

Trade-off between thermodynamic enhancement and kinetic hindrance during phase inversion in the preparation of polysulfone membranes

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Abstract

Polysulfone membranes were prepared via the diffusion-induced phase inversion process from casting solutions consisting of polysulfone, dimethylformamide, and polyvinyl pyrrolidone as a polymeric additive. The effect of PVP added in casting solutions was analyzed by measuring the prepared membranes' morphology and water permeability. Variations in a casting solution's thermodynamic and kinetic properties caused by PVP addition suggest that the thermodynamic variation works in favor of the enhancement of demixing in the casting solution, but the rheological variation induces the opposite trend, or the delay of demixing. When prepared by the immersion coagulation into a water bath, the solidified membranes' structural and functional properties indicate that the coagulation of cast solutions was affected by the trade-off relationship between thermodynamic enhancement and kinetic hindrance. With a small amount of PVP in the casting solution, the thermodynamic driving force played a major role on solution demixing, inducing the demixing enhancement, corresponding to the acceleration of phase separation due to the PVP's nonsolvent effect. Consequently, the PVP acts as a phase separation enhancer, resulting in both macropore enlargement and permeate flux increase. With more addition of PVP, however, the macropore structure and the water permeability were suppressed rather than enlarged or increased. These phenomena reflect that the demixing of the cast solution was delayed, with the kinetic hindrance offsetting the thermodynamic effect for phase separation enhancement.

Keywords: Polymeric membrane; Phase inversion; Polysulfone; Polymer additive; Macropore; Permeability

1. Introduction

Many composite membranes, and almost all desalination membrane systems, consist of phase

inversion membranes, either as a main functional layer or just a supporting layer. In the preparation of phase inversion polymeric membranes [1,2], additives are commonly used, along with polymer and solvent, in a membrane formation system to improve morphology and function of resultant

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membranes. In general, additives work as a nonsolvent agent for reducing solvent power in the solution. Those additives are leached out of cast solution films, while exchanged with a coagulating medium during a solidification process. Analyzing a phase inversion process of a multi-component system containing an additive is very difficult because of many correlated factors such as various interactions, mutual diffusions, and specific bondings among components in the process. Nevertheless, there are two important factors that can be crucial for forming phase inversion membranes: thermodynamic phase equilibria and mutual diffusivities in a system.

A polymer solution can be phase-separated by inducing thermodynamic instability. A compositional change of constituents, as well as temperature variation, can cause phase separations, the demixing that leads to a homogeneous polymer solution into a heterogeneous one and, eventually, a solid polymeric structure [3–6]. Therefore, the constituents' thermodynamic stability is one of the critical factors determining membrane structure, which is defined during the phase inversion process.

Kinetic properties also have a significant effect in the formation of a phase inversion membrane. When prepared via diffusion-induced phase inversion processes such as either exposure in a nonsolvent vapor atmosphere or immersion into a nonsolvent bath, the prepared membrane structure and function can change depending on the rate of diffusion. However, it is very difficult to clarify the diffusion phenomena because of the solution's being heterogeneous like the nucleation of constituents and polymer collapsing due to a compositional change during the coagulation process. The addition of a polymer additive in a casting solution makes the phase inversion system more complicated because of the additive's nonsolvent and high molecular weight effects.

Polyvinylpyrrolidone (PVP) is one of the popular, high-molecular polymer additives applied in a casting solution in the preparation of phase inversion polysulfone (PSF) membranes. Its preference is due to good miscibility with PSF and high solubility in water, a common precipitating agent [7–10]. PVP as an additive induces significant variations in casting solution's characteristics: the increase in thermodynamic instability due to its nonsolvent property and the kinetic hindrance due to rheological variation by its high molecular weight. In terms of kinetic hindrance, it can work as an agent for suppressing macropore formation in the phase inversion membranes [11], but it can also function as a permeate flux enhancer. It has been reported that PVP addition can induce the enlargement of macrovoids in the membrane as well as a significant increase in membrane permeability [12].

The main reason PVP exerts so many influences over phase inversion is clearly due to its involvement with apparent physico-chemical variation that affects the thermodynamic and kinetic driving forces. In a previous study [13], we reported that in the *n*-methylpyrrolidone (NMP)-PVP-PSF system, the trade-off relationship between thermodynamic driving force and kinetic driving force can be found. As the PVP replaces NMP in a PSF casting solution, the homogeneous region of the mixed solution, including water, can be further reduced due to the PVP's nonsolvent effect, and the mutual movement can be hindered due to PVP's high molecular effect; but the membrane structure and function follow a combined effect of two factors. Therefore, it has been suggested that, if the PVP addition cannot come to terms with the demixing enhancement, it is not because the PVP fails to induce thermodynamic enhancement but because it is overwhelmed by kinetic hindrance.

Although it has been known that PVP has a great influence over membrane formation, the

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