

Diffusion in Multi-component Polymer Solutions

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Abstract: In the present work a comprehensive methodology is proposed for calculating the Fickian diffusion coefficients in a multi-component solvents-polymer system as a function of the solvents self-diffusion coefficients, the constituent chemical potentials and the process conditions. This methodology is based on the application of well established principles such as the Gibbs-Duhem theorem for diffusing systems along with the friction coefficients concepts. It is also shown, in the most general case of multi-component solutions that the cross friction factors (ζ_{ij} $i \neq j$) are related to the i -th and j -th substances friction coefficients (ζ_{ii} , ζ_{jj}) by the simple geometric rule ($\zeta_{ij}^2 = \zeta_{ii}\zeta_{jj}$) in order to simultaneously satisfy the Onsager reciprocal conditions and the Gibbs-Duhem equation. The case of constant friction coefficients ratios is re-examined leading to a screening of the existing theories for multi-component polymer systems. Finally, the described methodology is applied to the formamide-acetone-cellulose acetate (CA) system which is used in the asymmetric membrane manufacture. The acetone evaporation process from this system is studied as one-dimensional numerical experiment. For this purpose, the evaporation process is modeled as a coupled heat and mass transfer problem with a moving boundary and the Galerkin finite element method is used to solve simultaneously the non-linear governing equations. All the model parameters were estimated from literature measurements leading to a fully predictive model. The model predictions are in excellent agreement with experimental data for polymer solution weight and surface temperature vs. time thus validating the applied methodology for the calculation of friction coefficients.

Key-Words: Multi-component Diffusion, Friction Coefficients, Free Volume Theory, Solvent Evaporation, Coatings, Asymmetric Membrane Formation -

1 Introduction

The multi-component diffusion in solvents-polymer systems is a process of major importance in many industrial processes, including membrane, foam and coating formation, de-volatilization, effectiveness of polymerization reactors at high conversion. The importance of the multi-component diffusion has led to numerous physical theories for solvent(s)-polymer systems¹⁻⁶. Most theories utilize the free volume theory for the estimation of the solvent(s) self-diffusion coefficients⁷ along with the friction coefficients concepts⁸ to describe the dependence of Fickian diffusion coefficients on temperature and concentration. The main difficulty in this approach is that one has more unknowns to determine than available equations. To overcome this difficulty several workers⁴⁻⁶ developed physical theories relating the friction factors with pure substances properties such as the molecular weight, the molar volume etc. Most of these theories assume that the ratios of friction factors remain constant³⁻⁴.

In this work, the generalized friction coefficients formalism along with the various theories for friction coefficients determination is briefly reviewed, the corresponding equations relating the friction factors with solvent(s) self-diffusion coefficients are derived and the special case of constant friction factors ratios is re-examined. Finally, the above theory is validated against established experimental data for the acetone evaporation from the formamide-acetone-cellulose acetate system which is widely used in asymmetric membrane preparation, results are presented and conclusions are drawn.

2. Problem Formulation

The origin of the friction coefficients concept can be found in the works of Einstein and Sutherland for the binary diffusion⁸. Onsager based on non-equilibrium thermodynamics applied for the first time the friction coefficient concepts in multi-component systems.⁸ According to Bearman⁹ the self diffusion coefficient of the i-th substance can be expressed as a function of the friction coefficients and the molar concentrations as:

$$D_1^* = \frac{RT}{N^2 \left(c_i \zeta_{i \cdot i} + \sum_{\substack{j=1 \\ j \neq i}}^N c_j \zeta_{ij} \right)} \quad (1)$$

$\zeta_{i \cdot i}$ represents the friction factor of i-th substance isotopes. In the above notation, a distinction was made between the isotopes friction coefficients as a result of the self-diffusion experimental measurement by the radiotracer technique. An extensive discussion of the subject is given by Tirrell and Harris⁸.

In the above equations, there are more friction coefficients to define than available equations (high degree of freedom). For example, in the ternary system (non)-solvent(1)-solvent(2)-polymer(3) system the ternary diffusion coefficients, D_{ij} , are related to the friction coefficients and the thermodynamic properties by the following equations:¹⁰

$$D_{11} = -\frac{V_1}{N^2 E} \left(E_{22} \frac{\partial \mu_1}{\partial u_1} - E_{12} \frac{\partial \mu_2}{\partial u_1} \right)$$

$$D_{12} = -\frac{V_2}{N^2 E} \left(E_{22} \frac{\partial \mu_1}{\partial u_2} - E_{12} \frac{\partial \mu_2}{\partial u_2} \right)$$

$$\begin{aligned}
 D_{21} &= -\frac{V_1}{N^2 E} \left(E_{11} \frac{\partial \mu_2}{\partial u_1} - E_{21} \frac{\partial \mu_1}{\partial u_1} \right) \\
 D_{22} &= -\frac{V_2}{N^2 E} \left(E_{11} \frac{\partial \mu_2}{\partial u_2} - E_{21} \frac{\partial \mu_1}{\partial u_2} \right)
 \end{aligned} \quad (2)$$

where N is Avogadro's number; E_{ij} and E are defined as

$$\begin{aligned}
 E_{11} &= \frac{V_1 u_2 \zeta_{12}}{v_2 u_3} - \frac{RTV_1(1-u_2)}{N^2 D_{T1} u_1 u_3} \\
 E_{12} &= \frac{(1-u_1)\zeta_{12}}{M_2 u_3} - \frac{RTV_2}{N^2 D_{T1} u_3} \\
 E_{21} &= \frac{(1-u_2)\zeta_{12}}{M_1 u_3} - \frac{RTV_1}{N^2 D_{T2} u_3} \\
 E_{22} &= \frac{V_2 u_1 \zeta_{12}}{v_1 u_3} - \frac{RTV_2(1-u_1)}{N^2 D_{T2} u_2 u_3} \\
 E &= -\frac{\zeta_{12}^2}{M_1 M_2 u_3} + \frac{R^2 T^2 V_1 V_2}{N^4 D_{T1} D_{T2} u_1 u_2 u_3} \\
 D_{Ti} &= \frac{D_i^*}{1 - (D_i^* / D_i^0)} \approx D_i^* \\
 D_i^0 &= \frac{RTM_i v_i}{u_i \zeta_{ii} N^2}
 \end{aligned} \quad (3)$$

Here, M_i and v_i are the molecular weight and pure molar volume of the i -th component, and ζ_{ij} represents the friction coefficient between components i and j , respectively. In the above equations u_i represents the volume fraction of the i -th substance respectively. The chemical potentials μ_i are directly calculated as function of polymer solution temperature and volume fractions in the ternary system using Flory-Huggins theory.¹¹

D_i^* represents the self diffusion coefficient of the i -th component in the ternary solution and are given as a

function of the process conditions by the free-volume theory⁷. In the equations (2)-(3) the Fickian diffusion coefficients D_{ij} are related not only to self-diffusion coefficients but also to the ζ_{12} friction coefficient which must be determined. This could be achieved by estimating ζ_{12} from binary diffusion coefficient data¹² for the solvent(1)-solvent(2) system or by applying physical theories¹⁻⁶.

The aim of this work is to overcome these difficulties and suggest a unique theory for the diffusion in multi-component polymer solutions.

3. Problem Solution

The starting point in our analysis is the definition of Onsager L_{ij} mobility coefficients. Following Onsager we shall assume that the molar fluxes J_i in a n -component system can be expressed as a linear combination of the vector of chemical potential gradients X_i and a $N \times N$ matrix of Onsager L_{ij} mobility coefficients:

$$\begin{aligned}
 J_i &= \|L_{ij}\| X_i \\
 X_i &= -\text{grad} \mu_i \quad J_i = c_i (v_i - v^R)
 \end{aligned} \quad (4)$$

Where v^R refers to the velocity of an arbitrary reference framework, c_i is the molar concentration. By inverting the above equations one gets:

$$\begin{aligned}
 X_i &= \|L_{ij}\|^{-1} J_i = \|\zeta_{ij}\| J_i \\
 i &= 1, 2, \dots, N \quad ; \quad j = 1, 2, \dots, N
 \end{aligned} \quad (5)$$

By applying the Gibbs-Duhem theorem for isothermal and isobaric systems the following equations hold:⁸

$$\sum_{i=1}^N x_i d\mu_i = \sum_{i=1}^N c_i \frac{d\mu_i}{dz} = 0 \quad \text{or}$$

$$\sum_{i=1}^N \sum_{j=1}^N \zeta_{ij} c_i J_j = \sum_{j=1}^N J_j \sum_{i=1}^N c_i \zeta_{ij} = 0$$

$$\sum_{i=1}^N c_i \zeta_{ij} = 0 \quad j=1,2..N \quad (6)$$

By multiplying the above equation by $(v_i - v^R)$ and subtract the product from equation (5) the following equation is derived: ⁸

$$\frac{d\mu_i}{dz} = - \sum_{k=1}^N c_k [\zeta_{ik} (v_i - v_k)] \quad (7)$$

Finally, Miller (Ref. 8, p. 50) using equations (6) and (7) derived the Onsager reciprocal conditions:

$$\zeta_{ik} = \zeta_{ki} \quad i = 1,2,..N; \quad k=1,2 ..N \quad (8)$$

By eliminating the molar concentration in equation (6) and apply the Onsager reciprocal rule (Eq. 8) the following equation is derived:

$$\zeta_{ij}^2 = \zeta_{ii} \zeta_{jj} \quad (9)$$

This equation was also proposed by Price and Romdhane¹³The importance of the above equation is shown in the next paragraph. Equation (6) can be re-written as

$$\zeta_{ii} + \sum_{\substack{j=1 \\ j \neq i}}^n \zeta_{ji} (c_j / c_i) = 0 \quad i=1,2..N \quad (10)$$

The following equation also holds:⁸

$$\sum_{i=1}^n c_i v_i = 1 \quad (11)$$

By substituting equations (11) and (9) into equation (10), taking into account constant ratio of friction coefficients (arbitrary physical constants) and taking the derivatives with respect to molar concentration, one directly derives the following equation for the ratio of friction coefficients:

$$(\zeta_{ii} / \zeta_{jj})^{0.5} = v_i / v_j$$

$$\zeta_{ik} / \zeta_{jk} = v_i / v_j \quad (12)$$

This equation proposed also by Alsoy and Duda³, satisfies simultaneously the Onsager reciprocal condition as well as the Gibbs-Duhem relation along with the concept of constant friction coefficients ratio.

Regarding the multi-component system consisting of n-1 low molecular weight substances and a polymer, the application of the Gibbs-Duhem theorem leads to the calculation of the friction coefficients if the low molecular weight substances self diffusion coefficients are known.

For example the Gibbs-Duhem equations (Eq. 6) for a diffusing ternary system are written as:

$$\zeta_{12} = \sqrt{\zeta_{11} \zeta_{22}}$$

$$\begin{aligned} c_1 \zeta_{11} + c_2 \zeta_{12} + c_3 \zeta_{13} &= 0 \\ c_2 \zeta_{22} + c_1 \zeta_{12} + c_3 \zeta_{23} &= 0 \\ c_3 \zeta_{33} + c_2 \zeta_{23} + c_3 \zeta_{13} &= 0 \end{aligned} \quad (13)$$

The friction coefficients ζ_{13} and ζ_{23} are related to ζ_{12} in terms of the respective Bearman equations for the self-diffusion coefficients (eq. 1) as follows: ¹⁰

$$\zeta_{13} = \frac{v_3}{u_3} \left(\frac{RT}{N^2 D_{T1}} - \frac{u_2}{v_2} \right)$$

$$\zeta_{23} = \frac{v_3}{u_3} \left(\frac{RT}{N^2 D_{T2}} - \frac{u_1}{v_1} \right) \quad (14)$$

The D_{Ti} are given in Eq. 3 Equations (13)-(14) result for a ternary system in a simple quadratic equation which is directly solved to calculate ζ_{12} and consequently D_{ij} in terms of the self-diffusion coefficients and the process conditions.

Finally, the described methodology is applied to the formamide-acetone-cellulose acetate (CA) system which is used in the asymmetric membrane manufacture. The acetone evaporation process from this system is studied as one-dimensional numerical experiment. For this purpose, the evaporation process is modeled as a coupled heat and mass transfer problem with a moving boundary and the Galerkin finite element method is used to solve simultaneously the non-linear governing equations.¹² All the model parameters were estimated from literature measurements leading to a fully predictive model. In Figure 1 the model predictions are compared with experimental data for polymer solution weight. It was found convenient to represent polymer solution weight as the ratio of the acetone plus formamide weight to the cellulose acetate weight in the polymer solution. The experimental data & conditions of Ohya nad Sourirajan¹⁴ were used in our numerical experiments The model predictions are in excellent agreement with

experimental data¹⁴ for polymer solution weight (see Fig 1) and surface temperature vs. time thus validating the applied methodology for the calculation of friction coefficients.

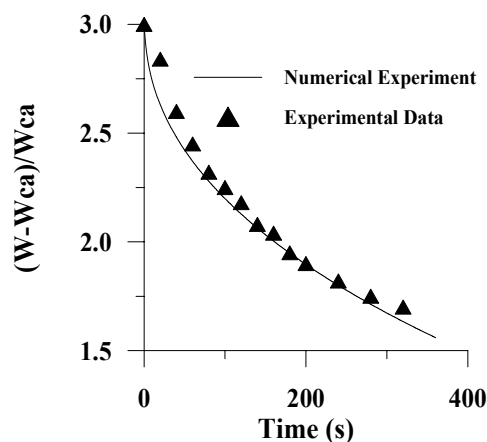


Figure 1. Comparison of model predictions for polymer solution weight with experimental data¹⁴

4 Conclusions

In the present work it is shown in the most general case of a diffusing multi-component solutions that application of the Gibbs-Duhem theorem leads to a simple geometric rule ($\zeta_{ij}^2 = \zeta_{ii}\zeta_{jj}$) between the cross friction coefficients (ζ_{ij} $i \neq j$) and the pure substances friction coefficients (ζ_{ii}). In addition, if the ratios of friction factors remain constant the following equation holds: $(\zeta_{ii}/\zeta_{jj})^{0.5} = v_i/v_j$. Where v_i is the molar volume of i -th substance in the solution.

It is also shown, that application of Gibbs-Duhem theorem along with the above simple geometric rule to a multi-component system solvent (1)-solvent(2)-....-solvent(n-1) - polymer(n) leads to further estimation of the Fickian diffusion coefficients as a function of the solvents self diffusion coefficients, chemical potential as well as process conditions.

Finally, the above theory was validated against established experimental data for the acetone evaporation from the ternary formamide-acetone-cellulose acetate system which is important in asymmetric membrane preparation. The model predictions are in excellent agreement with experimental data for polymer solution weight and surface temperature thus validating the applied methodology for the calculation of friction coefficients.

The described methodology may be applied to processes such as asymmetric membrane formation, controlled drug release and reverse osmosis that exhibit similar multi-component diffusion phenomena thus leading to a more rational design of processes and products.

Acknowledgments

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