



Mass and heat diffusion in ternary polymer solutions: A classical irreversible thermodynamics approach



S. Shams Es-haghi, M. Cakmak*

Department of Polymer Engineering, 250 S. Forge St., The University of Akron, Akron, OH 44325-0301, USA

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ABSTRACT

Governing equations for evolution of concentration and temperature in three-component systems were derived in the framework of classical irreversible thermodynamics using Onsager's variational principle and were presented for solvent/solvent/polymer and solvent/polymer/polymer systems. The derivation was developed from the Gibbs equation of equilibrium thermodynamics using the local equilibrium hypothesis, Onsager reciprocal relations and Prigogine's theorem for systems in mechanical equilibrium. It was shown that the details of mass and heat diffusion phenomena in a ternary system are completely expressed by a 3×3 matrix whose entries are mass diffusion coefficients (4 entries), thermal diffusion coefficients (2 entries) and three entries that describe the evolution of heat in the system. The entries of the diffusion matrix are related to the elements of Onsager matrix that are bounded by some constraints to satisfy the positive definiteness of entropy production in the system. All the elements of diffusion matrix were expressed in terms of derivatives of exchange chemical potentials of the components with respect to concentration and temperature. The spinodal curves of ternary polymer solutions were derived from the governing equations and their correctness was checked by the Hessian of free energy density. Moreover, it was proved that setting cross-diffusion coefficients to zero results in a contradiction, and the governing equations without cross-diffusion coefficients do not express the actual phase behavior of the system.

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1. Introduction

Mass and heat diffusion in polymer solutions is of great importance in the technologies related to painting, coating, inkjet printing, plastic films and production of electronic devices [1]. Diffusion processes also play a key role in self-assembly [2] and important areas of study in soft matter physics [3]. A proper understanding of diffusion phenomena in polymer solutions is required in order to have a control on the processes involving polymer solutions.

Polymer solutions commonly used for industrial purposes are generally multi-component systems, i.e., ternary polymer solutions of one polymer in two solvents or two polymers in one solvent [4]. Most of the experimental and theoretical studies thus far, have been about diffusion in binary systems, and despite the broad range of applications involve ternary polymer solutions [4–14] there is no

theoretical work that formulates thermodynamically consistent governing equations for mass and heat diffusion in ternary polymer solutions in a way that all the mass and thermal diffusion coefficients necessary to describe the transport phenomena are derived in terms of thermodynamic variables.

By increasing the number of components in a mixture and emergence of cross-diffusion effects, the transport phenomena become very complex. As a result, a large number of mass diffusion coefficients are required to describe the mass transport [2]. This complexity will increase by adding a spatially varying temperature field to the system, since the effect of thermal diffusion and contributions of mass fluxes to the heat flow must also be considered. Mass and heat diffusion are irreversible phenomena and they contribute to entropy production in the system. Hence, the governing equations for mass and heat evolution in ternary polymer solutions must be derived in the framework of classical irreversible thermodynamics in which the balance of entropy plays a crucial role. An overview of the governing equations formulated for mass and heat diffusion in ternary polymer solutions indicates that these

* Corresponding author.

E-mail address: cakmak1@uakron.edu (M. Cakmak).

equations were derived without considering the balance of entropy in the system. Vrentas et al. [15] derived governing equations for isothermal mass diffusion in ternary polymer solutions based on a theory due to Bearman [16]. They considered a ternary polymer system containing one polymer and two solvents. In that system, the concentration of solvents was much lower than that of the polymer. They set the cross-diffusion coefficients to zero and estimated the principal mass diffusion coefficients by the self-diffusion coefficients of the solvents. Using the same approach based on the statistical theory of Bearman [16], Shojaie et al. [17] developed a model for non-isothermal mass diffusion in a ternary polymer solution containing a polymer and two solvents. The heat transfer in their model was described by the Fourier's law of heat conduction. Alsoy and Duda [18] studied the drying of ternary polymer solutions using a model in which the mass diffusion coefficients were expressed in terms of self-diffusion coefficients of the solvents. In that model they assumed temperature to be temporally dependent and spatially independent. Dabral et al. [4] modeled the drying process of a ternary polymer solution as an isothermal mass diffusion problem. Due to the lack of reliable experimental data and the absence of a suitable predictive theory, they set the cross-diffusion coefficients to zero. In the above-mentioned formulations, there is no criterion that guarantees the governing equations are thermodynamically consistent. An analysis of these models developed for diffusion in multi-component systems indicates that some of them are not consistent with the Onsager reciprocal relations [19]. Moreover, in these studies, contribution of temperature gradient to mass diffusion in ternary polymer solutions was neglected. Furthermore, the heat transfer was modeled using the Fourier's law of heat conduction. This formulation does not take into account the effect of mass diffusion on the heat transfer and the coupling between mass and heat transfer is only due to the temperature dependency of mass diffusion coefficients.

Recently, we developed a thermodynamically consistent model of mass and heat diffusion in binary polymer solutions [20]. In this paper, we focus on generalization of this model to ternary polymer solutions. Although this study aims to develop a theoretical understanding of diffusion in ternary polymer solutions, the governing equations derived herein can be used for any ternary system. Since, the governing equations have been formulated for the general case of non-isothermal three-component systems, the effect of temperature gradient on the evolution of concentration of the components was shown by derivation of thermal diffusion coefficients in terms of phenomenological coefficients and derivatives of exchange chemical potentials of the components with respect to temperature. Moreover, it was proved that cross-diffusion coefficients play a crucial role in expressing the phase behavior of a ternary system and setting the cross-diffusion coefficients to zero leads to a contradiction.

2. Theory

We consider a non-reacting ternary system in which non-convective mass diffusion and heat conduction occur. The system is considered to be in one phase, far from the critical region of phase separation. We also assume the system is in mechanical equilibrium. The hypothesis of local equilibrium allows the fundamental equation of classical thermodynamics to be valid for every volume element in the system, although the whole system is not in equilibrium [21]. Using this hypothesis and Prigogine's theorem for systems in mechanical equilibrium, the rate of change of entropy per unit volume for a three-component system such as solvent/solvent/polymer or solvent/polymer/polymer is given by (see Appendix A)

$$\frac{ds}{dt} = -\nabla \cdot \left(\frac{J_q - \mu_{1,3}J_1 - \mu_{2,3}J_2}{T} \right) - \frac{1}{T^2} \nabla T \cdot (J_q - \mu_{1,3}J_1 - \mu_{2,3}J_2) - \frac{1}{T} J_1 \cdot \nabla \mu_{1,3} - \frac{1}{T} J_2 \cdot \nabla \mu_{2,3}, \quad (1)$$

where s, J_q, J_1, J_2 and T are entropy per unit volume, heat flux, mass flux of component 1, mass flux of component 2 and absolute temperature, respectively. $\mu_{1,3}$ and $\mu_{2,3}$ are exchange chemical potentials of components 1 and 3, and 2 and 3, respectively.

Equation (1) represents the rate of change of entropy per unit volume of the mixture in terms of divergence of entropy flux and rate of entropy production per unit volume of the system σ , which can be presented in the bilinear form of thermodynamics forces

$$\underline{X} = \left(-\frac{1}{T} \nabla \mu_{1,3}, -\frac{1}{T} \nabla \mu_{2,3}, -\frac{1}{T^2} \nabla T \right) \text{ and the conjugated fluxes } \underline{J} = (J_1, J_2, J_q - \mu_{1,3}J_1 - \mu_{2,3}J_2),$$

$$\sigma = -\frac{1}{T^2} \nabla T \cdot (J_q - \mu_{1,3}J_1 - \mu_{2,3}J_2) - \frac{1}{T} J_1 \cdot \nabla \mu_{1,3} - \frac{1}{T} J_2 \cdot \nabla \mu_{2,3}. \quad (2)$$

As one can see due to a constraint for the fluxes, in a ternary system the mass flux of two components are expressed explicitly in the rate of entropy production. In effect, for a general case of an n -component system, $n-1$ equation are required to describe the mass diffusion in the system.

The governing equations can be found using linear flux–force relationships considering the Onsager reciprocal relations and also they can be derived from Onsager's variational principle [22] by maximizing $(\sigma - \psi)_j$, the difference between rate of entropy production in the system and a dissipation function ψ presented in terms of thermodynamic forces in the system

$$\psi(X_1, X_2, X_3) = \frac{1}{2} \sum_{i,k=1}^3 L_{ik} X_i X_k \geq 0, \quad (3)$$

here L_{ik} are phenomenological coefficients. Using linear flux–force relationships, the fluxes can be written in terms of the forces as shown in Eqs. (4)–(6) which in matrix presentation would yield Eq. (7)

$$J_1 = l_{11} \left(-\frac{1}{T} \nabla \mu_{1,3} \right) + l_{12} \left(-\frac{1}{T} \nabla \mu_{2,3} \right) + l_{13} \left(-\frac{1}{T^2} \nabla T \right), \quad (4)$$

$$J_2 = l_{21} \left(-\frac{1}{T} \nabla \mu_{1,3} \right) + l_{22} \left(-\frac{1}{T} \nabla \mu_{2,3} \right) + l_{23} \left(-\frac{1}{T^2} \nabla T \right), \quad (5)$$

$$J_q - \mu_{1,3}J_1 - \mu_{2,3}J_2 = l_{31} \left(-\frac{1}{T} \nabla \mu_{1,3} \right) + l_{32} \left(-\frac{1}{T} \nabla \mu_{2,3} \right) + l_{33} \left(-\frac{1}{T^2} \nabla T \right), \quad (6)$$

$$\begin{pmatrix} J_1 \\ J_2 \\ J_q - \mu_{1,3}J_1 - \mu_{2,3}J_2 \end{pmatrix} = \begin{pmatrix} l_{11} & l_{12} & l_{13} \\ l_{21} & l_{22} & l_{23} \\ l_{31} & l_{32} & l_{33} \end{pmatrix} \begin{pmatrix} -\frac{1}{T} \nabla \mu_{1,3} \\ -\frac{1}{T} \nabla \mu_{2,3} \\ -\frac{1}{T^2} \nabla T \end{pmatrix}. \quad (7)$$

Entries of matrix $L=(l_{ij})_{3 \times 3}$ are Onsager's coefficients and based on Onsager's reciprocity relations, matrix L is a symmetric matrix [23]. In conditions for which linear flux–force relations are valid,

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