the casting process. Phase separation occurs when the non-solvent additive causes a demixing of the polymer-solvent system, leading to the formation of distinct polymer-rich and non-solvent-rich domains within the casting solution. The result of the casting process for the dope solution with PSf concentration of 2% and 6% was shown in Figure 5 below.



(a) 2 (b) 6
% PSf % PSf

Fig. 5 *Membrane casting result for dope solution with low concentration of PSf*

The membrane was successfully cast when a greater concentration of PSf was utilized. In general, higher polymer concentrations in the dope solution result in increased solution viscosity. The higher viscosity reduces the rate of solvent evaporation, allowing the polymer chains more time to reorganize and produce a well-structured membrane. The increased viscosity can also impede polymer chain mobility, preventing them from diffusing away from the casting solution and increasing membrane development. This conforms to a finding made by Holda et al. [6], which entails that highly concentrated polymer solutions exhibit slowed kinetics due to increased viscosity thus evidently delaying the membrane formation process. Likewise, more polymer chains are present in the casting solution at greater polymer concentrations, resulting in a larger density of nucleation sites for membrane development. The early production of solid structures inside the casting solution is referred to as nucleation. The presence of a higher concentration of polymer chains increases the probability of nucleation events, leading to the formation of a membrane structure. The produced membrane was shown in Figure 6 below.



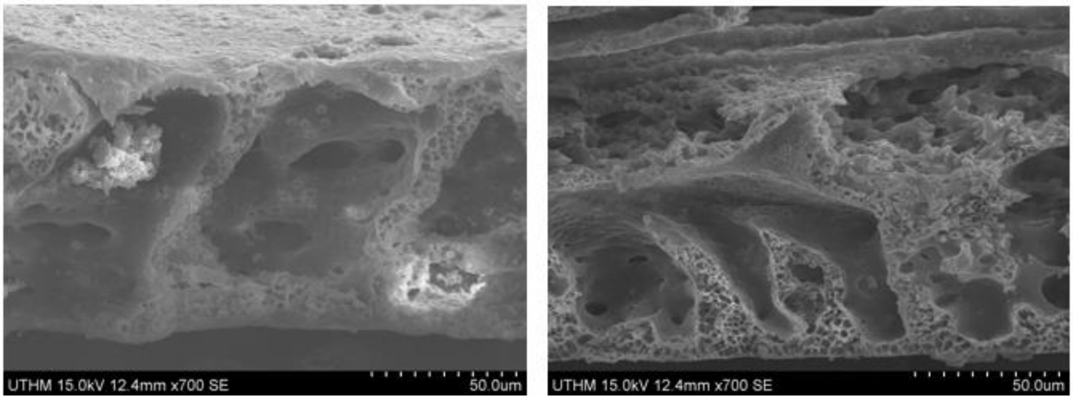
(a) 10% PSf/NMP/$ZnCl_2$ (b)10% PSf/NMP/$Zn(NO_3)_2$

(c) 10% PSf/NMP/$Zn(CH_3CO_2)_2$

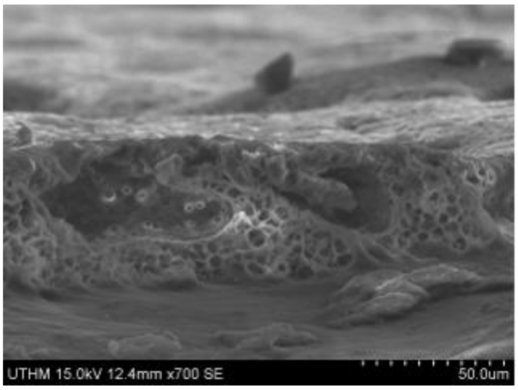
Fig. 6 *Membrane casting results for dope solution with higher PSf concentration*

3.4 Morphology Analysis

Figure 3.6 illustrates the impact of various zinc salts on the PSf membrane. The introduction of ZnCl2, Zn(NO3)2, and Zn(CH3CO2)2 into the dope solution caused notable changes in the membrane structure. When the zinc salt was added at the same concentration as PSf, the sublayer became more porous, exhibiting larger irregular finger-like holes. The skin layer acted as a separator, while the support layer provided mechanical strength to the membrane. The presence of Zn(CH3CO2)2 in the depicted sample indicated the absence of a continuous phase in the sublayer of the membrane. The addition of zinc salt expanded the membrane pores, resulting in increased porosity. This outcome could be attributed to a reduction in the membrane's thermodynamic stability, as evidenced by the ternary diagram data shown in Figure 3.1. Additionally, as described by Razali et al. [7], the rapid phase inversion process led to the formation of large pores and sponge-like structures within the membrane. This behaviour has the potential to enhance membrane permeability.



PSf/NMP/$ZnCl_2$ PSf/NMP/$Zn(NO_3)_2$



PSf/NMP/$Zn(CH_3CO_2)_2$

Fig. 7 *Cross-section for three membranes with different compositions*

4. Conclusions

In conclusion, the PSf/zinc salt membrane was manufactured using the phase inversion method, but lower concentration dope solutions with comparable amounts of polymer and zinc salt were unable to form suitable membranes due to their instability. The thermodynamic stability of the PSf/zinc salt system was evaluated using a ternary phase diagram, indicating that the cloud point measurements showed phase separation and instability. The resulting membranes had a porous structure with enlarged holes due to the addition of zinc salt. Overall, the objectives were partially achieved, and further experimentation can improve the results.

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