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Mathematical calculation of binodal curves of a polymer/solvent/nonsolvent system in the phase inversion process

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Abstract

Four methods of calculating Flory–Huggins interaction parameters from solubility parameters were examined by comparing calculated binodal curves with experimental data. This is a promising method to calculate interaction parameters from solubility parameters because of the wide use of solubility parameters. The fitting results were satisfactory after the optimization of the correction constant according to the membrane casting systems mentioned. The optimized correction constants were 0.09 and 1.01 for the polymer/solvent and polymer/nonsolvent, respectively. The constants were obtained from PES/solvent and PSF/solvent systems and checked with PSF/DMAc/nonsolvent systems. Calculation was carried out, based on Flory–Huggins solution theory, to analyze the behavior of the polymer/solvent/nonsolvent system phase diagram with the influence of parameter sets in a wide range. It was found that with the increment of solvent/polymer interaction parameters or nonsolvent/polymer interaction parameters the miscibility gaps decreased. However, the miscibility gaps increased with the increment of nonsolvent/solvent interaction parameters.

Keywords: Binodal curve; Flory–Huggins; Interaction parameter; Solubility parameter; Ternary phase diagram; Miscibility gap

1. Introduction

The phase separation process is one of the main methods for the preparation of asymmetric polymer membranes. A ternary phase diagram is very useful in the description of the thermodynamic properties of a three-component system of polymer/solvent/nonsolvent which is usually used to make asymmetric membranes by immer-

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sion precipitation [1,2], the essential means to prepare the membrane with phase separation induced by changing the concentration of the solution. Different ternary systems result in different membranes with different structures.

Altena et al. [2] proposed the following explanation: (1) the equilibrium thermodynamic properties of a three-component system of polymer/solvent/nonsolvent, such as a liquid–liquid phase separation and gelation; (2) the exchange of solvent and nonsolvent during membrane formation and the effect on the kinetics of the above-mentioned demixing phenomena. A proper model for the formation process of asymmetric membranes should, of course, include both sets of factors. Koenhen et al. [3] and Broens et al. [4] suggested that the porosity of the sublayer was ascribed to liquid–liquid phase separation and the pores were formed most probably by nucleation and growth of the dilute polymer phase. Cohen et al. [5] proposed a different model for the formation of porous structures in the coagulation step during membrane formation. Their model was based on diffusion-induced phase separation at the spinodal in the ternary system.

The thermodynamic properties of the casting solution and coagulation pairs play a very important role on the structure and performance of a membrane prepared by immersion precipitation. Altena et al. [2] calculated the binodal curves of two membrane-forming systems: cellulose acetate/solvent/water and polysulfone/solvent/water. During their calculation, the interaction parameter (g_{12}) of nonsolvent and solvent was taken to be concentration-dependent, and the other interaction parameters of polymer with solvent (g_{23}) and with nonsolvent (g_{13}) were kept constant. Based on the Flory–Huggins theory, the relation between the behavior of the ternary phase diagram for the typical membrane-forming systems and various parameters was analyzed by Yilmaz et al. [1]. The importance of various parameters in controlling the phase-diagram behavior was demonstrated. It was concluded that g_{23} should also be considered as concentration-dependent. And the concentration dependency of the solvent/polymer interaction parameter (g_{23}) played a critical role in affecting the nature of the miscibility gap. Also the effect of the chain length distribution on the phase behavior of polymer solutions in a single solvent was described qualitatively [6]. The influences of molecular weight and molecular weight distribution appear to be strongest in the region of low m_n [7], but unfortunately, the data for the concentration dependency and molecular weight distribution dependence of g_{23} is quite limited, which holds back the application.

In this paper the Flory–Huggins interaction parameter from solubility parameters [8–11] was calculated, and the correction constant was optimized on the basis of polyethersulfone (PES)/solvent/water systems, polysulfone (PSF)/solvent/water systems and was checked by PSF/solvent/nonsolvent systems. The involved nonsolvents were water, ethanol, butanol and pentanol; the involved solvents were N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and 1-methyl-2-pyrrolindone (NMP). In addition, the behavior of the polymer/solvent/nonsolvent system phase diagram with the effects of parameter sets in a wide range was analyzed.

2. Calculation of binodal curves of the polymer/solvent/nonsolvent system in the phase inversion process

2.1. Thermodynamics of polymer/solvent/nonsolvent system

The Flory–Huggins theory [12] for polymer solutions was extended to a three-component system by Tompa [13] and was widely used to describe the ternary phase diagram of the membrane casting system: polymer/solvent/nonsolvent [1,2].

The Gibbs free energy (ΔG_m) of the mixing of the membrane casting system is as follows: