Demixing behavior of binary polymer mixtures

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ABSTRACT

In this work the density gradient theory in combination with different Gibbs excess energy (G^E) models is used to model the demixing behavior of binary polymer mixtures. The investigated polymer mixtures are Polydimethylsiloxane/Polytetramethyldisiloxanylethylene, Phenylethylether/Polydimethylsiloxane and Boltorn U3000/propanol. As G^E-models, the Koningsveld–Kleintjens model and the Lattice Cluster Theory combined with the extended chemical association lattice model were used. So we could show that the density gradient theory combined with different G^E-models to consider molecular influences, as association or molecular architecture, can model the demixing of polymer mixtures. The influence parameter required by the density gradient theory was fitted to experimental interfacial tension data. We have shown that the density gradient theory allows modeling the experimentally observed phenomena known from phase equilibria measurements as longer demixing times near the spinodal curve and for shorter tie lines. Moreover, the density gradient theory predicts a change in the interfacial composition near the equilibrium. But this composition change cannot be considered by common sharp interface models assuming a stable interface during the whole separation process.

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1. Introduction

The characteristics of the interface between two fluids have been the subject of scientific discussions for a long time. At the beginning of the 18th century, Young, Laplace, and Gauss [1] regarded the interface between two phases as an interface of zero thickness; whereas physical quantities such as density were assumed to be discontinuous across the interface. Later Poisson [2], Maxwell [3], and Gibbs [4] assumed that the interface actually describes a smooth transition of physical properties between the bulk fluid values. Gibbs [4] has introduced the notion of a dividing surface. At this surface, there is a discontinuity of physical quantities and surface excess quantities are introduced in order to develop the equilibrium thermodynamics of interfaces. The concept of a smooth interface with a non-zero thickness was derived by Lord Rayleigh [5] and van der Waals [6] proposed gradient theories to model the interfacial region based on thermodynamic principles. Especially, van der Waals developed a theory of the interface on the basis of his equation of state. He used this theory to calculate the thickness of the interface, which becomes infinite by approaching the critical temperature.

Cahn and Hillard [7] rediscovered the theories of Van der Waals and Rayleigh and they developed the density gradient theory (DGT). It is a mean field approximation leading to a general expression of Helmholtz free energy of an inhomogeneous system. In equilibrium interfacial/surface tension and density/concentration profiles can be calculated by using the stationary form of density gradient theory in combination with an equation of state (EOS) or a Gibbs excess energy (G^E)-model [8]. The surface tension can be modeled for pure liquids or liquid mixtures. In literature there are several works dealing with the calculation of interfacial properties in equilibrium [9–16]. To model the mass transfer across the interface and the phase decomposition, the non-steady form of the density gradient theory is used [17–19]. In literature this is often called the "spinodal decomposition", which is understood as demixing of a liquid in two coexisting phases. However, this name is somehow confusing as the binodal curve describes the two coexisting phases in equilibrium, but not the spinodal curve. As mentioned, density gradient theory is grounded on a model describing the thermodynamic equilibrium using an EOS or a G^E-model. We have decided to use G^E-models as in this case no high pressure regions are considered, the pressure does not play an important role in the demixing of liquids.

In the 1940s, it was recognized that the thermodynamics of polymeric systems need to be treated in a special way. It was found that experimental data of vapor–liquid equilibria and Raoult's law predictions for an ideal solution were inconsistent. To understand non-ideal polymer solutions Flory and Huggins independently developed a simple lattice theory [20,21]. Their theory is based on the assumption that a lattice is occupied by large molecules with differences in size. By segmenting the molecules an expression for the mixing entropy is derived. Flory and Huggins imaginary filled the lattice with polymer molecules segment by segment and afterwards with the solvent molecules counting the possibilities of positioning. Apart from the combinatorial part of the Gibbs mixing energy, also the residual part has to be calculated. In the Flory–Huggins theory the residual part is given as a purely enthalpic contribution based on the Flory–Huggins

χ-parameter dependent on temperature. But experiments have shown that the χ-parameter is also dependent on concentration. For this reason Koningsveld and Kleintjens [22] developed an expression for the χ-parameter, which is also dependent on the segment fraction. With this extension of the Flory–Huggins theory the Koningsveld–Kleintjens (KK) model is able to describe the liquid–liquid equilibrium (LLE) of different molecules as linear polymers or small molecules, but the chemical structure of the polymer is not explicitly considered. For this reason, Freed and coworkers [23,24] developed the Lattice Cluster Theory (LCT) which is based on the Flory–Huggins theory [16]. Similar as the Mayer Expansion of real gases, correction terms to the Flory–Huggins theory were calculated. Using these expansions the polymer architecture can directly be considered in the Helmholtz free energy. Zeiner et al. [25] have published a reviewed version of the LCT. By the LCT the critical concentration was predicted and with help of one adjustable parameter the critical temperature could also be calculated. Moreover, the phase with low concentration of the hyperbranched polymer could be modeled in good agreement with experimental data, but there was a deviation between the calculated high concentrated phase and the experimental data. One way to improve the model is the consideration of associative interactions. Therefore the LCT was combined with different association theories [26–29]. By this combination a good accordance between experimental data and calculations could be achieved. Furthermore, the LCT was also used to model high pressure phase equilibria of hyperbranched polymer solutions [30], using the LCT-equation of state [30–32].

In the works focusing on the spinodal decomposition [17–19] just the Flory Huggins theory has been used so far to describe the thermodynamic behavior. For this reason we want to show that also more complex thermodynamic models allowing incorporating different molecular characteristics as association phenomena and different architectures of the molecules can be used for the calculation of the demixing behavior. Moreover, the gap between the application of the DGT in equilibrium and in non-steady state is closed.

2. Theoretical background

2.1. G^E-models

This work focuses on the investigation of polymer blends/solutions. For the use of G^E-models, the molecules have to be divided in segments and all thermodynamic quantities will be considered to be dependent on the segment-molar instead of molar fraction. For this reason the segment molar fraction of component i, ϕ_i, is introduced, which is defined as follows:

$$\phi_i = \frac{M_i n_i}{N_L} \tag{1}$$

where n_i is the number of molecules i, N_L is the number of lattice sites to be occupied and M_i is the number of segments of component i.

2.1.1. Koningsveld–Kleintjens model

Similar as in the Flory–Huggins theory, the ideal-athermal mixture is chosen as a standard state in the KK-model. So the KK-model for a binary mixture can be expressed as follows [22]:

$$\frac{\Delta g_{KK}}{RT} = \frac{\phi_1}{M} \ln(\Phi_1) + \frac{\phi_2}{M_2} \ln(\phi_2) + \chi \phi_1 \phi_2. \tag{2}$$

Koningsveld and Kleintjens [22] developed a model where the Flory–Huggins χ-parameter is expressed as follows:

$$\chi = \frac{\beta(T)}{1 - \gamma \phi_2}. \tag{3}$$

Here the function $\beta(T)$ can be expressed as:

$$\beta(T) = \beta_0 + \frac{\beta_1}{T}. \tag{4}$$

The KK-model shows a physical meaning as the function $\beta(T)$ describes the contact energy of the molecules and the parameter γ expresses the ratio of the segment surfaces σ_i of the components:

$$\gamma = 1 - \frac{\sigma_{Polymer}}{\sigma_{Solvent}}. \tag{5}$$

In this work, all three parameters β_0, β_1 and γ were fitted to experimental data.

2.1.2. Lattice Cluster Theory

Freed and coworkers [23,24] developed the LCT to overcome the limitations of the Flory–Huggins theory [20,21], which are the overestimation of the state of the segments on the lattice and the ignored molecule architecture. Inspired by the work of de Gennes [33], who treated the long chains as a self-avoiding walk on a lattice by the use of spines for each component, Freed and Dudowicz [24] developed the LCT for an arbitrary chain structure. The considered chain consists of a number of monomer units (or segments) of the same type. The LCT is a cluster expansion in the inverse coordination number $1/z$ and the reduced interaction energy ε/kT (k — Boltzmann constant; T — temperature). This cluster expansion is truncated at second order, because higher contributions are numerically irrelevant [24]. Here the interaction energy ε is calculated as follows:

$$\varepsilon = \varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12} \tag{6}$$

where ε_{11} and ε_{22} are the interaction energy between two polymer segments of the same kind and ε_{12} is the interaction energy between two polymer segments of different kinds. The interaction energy ε is related to the usual χ-parameter of the Flory–Huggins theory by $\chi = \frac{2z\varepsilon}{k_B T}$. The interaction parameter ε relates to one contact point, but the quantity $z\varepsilon$ to one segment. Therefore, in the limit of an infinite number of contact points ($z \to \infty$) ε goes to zero but $z\varepsilon$ remains finite. For $z \to \infty$, all terms (Eq. (7)) except the $z\varepsilon$ terms vanish. So the Flory–Huggins limit is reached.

The segment-molar Gibbs energy Δg_{LCT} (without the pure component contributions) is written as:

$$\frac{\Delta g_{LCT}}{RT} = \frac{\phi_1}{M_1} \ln(\phi_1) + \frac{\phi_2}{M_2} \ln(\phi_2) + \sum_{i=1}^{6} \alpha_i \phi_1^i. \tag{7}$$

The first two terms of Eq. (7) are the well-known athermal Flory–Huggins contribution. The last term with the quantities α_i with i running from 1 to 6 takes the architecture of the molecules into account and represents the correction to Flory–Huggins theory. The expressions for the α_i can be found in [25]. The polymer can form a chain of M_i-segments having an arbitrary structure. To characterize the chain architecture, three architectural properties are required. Similar as in the Flory–Huggins theory [20,21] a chain is built-up of segments. Here the architectural properties are: the number $N_{1;i}$ of bonds, the number $N_{2;i}$ of two consecutive bonds, and the number $N_{3;i}$ of three consecutive bonds between segments of chain i. These parameters can be estimated a priori knowing only the chemical structure of the molecule.

2.1.3. Extended chemical association lattice model

In literature two different possibilities of describing the association are described. One way is the "physical theory", where the associative contributions are calculated by integral equations including an associative interaction potential. The second way is the assumption of a chemical