Phase diagram of ternary polymeric solutions containing nonsolvent/solvent/polymer: Theoretical calculation and experimental validation

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ABSTRACT

Mathematical modeling of phase inversion membrane fabrication has been focused by many researchers, as the experimental study of phenomenological events is almost impossible, mainly, due to the high rate of exchanges and the small thickness of cast film. The appropriate coupling of conservation law of mass and thermodynamic stability boundaries and their consequent kinetic mechanisms is the only way to establish a rigorous thermo-kinetic predictive model. In this work, we focused on development of a reliable method of phase diagram construction i.e. determination of thermodynamic boundaries, where a compressible regular solution theory based model (CRS) has been used to resolve the essence of experimental knowledge on interaction parameters of models such Flory−Huggins. Attempts were made to develop thermodynamic regions such as binodal, spinodal, gelation, vitrification and etc. For validation of calculation results, required experimental phase diagram and thermodynamic boundaries were retrieved from literature. Ternary systems of (1) polyethersolfune/N-methylpyrrolidone/water and (2) cellulose acetate/acetone/water were considered as the case study, here, for which the methodology can be extended then to other amorphous polymer containing systems.

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1. Introduction

The remarkable work of Loeb and Sourarijan on fabrication of polymeric membranes using phase inversion technique was followed by both industry and academia, and found many applications in commercial membrane fabrication [1−3]. The wet casting (immersion precipitation) technique is of the most applied methods of membrane fabrication to obtained a wide variety of final membrane morphologies [1]. To enhance theoretical knowledge, improve design and plan control strategies regarding membrane fabrication, many researchers devoted their focus on the modeling and computer based numerical simulation of phase inversion and consequent thermo-kinetic events involved with the help of conservation law of mass and thermodynamic phase equilibria [4−20].

A rigorous mathematical model, which includes all possible thermodynamic and kinetic considerations regarding the phase inversion phenomenon, has never been established so far. Such mathematical model could successfully explain many experimental observations and would result in appropriate understanding of fundamental events involved during the phase inversion. To establish such a practical predictive model, one should consider many thermo-kinetic equations corresponding to all possible thermodynamic regions of a ternary system of interest, together with the components conservation governing equations (i.e. PDEs).

The mathematical modeling of component interphase transfer and composition changes results in the describing (governing) partial differential equations (PDEs) that must be solved using appropriate initial and boundary conditions by means of reliable calculation routines concerning dynamic compositional changes of thin film cast polymeric membranes by phase inversion technique (like the well-known precipitation path).

The development and solution of such PDEs have been focused in our forthcoming paper, and in this work, we narrowed our attention to theoretically develop a method of phase diagram construction by considering the possibility of incorporating

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phenomenological events involved such as gelation, nucleation and growth, spinodal demixing, macrovoid formation and etc. to be used for establishing of desired rigorous mathematical thermo-kinetic model of phase inversion for membrane fabrication. For validation of calculation results, required experimental phase diagrams having thermodynamic boundaries were retrieved from literature. Ternary systems of (1) polyethersolfune/N-methylpyrrolidone/water and (2) cellulose acetate/acetone/water were considered as the case study, here, for which the methodology can be extended then to other amorphous polymer containing systems.

2. Phase inversion for membrane fabrication; focusing on thermo-kinetic modeling

For the preparation and manufacturing of polymeric membranes by phase inversion, there are two commonly used methods (Fig. 1) i.e. dry casting and wet casting, which have been extensively studied both using theoretical and experimental methods [15,16,19–22]. Obviously, the mathematical studies would be of more interest as they could reduce the cost of extensive trial-and-error experiments and make prior investigations possible on the influencing parameters on the final membranes morphology. Besides all the beneficiating features of a well-developed mathematical model, the rapid rate of exchanges and the small thickness of casted films makes it hard (if not to say impossible) to experimentally study various phenomena that are not well understood, especially for studies on wet casting.

To develop the most rigorous model of interest in phase inversion, two different sets of mathematical equations must be considered;

(i) Thermodynamic Equations; The thermodynamic model which is able to describe the equilibrium at the interface of two phases and criteria regarding different possible thermodynamic regions with desirable accuracy (Fig. 2), and

(ii) Kinetic Equations; Conservation equations for components mass transport, which might be held until the thermodynamic boundaries are reached (such as binodal or any others), after which appropriate kinetic equations regarding the instantaneous thermodynamic state of solution (Fig. 3) and based on the thermodynamic equations (i) must be incorporated.

In present work, we narrowed our focus on a thermodynamically study to describe thermodynamic equations for ternary phase diagram construction in terms of Gibbs free energy. By selection of a reliable Gibbs free energy model, the binodal, spinodal, vitrification, gelation and other boundaries can be established, in addition, the instantaneous local thermodynamic states of solution (stable, unstable, metastable) might be determined. Each
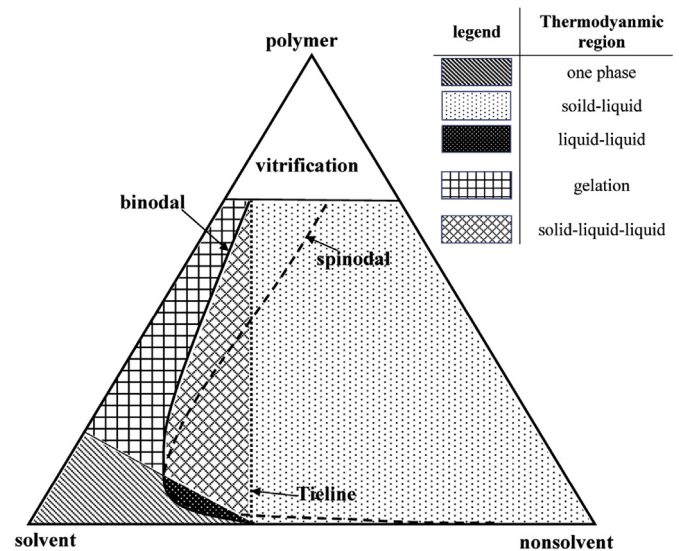
Fig. 2. Schematic representation of different possible thermodynamic regions for a ternary semicrystalline polymeric system [1,3,23].

thermodynamic region between these boundaries has distinct kinetic relationship, which must be considered to establish the rigorous model of interest that will be covered in our forthcoming paper. In other words, the governing equations (PDEs) resulting from the conservation law of components are appropriate for the one phase region (Fig. 2) while, upon the binodal boundary (or any other boundary) reaches, the contribution of events such as nucleation and growth and their relative magnitude of changes must be considered.

For a ternary system of solvent, nonsolvent and (semi-crystalline) polymer, the phase diagram is illustrated in Fig. 2 schematically [1,3,23] (more thermodynamic region can be observed in such as system, the amorphous polymer containing schematic phase diagram is covered in next paragraphs). Different possible phase boundaries are depicted in this figure. For any system of interest, mostly based on the polymer type and nature, a completely/slightly distinct phase diagram would be expected [24]. The instantaneous local situations of stable, unstable and metastable can be determined using the Gibbs free energy equation and its first and second derivation with respect to composition (mathematically the volume fraction) as illustrated schematically in Fig. 3 [1].

Considering the time scale and dynamic evolution of compositions, the film points, from the interface of two phases to the underlying support layer, will experience different states of stable, unstable and metastable which finally results in completely different morphologies and internal structure of membranes (Fig. 3). Such dependency of morphology and internal structure and
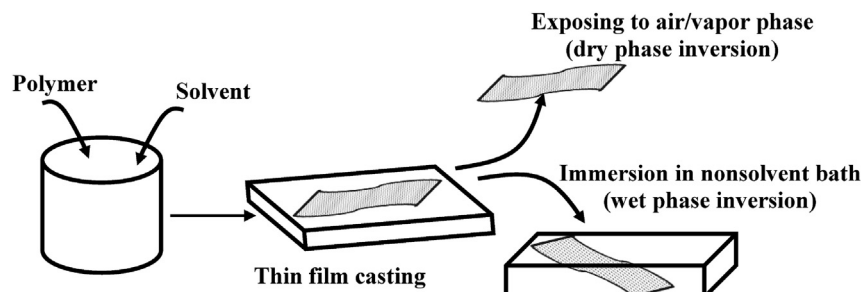
Fig. 1. Phase inversion membranes fabrication.