



Thermal diffusion in polymer solutions: Approaching spinodal



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ABSTRACT

This paper aims to theoretically explain the behavior of thermal diffusion coefficient in polymer solutions; specifically, in the vicinity of the unstable regions of phase diagrams. Based on an equation that was derived in the framework of classical irreversible thermodynamics, a dimensionless number was introduced that plays a crucial role in determining the thermal diffusion in polymer solutions. The behavior of thermal diffusion coefficient in various phase diagrams was investigated by changing the Flory-Huggins interaction parameter to include concentration and temperature dependencies using Koningsveld interaction factor. It was shown that irrespective of the types of phase diagrams, the proposed equation for thermal diffusion becomes zero at infinite dilution and takes finite values on the spinodal line. Moreover, it was illustrated that in a binary polymer solution the Soret coefficient (the ratio of the thermal diffusion coefficient to the mutual diffusion coefficient) diverges at the critical point, and more importantly it was predicted that the divergent behavior of the Soret coefficient is observed at all the points of the spinodal line.

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1. Introduction

Mass diffusion in a multi-component system generated by applying a temperature gradient is called thermal diffusion or Soret effect [1]. This phenomenon was first discovered and reported by Ludwig, but it is called "Soret effect" because several years later Soret performed more detailed experiments and showed that a temperature gradient in some aqueous solutions results in a concentration gradient [2]. In multi-component mixtures containing macromolecules such as polymer solutions the Soret-type diffusion can be exploited in the so-called thermal field flow fractionation (TFFF) to separate polymer chains over a wide range of molecular weights [3–5]. In effect, TFFF is a powerful technique for characterization of polymers. It has a number of advantages over the size-exclusion chromatography (SEC) [6]; for example, it gives a better resolution for characterizing ultrahigh molecular-weight polymers [5,6]. Moreover, recent studies by Greyling and Pasch showed that TFFF is an effective tool for separation of polymer chains based on their microstructure [7–9]. Due to the practical importance of thermal diffusion, a good understanding of this phenomenon in

polymer solutions is needed to have a better control of practical applications. During the past decades thermal diffusion in polymer solutions has been studied extensively [10–16], however, the physics underlying this phenomenon is not fully understood [17]. According to the recent experiments, thermal diffusion of short polymer chains increases by increasing the molecular weight and reaches a plateau at very high molecular weights [12–15]. Moreover, a reciprocal relation was found between the thermal diffusion and solvent viscosity [14]. It was also observed that rigid polymer chains have higher thermal diffusion coefficients than more flexible ones [13,14,16].

Recently, the governing equations for mass and heat evolution in binary polymer solutions were derived in the framework of classical irreversible thermodynamics and the effect of thermal diffusion on the concentration profiles during the course of evaporation of the solvent was studied [18,19]. Consistent with the experimental observations, the simulation results showed that when a polymer solution is exposed to a temperature gradient, the polymer that has a positive thermal diffusion coefficient tends to migrate to the cold side of the temperature gradient [18,19]. Moreover, based on the equation that was derived for the thermal diffusion in polymer solutions, the above-mentioned experimental observations related to the effect of molecular weight, polymer chain rigidity and viscosity of the solvent on the thermal diffusion

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were explained qualitatively [18,19].

One of the important questions regarding the transport coefficients in multi-component systems is their behavior near the critical points or the unstable regions of phase diagrams. Unfortunately, studies related to the critical behavior of thermal diffusion coefficient in multi-component systems containing macromolecules are limited to a few studies in critical polymer blends [20–23]. Even in the case of multi-component systems of simple fluids, there are only a few investigations on the thermal diffusion in the neighborhood of critical points [24]. It is interesting to note that irrespective of the system in question, the Soret coefficient (the ratio of the thermal diffusion coefficient to the mutual diffusion coefficient) exhibits a divergent behavior near the critical points. Due to lack of theoretical understanding of the critical behavior of Soret effect in the polymer solutions and also knowing the fact that different polymer phase diagrams have been observed for polymer solutions, it is important to study the critical behavior of the Soret effect in polymer solutions. Therefore, the objective of this paper is to study the behavior of thermal diffusion coefficient in polymer solutions in different phase diagrams and to explain and predict the behavior of the thermal diffusion in the vicinity of the unstable regions of phase diagrams.

2. Theoretical considerations

Based on the governing equations for mass and heat transport derived in the framework of classical irreversible thermodynamics, mutual diffusion coefficient D_M , thermal diffusion coefficient $D_{thermal}$, and thermal conductivity k in a binary polymer solution are given by Refs. [18,19].

$$D_M = \alpha \left(\frac{\partial \mu}{\partial \varphi_1} \right)_T, \quad (1)$$

$$D_{thermal} = \alpha \left(\frac{\partial \mu}{\partial T} \right)_{\varphi_1} + \beta, \quad (2)$$

$$k = \gamma - \frac{\beta^2}{\alpha} T, \quad (3)$$

where α , β and, γ are the phenomenological coefficients that are restricted by constraints

$$\alpha > 0, \quad \gamma > 0, \quad |\beta| < \sqrt{\alpha \gamma T^{-1}}, \quad (4)$$

to satisfy the positive-definiteness of entropy production in the system. μ is the exchange chemical potential of the components and is given by

$$\mu = \frac{1}{M_1} \left(\mu_1 - \frac{1}{N} \mu_2 \right), \quad (5)$$

where M_1 , μ_1 , μ_2 and N are molecular weight of the solvent, chemical potential of solvent, chemical potential of polymer and ratio of the molar volume of the polymer to that of the solvent, respectively. T is the absolute temperature and φ_1 is the volume fraction of the solvent. Hereafter, the subscript 1 and 2 are used to show solvent and polymer, respectively. The behavior of mutual diffusion coefficient in different hypothetical phase diagrams of polymer solutions was studied recently [25]. In this paper, we focus on the thermal diffusion coefficient and study the behavior of thermal diffusion in polymer solutions in different phase diagrams. As will become clear later in this paper, the previous study on mutual diffusion coefficient will be exploited once we explain the

critical divergent behavior of the Soret coefficient. As discussed in the previous works [18,19], in Eq. (2), the value of β is negligible as compared to the derivative of exchange chemical potential with respect to the temperature. It is important to note that β which is a phenomenological coefficient that appears in the model derivation as the multiplier of the temperature gradient is several orders of magnitude smaller than α [1]. It should be noted that a recent comparison of the model described in Refs. [18,19], where β was neglected, with the real-time drying data showed that the model can successfully describe the experimental data obtained in different processing conditions without using any fitting parameters [26]. Since γ is positive, neglecting β also guarantees the positive definiteness of thermal conductivity. In effect, this is one manifestation of the consistency with the second law of thermodynamics that the thermal conductivity is proved to be a positive definite quantity. The phenomenological coefficient α , in general, is a function of concentration and temperature and it expressed as a dimensionless form [18,19].

$$\alpha/\alpha' = \frac{\varphi_1(1-\varphi_1)}{\theta}, \quad \alpha' = \frac{D_0 M_1}{RT_0} \quad (6)$$

where $\theta = T/T_0$, is the dimensionless temperature, R is the gas constant, and $[\alpha'][\mu] = L^2 T^{-1}$, indicating that Eq. (1) has the dimensionality of the diffusion coefficient.

Due to a constraint between mass fluxes of components in a multi-component system [18,19], only one governing equation is required to describe the mass transport in a binary system. Therefore, the thermal diffusion coefficient is expressed with respect to the component where the mass flux is expressed in terms of it. For example, if we express the mass flux in the system using the flux of component 1

$$J_1 = -D_M \nabla \varphi_1 - D_{thermal} \nabla T, \quad (7)$$

$D_{thermal}$ will be the thermal diffusion of solvent. If the thermal diffusion coefficient of component 1 is negative, upon applying a temperature gradient to the system, the component 1 will diffuse to the warm side of the temperature gradient. In such a case the second component will have a positive thermal diffusion coefficient and migrates to the cold side of the temperature gradient [27]. In the binary polymer solutions, polymers almost always have a positive thermal diffusion coefficient [10]. Due to the constraints between the mass fluxes and also the relation between thermal diffusion of the components as mentioned above, herein we picked the thermal diffusion of the solvent for analysis. This provides us with a more general picture since in real processing conditions including drying of polymer solutions, the governing equations and boundary conditions must be described in terms of the flux of the solvent [18,19].

It is important to note that, considering the Gibbs original idea indicating that the driving force for diffusion is the gradient of chemical potential [28], one can easily reach the contribution of temperature gradient to the mass flux without resorting to the details of the theory of classical irreversible thermodynamics. Since the chemical potential is a function of both concentration and temperature, the gradient of chemical potential reads

$$\nabla \mu = \left(\frac{\partial \mu}{\partial \varphi} \right)_T \nabla \varphi + \left(\frac{\partial \mu}{\partial T} \right)_\varphi \nabla T. \quad (8)$$

The gradient of chemical potential has two contributions: one from the gradient of concentration and the other from the gradient of temperature. The mutual diffusion coefficient originates from the variation of chemical potential with concentration, and thermal

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