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Thermodynamic and kinetic study of spinodal phase separation in heptane–phenol system

Yuechan Li

Department of Materials Science and Engineering, Xiamen University of Technology, Xiamen 361024, People's Republic of China

ABSTRACT

The Flory–Huggins theory and phase-field method were used for thermodynamic optimization and kinetic simulation of spinodal phase separation in heptane–phenol binary system in this paper, respectively. The interaction parameter χ_{12} was optimized, and the calculated phase diagram was in good agreement with experimental data. The kinetic simulations indicated that the speed of spinodal phase separation is significantly affected by the quench temperature and the resultant morphology is determined by the initial average concentration. The results obtained could shed light on investigating phase separation patterns in immiscible organic systems.

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1. Introduction

Spinodal phase separation is ubiquitous in the liquid or solid phase in many systems, such as metallic systems Bi–Zn, Cu–Ni–Sn, organic systems phenol–heptane, methanol–CS_2, polymer systems polybutadiene–polystyrene, polystyrene–tetramethylbisphenol A polycarbonate, even glasses B_2O_3–SiO_2–Na_2O. The spinodal decomposition may be used to manufacture products with predefined mechanical, thermal, chemical and/or electrical properties, since they can exhibit very fine scale composition modulations [1]. For example, Cu–Ni–Sn alloys can be hardened by spinodal phase separation and are used in electrical contact materials that grip by elastic springback, such as in computer connectors [2]. A number of functional materials can also be fabricated by spinodal decomposition, for example, a porous, high-silica skeleton formed from B_2O_3–SiO_2–Na_2O system [3], a unique microporous structure of PS/PEG200 via two step phase separation [4]. Another important and up-to-date application concerns the sol–gels for the production of nanoparticles and membranes [1]. Guo et al. [5] prepared monolithic cordierite with a cocontinuous macroporous structure by sol-gel process accompanied by phase separation in MgO–Al_2O_3–SiO_2 ternary system. Wang et al. [6] used the immersion phase inversion process to prepare organic–inorganic-blended ultrafiltration membranes. Besides, a temperature gradient plays an important role in the phase-separated structures. Jiang et al. [7] found that the orientation of phase-separated domains can respond quickly to the change in the direction of external temperature gradient field.

However, the mechanisms and the formation kinetics of different morphologies during liquid spinodal decomposition are still unclear. Therefore, a detailed understanding of liquid spinodal phase separation in organic systems is of both fundamental interest and practical importance.

CALPHAD (*Cal*culation of *Pha*se *Di*agrams) method [8] is an important tool for designing new materials because it can significantly decrease cost and time during development of materials and provide a clear guide line for material design. The phase-field method is a powerful tool for modeling and understanding the phase transformations and microstructure evolutions. The temporal evolution of the morphology is described by a set of equations of the field variables, which are Cahn–Hilliard equations for conserved variants [9] and Ginzburg–Landau equations for nonconserved variables [10]. Combining of both thermodynamic calculation and kinetic simulation to investigate the pattern evolutions during spinodal phase separation is a general trend.

As one of the most important pollutant sources in water, phenolic compound is eliminated by organic solvent extraction method. The extraction process controlling depends on both thermodynamic and kinetic parameters. Therefore, it is important to find out the behavior of phase separation in phenolic systems. In this study, the phase diagram of heptane–phenol binary system was calculated using Flory–Huggins model [11] and the interaction parameter χ_{12} was optimized. According to the calculated thermodynamic parameters, spinodal phase separation of various initial average concentrations under different quench temperatures in this system is studied systemically via computer simulations using the phase-field method. The numerical results are presented and discussed, and conclusions are drawn.

E-mail address: liyuechan@xmut.edu.cn

2. Theory and calculation

2.1. Thermodynamic calculation

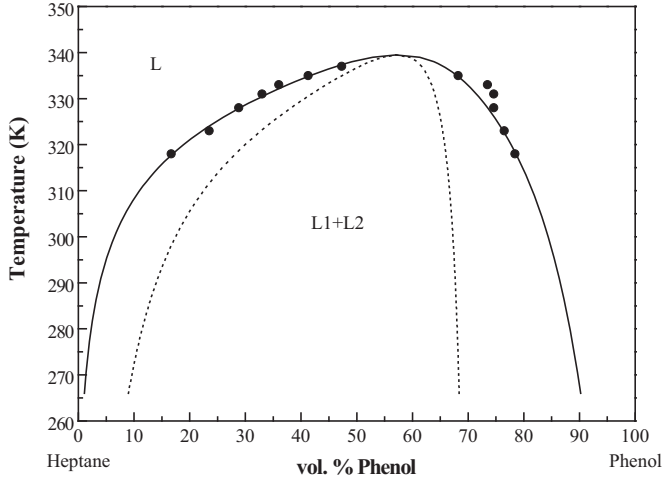The free energy density is described by the Flory–Huggins model [11]:

Fig. 1. Calculated phase diagram of heptane–phenol binary system.

$$f_{vol}(\varphi) = \frac{1}{V_m} f(\varphi) \tag{1}$$

with

$$f(\varphi) = RT((1 - \varphi)\ln(1 - \varphi) + \varphi \ln \varphi) + \chi_{12}\varphi(1 - \varphi) \tag{2}$$

where φ is volume fraction of phenol. V_m is the molar volume of the mixture and χ_{12} is the interaction parameter determining the enthalpy contribution toward mixing. χ_{12} is usually expressed as a function of temperature, T, in the following empirical form:

$$\chi_{12} = A + BT + (C + DT)*(1 - 2\varphi) \tag{3}$$

A, B, C, and D are parameters which need to be evaluated according to the CALPHAD method. On the basis of Eqs. (1)–(3), a binary phase diagram can be calculated.

2.2. Kinetic simulation

2.2.1. Cahn–Hilliard equation

According to Cahn–Hilliard theory [9], the diffusion equation describing phase separation kinetics can be written as,

$$\frac{\partial \varphi}{\partial t} = M\nabla^2\left(\frac{\partial(f_{vol}(\varphi))}{\partial \varphi} - 2\kappa\nabla^2\varphi\right) + \zeta(r, t) \tag{4}$$

where M is the chemical mobility (assumed to be composition-

Table 1
The calculated interaction parameter χ_{12} and critical points of heptane–phenol system.

System	Interaction parameter χ_{12}	Critical point Temperature (K)	Composition
Heptane–Phenol	$\chi_{12} = 15700 - 30T + (13000 - 40T)(\varphi_A - \varphi_B)$	339.5	0.570

Table 2
Some parameters of heptane and phenol.

	Density (g/cm³)	Molecular weight	Molar volume (m³/mol)
Phenol	1.071	94.11	$8.787*10^{-5}$
Heptane	0.68	100.21	$1.474*10^{-4}$

independent), $\zeta(r, t)$ is the noise term, κ is the gradient energy coefficient that can be derived from interface energy. According to Becker theory [12], interface energy between two liquids γ can be describe as follows

$$\gamma = \sigma_{12}^{L1L2} = \frac{K^`}{V_m^{2/3}}\chi_{12}\left(\varphi_1^{L1} - \varphi_1^{L2}\right)\left(\varphi_2^{L2} - \varphi_2^{L1}\right) \tag{5}$$
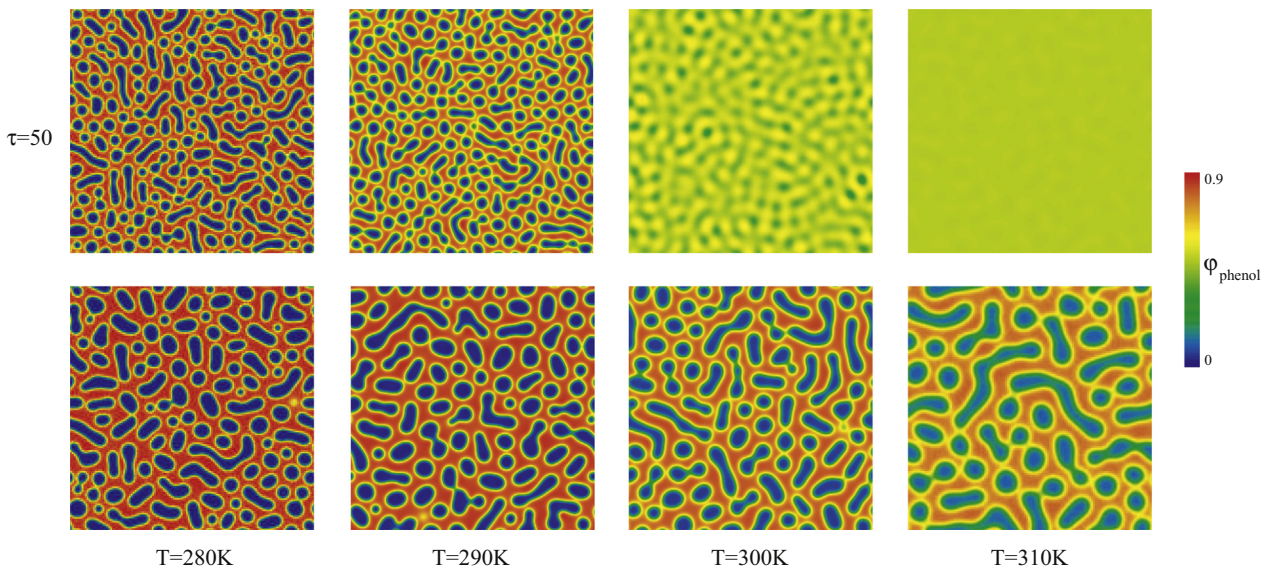

Fig. 2. Phase separation patterns at different quench temperatures in heptane–phenol system. (a) Time steps $\tau = 50$ and (b) final stage.