



Application of non-equilibrium thermodynamics and computer aided analysis to the estimation of diffusion coefficients in polymer solutions: The solvent evaporation method[☆]

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ABSTRACT

In this work, the solvent evaporation method for the estimation of the Fickian diffusion coefficients in binary and in multi-component solvent(s)–polymer systems is reviewed. The existing frameworks for multi-component diffusion are also examined in detail. The described methodology is applied to estimate the diffusion coefficients in the binary systems acetone/cellulose acetate (CA), solvent/poly(vinyl acetate) and in the ternary system water/acetone/cellulose acetate, which is widely used in asymmetric membrane manufacture. The solvent evaporation process from these systems is studied as a one-dimensional numerical experiment. For this purpose, the evaporation process is modeled as a coupled heat and mass transfer problem with a moving boundary. The Galerkin finite element method (GFEM) is used to simultaneously solve the non-linear governing equations. The model predictions are compared with experimental data for polymer solution weight vs. time during evaporation to estimate the unknown parameters of the Vrentas–Duda equation. The estimated diffusion coefficients were found to be in good agreement with those measured by other methods. It is believed that this review might contribute to a more rational design of industrial processes.

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1. Introduction

Diffusion in solvents–polymer systems is of major importance in a number of industrial processes, including membrane manufacture [1–4], foam and coating formation [5,6], de-volatilization [7] and the effectiveness of polymerization reactors at high conversion [8].

The industrial importance of diffusion has led to the development of numerous physical theories for the estimation of the diffusion coefficients in solvent(s)–polymer systems [9–17]. Most of these theories are based on sound principles such as the free-volume theory [18,19].

Traditional techniques to measure diffusion coefficients include sorption and desorption techniques, radiotracer methods, chromatography, and nuclear magnetic resonance (NMR) experiments

as reviewed by Crank and Park [20], Tyrrell and Harris [21].

The need for processes optimization in polymer industry along with the recent advances in computational methods [22,23] was the starting point for the solvent evaporation method. This method combines simple laboratory experiments with advanced modeling, in order to get accurate estimates of diffusion coefficients. In particular, laboratory experiments consist of gravimetric measurement of the solvent evaporation rate from appropriate cast polymer–solvent(s) films. The measured solvent evaporation rate is compared with model predictions in order to estimate the unknown parameters of the Vrentas–Duda equation [18,19]. The aim of this work is to review recent advances in the field of the estimation of diffusion coefficients by using the solvent evaporation method.

In the first part of this work the literature is reviewed and the fundamentals of diffusion as well as the free-volume theory are briefly discussed by using sound principles of non-equilibrium thermodynamics. In the second part, modeling equations for the solvent(s) evaporation from polymer solutions along with the Galerkin finite element method (GFEM) are examined. In Sections 3 and 4 of this work the solvent evaporation method is applied to binary and to ternary solutions, respectively. As main material

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the cellulose acetate (CA) has been selected, due to its importance in membrane manufacture. Finally, in Section 5 conclusions are drawn.

1.1. Diffusion fundamentals

1.1.1. Physical framework for diffusion

According to Truesdell [24] the diffusion theories can be classified as kinetic, hydrodynamic and thermodynamic models. The first theory developed is the kinetic model of Fick [25]. Fick [25], based on an asserted analogy of diffusion to heat flow, proposed the following equation for the mass flux j_i as a function of the mass density gradients in a binary mixture having uniform total density:

$$j_i = -D_{12} \text{grad} \rho_i; \quad i = 1, 2 \quad (1)$$

D_{12} is the Fickian phenomenological coefficient and ρ_i is the mass density of the i -th substance. The above equation can be generalized to multi-component mixtures also including the effects of temperature (Soret effect) on the mass flux (for a detailed review see Refs. [26,27]):

$$j_i = -D_i^T \text{grad} \ln T - \sum_{j=1}^{N-1} D_{ij} \text{grad} \rho_j; \quad i = 1, 2, 3, \dots, N \quad (2)$$

where D_i^T represents the multi-component thermal diffusion coefficients, T is the absolute temperature, and D_{ij} is the Fickian phenomenological coefficient between the i -th and j -th substance.

The most representative model for the hydrodynamic theories is the Maxwell–Stefan formulation [28–32] which generated considerable interest in the literature [33–35]. As reviewed by Cussler [36,37], Taylor and Krishna [38], Matuszak and Donohue [39] the Stefan–Maxwell formulation was applied in many areas including membrane and film science, chromatography, controlled-release, adsorption, catalysis, extraction and absorption, and distillation.

The thermodynamic theories include the Onsager–Fuos model [40–43] for diffusion:

$$\frac{d\mu_i}{dz} = -\sum_{k=1}^N c_k R_{ik} (v_i - v_k); \quad i = 1, 2, \dots, N \quad (3)$$

where μ_i and c_i are the chemical potential and the molar concentration of the i -th substance and R_{ij} are the resistance (friction) coefficients. Most workers in the area, assume the R_{ij} coefficients to be symmetrical according to the Onsager principle [44,45]:

$$R_{ij} = R_{ji}; \quad i, j = 1, 2, \dots, N \quad (4)$$

The underlying relations between the various diffusion models were investigated by many researchers [35,39,46].

Regarding membrane and film formation modeling, most work relies on the Fick law combined with the Onsager–Fuos model [47,48]. More specifically, the resistance coefficients defined in Eq. (3) are related to the usual Fickian diffusion equations (Eq. (1)) by using the definition of the diffusion molar flux (J_i^V) relative to the volume average velocity v^V [26,27]:

$$J_i^V = -\sum_{j=1}^{N-1} D_{ij} \text{grad} c_j = c_i (v_i - v^V); \quad v^V = \sum_{i=1}^N u_i v_i; \quad \sum_{i=1}^N J_i^V V_{Mi} = 0; \quad c_1 V_{M1} + c_2 V_{M2} = 1 \quad (5)$$

where c_i is molar concentration, V_{Mi} represents specific partial molar volume and u_i stands for the volume fraction of the i -th substance, respectively. By subtracting and adding the volume-average velocity v^V in Eq. (3), we can give write the diffusion coefficients, D_{ij} , in terms of the resistance coefficients R_{ij} .

However, the dependence of the resistance coefficients on concentration and temperature is not known. To reduce the high degree of freedom one has to resort to the self-diffusion coefficients.

1.1.2. Self-diffusion coefficients

The self-diffusion coefficients stand for the mass transfer in the absence of external gradients (temperature, concentration, etc.) [49]. They are usually measured by studying the movement of labeled compounds in chemically uniform systems. The self-diffusion coefficients D_1, D_2 for a binary solution can be written as a function of the resistance coefficients (friction) and the molar concentrations as [21]:

$$D_1 = \frac{RT}{c_1 R_{1*1} + c_2 R_{12}}; \quad D_2 = \frac{RT}{c_2 R_{2*2} + c_1 R_{12}} \quad (6)$$

Here R represents the universal gas constant, T stands for temperature in Kelvin and $R_{i,i}$ represents the resistance (friction) coefficient of i -th substance isotopes. The above equation gives the self-diffusion coefficient as experimentally determined in a ternary radiotracer experiment. In fact self-diffusion coefficients are measured by labeling some molecules of one component, say component 1, and following the diffusion of the labeled and unlabeled molecules through a chemically homogenous solution. The system can be treated as a ternary one consisting of unlabeled component 1, labeled component 1 designated as 1* and component 2 (Ref. [21], p. 81). In the above equation c_1 represents total molar concentration (labeled + unlabeled) of species type 1.

In order to measure self-diffusion coefficients in a ternary system (e.g. formamide–acetone–polymer) one has to take into account a quaternary system (Experiment A: labeled formamide 1*, formamide 1, acetone 2, polymer 3, Experiment B: formamide 1, labeled acetone 2*, acetone 2, polymer 3) and the following equations are directly derived [16]:

$$D_1 = \frac{RT}{c_1 R_{1*1} + c_2 R_{12} + c_3 R_{13}}; \quad D_2 = \frac{RT}{c_2 R_{2*2} + c_1 R_{12} + c_3 R_{23}} \quad (7)$$

In the above the resistance coefficients between isotopes (R_{1*1}, R_{2*2}) are not equal to the resistance coefficients of the unlabelled compounds (R_{11}, R_{22}) [21].

Regarding the relation of self-diffusion diffusion coefficients to the Fickian diffusion coefficients for binary solutions, the following equation is derived for the Fickian diffusion by using Eqs. (5) and (6):

$$D_{12} = \frac{V_{M2}}{R_{12}} \left(\frac{\partial \mu_1}{\partial \ln c_1} \right)_{T,P} \quad (8)$$

There are two distinct cases: the case of constant resistance coefficient ratio and the case of moderate solvent concentration. Bearman [50] has shown that the following equation holds for the case of constant resistance coefficient ratio:

$$\sqrt{\frac{R_{22}}{R_{11}}} = \sqrt{\frac{R_{22}}{R_{1*1}}} = \frac{V_{M2}}{V_{M1}} \quad (9)$$

By using Eqs. (8) and (9) along with the geometric rule ($R_{12} = \sqrt{R_{11} R_{22}}$), one directly shows that the mutual diffusion coefficient is given as a function of solvent molar concentration c_1 , chemical potential μ_1 and the self-diffusion coefficient D_1 by the

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