Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 46 (2005) 12626–12636

polymer

www.elsevier.com/locate/polymer

Multi-component diffusion in polymer solutions[☆]

George D. Verros [a,*], Nikolaos A. Malamataris [b]

[a] Department of Electrical Engineering, Technological Educational Institute of Lamia, GR-351 00 Lamia, Greece
[b] Department of Mechanical Engineering, Technological Educational Institute of W. Macedonia, GR-501 00 Kila, Greece

Received 19 July 2005; received in revised form 31 October 2005; accepted 1 November 2005

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 coefficient concepts. The case of constant friction coefficient 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 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 is used to simultaneously solve 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.

Keywords: Multi-component diffusion; Friction coefficients; Free volume theory

1. Introduction

Multi-component diffusion in solvent–polymer systems is of major importance in a number of industrial processes, including membrane manufacture [1–6], foam and coating formation [7], de-volatilization [8] and effectiveness of polymerization reactors at high conversion [9–14].

The industrial importance of the multi-component diffusion has led to the development of numerous physical theories for solvent(s)–polymer systems [15–19] by using the well known free volume theory [20]. Most theories [16–19] assume constant friction coefficient ratios and relate friction coefficients [21–23] with pure substance properties such as molecular weight, molar volume etc to describe the dependence of Fickian diffusion coefficients on temperature and concentration.

In this work a novel theory is proposed for multi-component diffusion in polymer solutions. This theory is based on the Onsager reciprocal conditions [21–23] and the Gibbs-Duhem equation [24]. In addition, it is shown for the case of constant friction coefficients ratios that the following equation holds: $(\zeta_{ij}/\zeta_{kj}) = v_i/v_k$ where v_i is the molar volume of ith substance in the solution.

In this work, the generalized friction coefficient 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 coefficient ratios is re-examined. Finally, the above theory is validated against established experimental data for 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. Friction coefficients formalism

The origin of the friction coefficients concept can be found in the works of Einstein and Satherland for binary diffusion

---

[☆] A preliminary version of this work was presented in the 3rd IASME/WSEAS International Conference on Heat Transfer, Thermal Engineering and Environment, 21–23 August 2005, Corfu, Greece.

[*] Corresponding author. Address: P.O. Box 454, Plagiari Thessaloniki 57500, Epanomi, Greece. Tel.: +306972722651; fax: +302231022465.

E-mail addresses: verros@eng.auth.gr (G.D. Verros), gdverros@otenet.gr (G.D. Verros).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.11.004

Notation section

a	free volume theory proportionality constant (mol/m^3)
c_i	molar concentration of the ith substance (mol/m^3)
C_i	auxiliary parameter, dimensionless
C_p	specific heat capacity, J/(kg K)
D_0	scaling factor (m^2/s)
D_{ij}	diffusion coefficient (m^2/s)
D_{Ti}	auxiliary parameter (m^2/s)
D_i^0	auxiliary parameter (m^2/s)
D_i^*	self diffusion coefficient of the ith substance (m^2/s)
D_{0i}	pro-exponential factor (m^2/s)
E	auxiliary parameter (J^2 m^2 s^2 mol^2/kg^2)
E_{ij}	auxiliary parameter (J m s mol/kg)
F	dissipation function (J/(m^3 s))
h	heat transfer coefficient (W/(m^2 K))
J_i	molar flux (mol/(m^2 s))
$j_i^{\neq}$	mass flux (kg/(m^2 s))
k	thermal conductivity (W/(m K))
K_{1i}	free volume parameter (m^3/(kg K))
K_{2i}	free volume parameter (K)
L_0	polymer solution initial axial length (m)
L_{sup}	support axial length (m)
L_{ij}	onsager mobility coefficient (mol^2/(J m s))
M_i	molecular weight of the ith substance (g/mol)
N	number of the constituents in the solution, dimensionless
N_{A}	avogadro number
R	universal gas constant (J/(mol K))
R^i	weighted residual, dimensionless
s	position of the moving boundary, dimensionless
T	temperature (K)
T_{g}	glass transition temperature (K)
u_i	volume fraction of ith substance, dimensionless
V_i	local velocity (m/s)
V^{R}	velocity of an arbitrary framework (m/s)
$V^{\neq}$	volume average velocity (m/s)
$V(0)$	solvent molar volume at 0 K (m^3/mol)
V_{FH}	average hole free volume per kilogram of solution (m^3/kg)
V_i^*	specific critical hole free volume of the ith substance (m^3/kg)
$\bar{V}_i$	specific volume of the ith substance (m^3/kg)
z	axial coordinate (m)

Greek letters

α	auxiliary parameter to scale friction coefficients
γ	overlap factor, dimensionless
ΔH_i	ith substance latent heat of vaporization (J/kg)
ε	emissivity of the polymer solution, dimensionless
ζ_{ij}	friction coefficient between the ith and jth substance (J m s/mol^2)
η	dimensionless axial length
Θ	dimensionless temperature
λ	auxiliary function, dimensionless
μ_i	chemical potential of the ith substance, J/mol
ξ	ratio of the critical molar volume of the solvent jumping unit to the polymer jumping unit critical molar volume, dimensionless
ρ	density (kg/m^3)
ρ_i	mass concentration of the ith substance (kg/m^3)
σ	Stefan-Boltzman constant (W/(m^2 K^4))
τ	dimensionless time
v_i	molar volume of the ith substance (m^3/mol)
ϕ^i	quadratic basis function, dimensionless
χ_{ij}	Flory–Huggins interaction parameter
ω_i	weight fraction of the ith substance

Subscript

0	initial condition
int	gas phase-polymer solution interface
s	polymer solution
sup	support

[22]. Onsager [25], based on non-equilibrium thermodynamics, applied for the fist time the friction factor concepts in multi-component systems. In his view, the dissipation function F, representing the free energy variation rate as a function of the local molar flux densities (J_i, J_k) and the friction factors (ζ_{ik}) is given as:

$$F=\frac{1}{2}\sum_{i=1}^{N}\sum_{k=1}^{N}\zeta_{ik}(J_iJ_k)=\frac{1}{2}\sum_{i=1}^{N}\sum_{k=1}^{N}\zeta_{ik}c_ic_k(V_iV_k) \tag{1}$$

where the local velocity vector V_i is defined as J_i/c_i, where c_i is the molar concentration of the ith substance.

When all the components in the mixture have the same velocity V, the free energy density remains constant and the dissipation function F is zero. Consequently,

$$\frac{1}{2}V^2\sum_{i=1}^{N}\sum_{k=1}^{N}\zeta_{ik}c_ic_k=0,\quad \sum_{k=1}^{N}\zeta_{ik}c_i=0 \tag{2}$$

$$k=1,2,\ldots,N;\quad i=1,2,\ldots,N$$

He also showed that the rate of free energy variation reaches a maximum when the local gradients of chemical potential have the following form:

$$\frac{\mathrm{d}\mu_i}{\mathrm{d}z}=-\sum_{k=1}^{N}c_k\zeta_{ik}(V_i-V_k)\quad i=1,2,..N \tag{3}$$

The friction coefficients defined in Eqs. (1)–(3) are related to the usual Fickian diffusion equations using the equations for the diffusion flux ($j_i^{\neq}$) relative to the volume average velocity $V^{\neq}$ [26]:

$$j_i^{\neq} = -\sum_{j=1}^{N-1} D_{ij}\nabla\rho_j = \rho_i(V_i - V^{\neq})V^{^1};\ = \sum_{i=1}^{N} u_i V_i;\ \sum_{i=1}^{N} j^{\neq}\bar{V}_i = 0 \tag{4}$$

where D_{ij} are the respective Fickian diffusion coefficients, $\bar{V}_i$ represents the specific volume and u_i stands for the volume fraction of the ith substance, respectively.

By using Eqs. (3) and (4), one can directly write the Fickian diffusion coefficients D_{ij} in terms of the friction coefficients ζ_{ij}. Unfortunately, the concentration and temperature dependence of the friction coefficients is still unknown. Therefore, one has to resort to additional relationships expressing the friction coefficients in terms of the well defined quantities such as the self-diffusion coefficients.

According to Bearman [27] the self diffusion coefficients D_1^*, D_2^* can be written as a function of the friction coefficients and the molar concentrations as:

$$D_1^* = \frac{RT}{N_\mathrm{A}^2(c_1\zeta_{11}^* + c_2\zeta_{12})} D_2^* = \frac{RT}{N_\mathrm{A}^2(c_2\zeta_{22}^* + c_1\zeta_{12})} \tag{5}$$

Here R represents the universal gas constant, T stands for temperature in Kelvin, $\zeta_{i\cdot i}$ represents the friction factor of ith substance isotopes and N_A is the Avogadro number. The above equations give the self-diffusion coefficient as experimentally determined in a ternary radiotracer experiment. More specifically, self-diffusion coefficients are measured by labeling some molecules of one component, say component 1, and following the diffusion of the labeled and unlabeled through the chemically homogenous solution. The system in a radiotracer experiment can be treated as a ternary one consisting of unlabeled component 1, labeled component 1 designated as 1* and component 2 (Ref. [22], p. 81). The above equations were derived to describe the radiotracer experiments. In Eq. (5), c_i represents the total molar concentration (labeled+unlabeled) of the ith substance. The proof of Eq. (5) using classical thermodynamics is given in two ways in Ref. [22] (p. 81–83) and its generalization to multi-component systems is obvious.

To measure the self diffusion coefficients in a ternary system (e.g. formamide–acetone–CA) one has to take into account a quaternary system (experiment A: labeled formamide 1*, formamide 1, acetone 2, CA 3, experiment B: formamide 1, labeled acetone 2*, acetone 2, CA 3) and the following equations are directly derived:

$$\begin{gathered} D_1^* = \frac{RT}{c_1\zeta_{11}^* + c_2\zeta_{12} + c_3\zeta_{13}}; \\ D_2^* = \frac{RT}{c_2\zeta_{22}^* + c_1\zeta_{12} + c_3\zeta_{23}} \end{gathered} \tag{6}$$

In Eqs. (5) and (6) the friction coefficients between isotopes (ζ_{1*1}, ζ_{2*2}) are not equal to the friction coefficients of the unlabelled compounds (ζ_{11}, ζ_{22}). Let us now assume that the self-diffusion in a usual ternary diffusion experiment (e.g. coating drying) can also be measured by a hypothetical self-diffusion experiment conducted under carefully controlled laboratory conditions using labeled compounds of the same concentration and in the same temperature conditions as in the usual ternary experiments. In this case, the self diffusion coefficient in the ternary diffusion experiment (e.g. coating drying) can be set equal to Eq. (6) which gives the self-diffusion coefficient as measured by the labeled compound experiments.

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 directly derived from Eqs. (3), (4) and (6) [28]:

$$D_{11} = -\frac{\bar{V}_1}{N_\mathrm{A}^2 E}\left(E_{22}\frac{\partial\mu_1}{\partial u_1} - E_{12}\frac{\partial\mu_2}{\partial u_1}\right) \tag{7}$$

$$D_{12} = -\frac{\bar{V}_2}{N_\mathrm{A}^2 E}\left(E_{22}\frac{\partial\mu_1}{\partial u_2} - E_{12}\frac{\partial\mu_2}{\partial u_2}\right) \tag{8}$$

$$D_{21} = -\frac{\bar{V}_1}{N_\mathrm{A}^2 E}\left(E_{11}\frac{\partial\mu_2}{\partial u_1} - E_{21}\frac{\partial\mu_1}{\partial u_1}\right) \tag{9}$$

$$D_{22} = -\frac{\bar{V}_2}{N_\mathrm{A}^2 E}\left(E_{11}\frac{\partial\mu_2}{\partial u_2} - E_{21}\frac{\partial\mu_1}{\partial u_2}\right) \tag{10}$$

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

$$E_{11} = \frac{\bar{V}_1 u_2\zeta_{12}}{v_2 u_3} - \frac{RT\bar{V}_1(1-u_2)}{N_\mathrm{A}^2 D_{T1} u_1 u_3} \tag{11}$$

$$E_{12} = \frac{(1-u_1)\zeta_{12}}{M_2 u_3} - \frac{RT\bar{V}_2}{N_\mathrm{A}^2 D_{T1} u_3} \tag{12}$$

$$E_{21} = \frac{(1-u_2)\zeta_{12}}{M_1 u_3} - \frac{RT\bar{V}_1}{N_\mathrm{A}^2 D_{T2} u_3} \tag{13}$$

$$E_{22} = \frac{\bar{V}_2 u_1\zeta_{12}}{v_1 u_3} - \frac{RT\bar{V}_2(1-u_1)}{N_\mathrm{A}^2 D_{T2} u_2 u_3} \tag{14}$$

$$E = -\frac{\zeta_{12}^2}{M_1 M_2 u_3} + \frac{R^2T^2\bar{V}_1\bar{V}_2}{N_\mathrm{A}^4 D_{T1} D_{T2} u_1 u_2 u_3} \tag{15}$$

$$D_{Ti} = \frac{D_i^*}{1-\left(D_i^*/D_i^0\right)} \approx D_i^*;\quad D_i^0 = \frac{RTM_i v_i}{u_i\zeta_{i*i}N_\mathrm{A}^2} \tag{16}$$

The chemical potentials μ_i are directly calculated as a function of polymer solution temperature and volume fractions in the ternary system using Flory–Huggins theory [24]. D_i^* represents the self diffusion coefficient of the ith component in the ternary solution and is given as follows [20]:

$$D_1^* = D_{01}\,\mathrm{e}^{\frac{-(\omega_1 V_1^* + \omega_2 V_2^* \xi_{13}/\xi_{23} + \omega_3 V_3^* \xi_{13})}{V_{\mathrm{FH}/\gamma}}} \tag{17}$$

$$D_2^* = D_{02}\,\mathrm{e}^{\frac{-(\omega_1 V_1^* \xi_{23}/\xi_{13} + \omega_2 V_2^* + \omega_3 V_3^* \xi_{23})}{V_{\mathrm{FH}/\gamma}}} \tag{18}$$

$$\frac{V_{\mathrm{FH}}}{\gamma} = \sum_{i=1}^{3} \frac{K_{1i}}{\gamma}(K_{2i} - T_{gi} + T)\omega_i \tag{19}$$

D_{0i} is a pro-exponential factor, V_{FH} is the average hole free volume per kilogram of the solution and γ is an overlap factor, which is introduced, because the same free volume is available to more than one molecule. V_i^* is the specific critical hole free volume of the *i*th component required for a diffusion jump and ξ_{i3} represents the ratio of the critical molar volume of the jumping unit of *i*th-solvent to that of the polymer. K_{1i} and K_{2i} are free volume parameters for the *i*th component and T_{gi} is the glass transition temperature. In the above equations ω_i represents the weight fraction of the *i*th substance.

In Eqs. (7)–(19) the Fickain 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 was the starting point for several workers [16–19] to develop theories relating the friction coefficients to standard properties such as molar volume, molecular weight etc. These theories have recently been reviewed by Price and Romdhane [29]. According to these workers the developed physical theories can be classified in terms of the following equation:

$$\frac{\zeta_{ij}}{\zeta_{ik}} = \frac{\alpha_j}{\alpha_k}\frac{\bar{V}_j}{\bar{V}_k}\frac{M_j}{M_k} \tag{20}$$

where α_i are physical constants or functions used to scale the friction coefficients and M_i stands for the molecular weight of the *i*th substance, respectively. The resulting theories for various α_i values are summarized in Table 1. It can be shown that most theories assume constant friction coefficient ratios. A deeper question arises from Eq. (20): Is the ratio of the friction coefficients constant in diffusing polymer solutions?

As was shown by Bearman [30], the mutual diffusion coefficient in the case of binary solutions and constant friction coefficient ratio is given as a function of solvent mass concentration ρ_1, chemical potential μ_1 and the self-diffusion coefficient D_1^* by the following equation [31]:

$$D_{12} = \frac{D_1^*}{RT}\frac{\partial \mu_1}{\partial \ln \rho_1} \tag{21}$$

This equation relates the mutual diffusion coefficient with the solvent self-diffusion coefficient. The authors are aware that more rigorous approaches correlating the self- and the binary diffusion coefficients over a wide solvent concentration range including the dilute region appeared in the open literature [32]. However, one could use Eq. (21) correlating the self-diffusion coefficient with the mutual diffusion coefficient to check the validity of the assumptions made in its derivation such as the constant friction coefficients ratio.

This task is achieved by using free-volume theory [33] to describe the dependence of the solvent self-diffusion coefficient on temperature and concentration as well as Flory–Huggins thermodynamics [24] for chemical potential. As it was shown by several workers, the mutual and self-diffusion coefficients for binary solvent–polymer systems are satisfactorily correlated by the above equation thus validating the assumption of constant friction coefficient ratio for the binary polymer–solvent systems [34,35].

However, Zielinski and Alsoy [36] in a subsequent work have raised doubts about the models based on the assumption of constant friction factor ratios in multi-component solutions. Moreover, there is no clear reason to apply one theory (Table 1) instead of another.

The aim of this work is to overcome these difficulties and suggest a unique theory for diffusion in multi-component polymer solutions. The starting point in our analysis is the definition of Onsager L_{ij} mobility coefficients [25]. 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:

$$J_i = \|L_{ij}\|X;\quad X_i = -\mathrm{grad}\mu_i;\quad J_i = c_i(V_i - V^R) \tag{22}$$

where V^R is the velocity of an arbitrary reference framework. By inverting the above equations one gets:

$$X_i = \|L_{ij}\|^{-1}J_i = \|\zeta_{ij}\|J_i;\quad i = 1,2,\ldots,N; \\ j = 1,2,\ldots,N \tag{23}$$

By applying the Gibbs-Duhem theorem for isothermal and isobaric systems Eq. (23) is written as [22]:

$$\sum_{k=1}^{N} c_k\frac{\mathrm{d}\mu_k}{\mathrm{d}z} = 0 \text{ or } \sum_{k=1}^{N}\sum_{i=1}^{N}\zeta_{ik}c_kJ_i \\ = \sum_{i=1}^{N} J_i \sum_{k=1}^{N} c_k\zeta_{ik} = 0 \text{ or } \sum_{k=1}^{N} c_k\zeta_{ik} = 0\quad i = 1,2,\ldots,N \tag{24}$$

Price and Romdhane [29] first showed the importance of the Gibbs-Duhem theorem. More specifically, they reported substantial errors in polymeric drying coating simulations by using literature models (Table 1) when this theorem was violated. The importance of this theorem is further shown in the subsequent paragraphs

Table 1
Models for multi-component diffusion

Model	References
$\alpha_i = 1,\ i = 1,2,\ldots,N$	Alsoy and Duda [16]
$\alpha_i = \bar{V}_i^{-1},\quad i = 1,2,\ldots N$	Zielinski and Hanley [17]
$\alpha_i = 0,\ i \neq N,\ \alpha_N \neq 0$	Dabral et al. [19]

By multiplying the above equation by $(V_i - V^R)$ and subtracting the result from Eqs. (3) and (23) is derived [22]:

$$\frac{\mathrm{d}\mu_i}{\mathrm{d}z} = -\sum_{k=1}^{N} c_k[\zeta_{ik}(V_i - V^R) - \zeta_{ik}(V_k - V^R)]$$
$$= -\sum_{k=1}^{N} c_k[\zeta_{ik}(V_i - V_k)] \tag{25}$$

Finally, Miller [37] (Ref. [22], p. 50) using Eqs. (22)–(25) derived the Onsager reciprocal conditions:

$$\zeta_{ik} = \zeta_{ki} \quad i = 1, 2, \ldots, N; \quad k = 1, 2, \ldots, N \tag{26}$$

The following equation between molar volumes and molar concentrations also holds [22]:

$$\sum_{i=1}^{N} c_i v_i = 1 \tag{27}$$

By using the above equation along with Gibbs-Duhem equations and by calculating the derivatives with respect to molar concentration, one directly derives the following equation for the case of the constant friction coefficient ratios:

$$\frac{\zeta_{ij}}{\zeta_{kj}} = \frac{v_i}{v_k} = \frac{\bar{V}_i}{\bar{V}_k}\frac{M_i}{M_k} \tag{28}$$

This equation proposed also by Alsoy and Duda (Table 1), simultaneously satisfies the Onsager reciprocal condition as well as the Gibbs-Duhem theorem along with the concept of constant friction coefficient ratios. Although the theory proposed by Alsoy and Duda [16] satisfies the Gibbs-Duhem theorem contrary to the other theories summarized in Table 1, doubts about this theory have been raised in the literature due to the assumption of constant friction coefficient ratios made [29]. The aim of the present work is to propose a theory based on the Gibbs-Duhem theorem without making the assumption of constant friction coefficient ratios.

By eliminating the molar concentrations in Eq. (24) and by applying the Onsager reciprocal rule the following equation is derived (Appendix A for a detailed proof):

$$\zeta_{ij}^2 = \zeta_{ii}\zeta_{jj} \tag{29}$$

This equation was also proposed by Price and Romdhane [29]. The above equation along with the Gibbs-Duhem equations is the key in our analysis for multi-component diffusing systems.

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. (24)) for a diffusing ternary system are written as:

$$\sum_{k=1}^{3} c_k\zeta_{ik} = 0 \quad i = 1, 2, 3 \quad \zeta_{12} = \sqrt{\zeta_{11}\zeta_{22}}$$

or

$$\begin{aligned} &c_1\zeta_{11} + c_2\zeta_{12} + c_3\zeta_{13} = 0, \\ &c_2\zeta_{22} + c_1\zeta_{12} + c_3\zeta_{23} = 0, \\ &c_3\zeta_{33} + c_2\zeta_{23} + c_3\zeta_{13} = 0 \end{aligned} \tag{30}$$

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. (6)) as follows [28]:

$$\zeta_{13} = \frac{v_3}{u_3}\left(\frac{RT}{N_\mathrm{A}^2 D_{T1}} - \frac{u_2}{v_2}\xi_{12}\right); \quad \zeta_{23} = \frac{v_3}{u_3}\left(\frac{RT}{N_\mathrm{A}^2 D_{T2}} - \frac{u_1}{v_1}\xi_{12}\right);$$
$$D_{Ti} = \frac{D_i^*}{1-(D_i^*/D_i^0)} \approx D_i^*; \quad D_i^0 = \frac{RTM_i v_i}{u_i\zeta_{i*i}N_\mathrm{A}^2}; \quad i = 1, 2 \tag{31}$$

According to Vrentas and Duda [28,33] one could assume $(D_i^*/D_i^0) = 0$ in the case of moderate concentrated solution ($\omega_3 > 0.2$) as the error introduced by the above simplification is quite small Eqs. (30) and (31) result in a simple quadratic equation which is directly solved to calculate ζ_{12} and consequently D_{ij} (Eqs. (7)–(19)) in terms of the self-diffusion coefficients and the process conditions. In the following section, the previously described methodology is applied to the evaporation process of the formamide–acetone–CA solution which is widely used in the asymmetric membrane manufacture.

3. Theory application to the formamide–acetone–CA system

Modeling multi-component diffusion is not an easy task. A typical example is the paradox of physically unrealistic concentrations in ternary diffusion [18]. More specifically, if ternary diffusion is considered as a one dimensional experiment then physically unrealistic concentrations are obtained for given initial concentrations and diffusion coefficients [18]. To illustrate this paradox a diffusion cell is considered. This cell comprises two compartments separated by a semi-permeable membrane which allows diffusion of the solutes A and B but not of the balancing component C. The diffusion cell is quite large so at the edges there is a constant concentration at any time. If we neglect the volume change of each compartment then analytical solutions of the resulting 1-dim problem are available [21]. These analytical solutions give reasonable results for small values of initial concentrations of solutes A and B. If higher concentrations of A and B are assumed then physically unrealistic concentrations of the balancing component C are observed [18]. Obviously, in this case the volume change of each cell compartment due to the mass transfer of A and B across the semi-permeable membrane can not be neglected and one has to consider the additional volume change in each compartment of the diffusion cell. Similar discrepancies (physically unrealistic concentrations) could occur due to the violation of the Gibbs-Duhem theorem or due to the assumption of constant friction coefficients ratios [29]. The aim of this work is to overcome these difficulties and propose a unique theory for multi-component diffusion in polymer solutions

3.1. The model equations

The system formamide–acetone–CA was the subject of extensive experimental investigation in asymmetric membrane formation [38–41]. Fig. 1 depicts the solvent evaporation process of the ternary system formamide–acetone–CA. The solution is spread on a solid support with thickness L_{sup}, which rests upon an insulating block. Heat is exchanged between the solution and the support as well as between the solution and the environment. Initially, the whole system (solution, ambient air, support) is at temperature T_0 and the polymer solution thickness is L_0. At time $t=0$ the ternary polymer solution is exposed to the environment and the solvent(s) begins to evaporate. At time t the polymer solution extends from coordinate $z=0$ at the upper glass plate to $z=L(t)$ at the gas–liquid moving interface, while the glass support has a constant thickness extending from $z=0$ to $z=-L_{\mathrm{sup}}$.

From a modeling point of view this is a coupled heat and mass transfer process with a moving boundary. Since diffusion is much slower than the relaxation mechanisms of the polymer chains in the solution, we assume pure Fickian diffusion [42–55] . Additionally, the process is considered as 1-dim model due to the relatively small initial thickness of the polymer solution (order of μm) compared to the width and length (order of cm) [42–55]. The dimensionless governing equations describing the conservation of mass and energy in an one phase ternary system and the support are written as follows [54]:

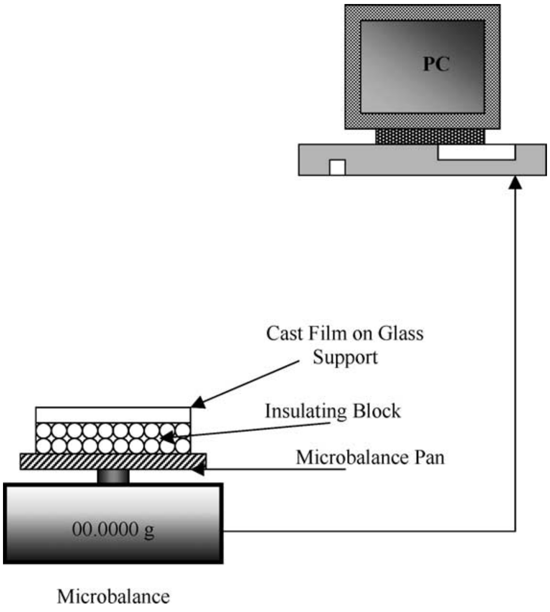

Fig. 1. Schematic representation of the solvent(s) evaporation process.

$$\frac{\partial u_1}{\partial \tau} = \frac{\partial}{\partial \eta}\left(C_1 \frac{\partial u_1}{\partial \eta}\right) + \frac{\partial}{\partial \eta}\left(C_2 \frac{\partial u_2}{\partial \eta}\right); \quad \eta = z/L_0;$$

$$t = D_0 t/L_0^2; \quad C_1 = \frac{D_{11}}{D_0}; \quad C_2 = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)\frac{D_{12}}{D_0}; \tag{32}$$

$$0 < \eta < s = \frac{L(t)}{L_0}$$

$$\frac{\partial u_2}{\partial \tau} = \frac{\partial}{\partial \eta}\left(C_3 \frac{\partial u_1}{\partial \eta}\right) + \frac{\partial}{\partial \eta}\left(C_4 \frac{\partial u_2}{\partial \eta}\right);$$
$$C_3 = \left(\frac{\bar{V}_2}{\bar{V}_1}\right)\frac{D_{21}}{D_0}; \quad C_4 = \frac{D_{22}}{D_0}; \quad 0 < \eta < s \tag{33}$$

$$C_5 \frac{\partial \Theta}{\partial \tau} = \frac{\partial}{\partial \eta}\left(C_6 \frac{\partial \Theta}{\partial \eta}\right); \quad \Theta = \frac{T}{T_0}; \quad C_5 = \frac{\rho_s C_{ps}}{\rho_0 C_{p0}};$$
$$C_6 = \frac{k_s}{D_0 \rho_0 C_{ps}}; \quad 0 < \eta < s \tag{34}$$

$$C_7 \frac{\partial \Theta_{\mathrm{sup}}}{\partial \tau} = \frac{\partial}{\partial \eta}\left(C_8 \frac{\partial \Theta_{\mathrm{sup}}}{\partial \eta}\right); \quad C_7 = \rho_{\mathrm{sup}} C_{\mathrm{psup}}/\rho_0 C_{\mathrm{p0}};$$
$$C_8 = k_{\mathrm{sup}}/\rho_0 C_{\mathrm{p0}} D_0; \quad -L_{\mathrm{sup}}/L_0 < \eta < 0 \tag{35}$$

In this work subscript 1 refers to formamide, 2 denotes acetone and subscript 3 represents CA. $\eta = z/L_0$ is the dimensionless space coordinate; $\tau = D_0 t/L_0^2$ is dimensionless time; $\Theta = T/T_0$ is the dimensionless temperature; $s = L(t)/L_0$ is the dimensionless position of the moving boundary. D_{ij} are the appropriate phenomenological diffusion coefficients for the ternary system. Equations for D_{ij} were presented in the previous section. T represents the temperature, t denotes time and D_0 is a scaling factor having the units of diffusion coefficient ρ_s, C_{ps} and k_s represent density, specific heat capacity and thermal conductivity of the polymer solution, respectively. C_{p0}, ρ_0 are scaling factors having units of specific heat capacity and density, respectively. Subscript ‘sup’ denotes properties and variables of the support.

Initial and boundary conditions for the diffusion equation:

$$u_1 = u_{10}; \quad u_2 = u_{20}; \quad \tau = 0 \tag{36}$$

$$C_1 \partial u_1/\partial \eta + C_2 \partial u_2/\partial \eta = C_9;$$
$$C_9 = -L_0 j^{\neq}_{\mathrm{F,int}} \bar{V}_1/D_0; \quad \eta = s \tag{37}$$

$$C_3 \partial u_1/\partial \eta + C_4 \partial u_2/\partial \eta = C_{10};$$
$$C_{10} = -L_0 j^{\neq}_{\mathrm{A,int}} \bar{V}_2/D_0; \quad \eta = s \tag{38}$$

$$\frac{\partial u_1}{\partial \eta} = 0; \quad \frac{\partial u_2}{\partial \eta} = 0 \quad \eta = 0 \tag{39}$$

Eq. (36) gives the initial concentration for formamide and acetone. Eqs. (37) and (38) are mass balances at the moving interface and Eq. (39) specifies zero mass flux at the glass plate.

$j^{\neq}_{\mathrm{A,int}}$ and $j^{\neq}_{\mathrm{F,int}}$ are the mass flux of acetone and formamide, at the gas–liquid interface.

Initial and boundary conditions for the energy equations:

$$\Theta = \Theta_{\sup} = 1 \quad \tau = 0 \tag{40}$$

$$\begin{aligned} &C_6 \frac{\partial \Theta}{\partial \eta} = C_{11}(\Theta_{\mathrm{s,int}} - 1) + C_{12}(1 - \Theta^4_{\mathrm{s,int}}) - C_{13}; \\ &\quad C_{11} = \frac{L_0 h}{D_0 \rho_0 C_{p0}}; \quad C_{12} = \frac{L_0 \varepsilon \sigma T_0^3}{D_0 \rho_0 C_{p0}}; \\ &\quad C_{13} = ((\Delta H_1) j^{\neq}_{\mathrm{A,int}} + (\Delta H_2) j^{\neq}_{\mathrm{F,int}}) L_0 / (T_0 D_0 \rho_0 C_{p0}); \quad \eta = s \end{aligned} \tag{41}$$

$$\frac{C_8 \partial \Theta_{\sup}}{\partial \eta} = \frac{C_6 \partial \Theta}{\partial \eta} \quad \eta = 0 \tag{42}$$

$$\frac{\partial \Theta_{\sup}}{\partial \eta} = 0 \quad \eta = -\frac{L_{\sup}}{L_0} \tag{43}$$

Eq. (40) gives the initial temperature in the support and the solution. Eq. (41) is an energy balance at the polymer solution–gas interface, taking into account heat transfer to the polymer solution, due to free convection and radiation as well as latent heat loss, due to acetone and formamide evaporation. Eq. (42) accounts for continuity of heat flux at the glass plate-polymer solution interface, while Eq. (43) stands for perfect insulation of the glass support lower surface. $\Theta_{\mathrm{s,int}}$ denotes the dimensionless temperature of the liquid–gas interface, h is the heat transfer coefficient, ε is the emissivity of the polymer solution, σ denotes the Stefan-Boltzman constant and ΔH_i is the ith substance latent heat of vaporization.

Finally, the instantaneous dimensionless solution thickness $s = L(t)/L_0$ is obtained from the following differential equation [54]:

$$u_3 \frac{\mathrm{d}s}{\mathrm{d}\tau} = C_9 + C_{10}; \quad \tau = 0, s = 1 \tag{44}$$

Eq. (44) defines the instantaneous position of the moving boundary in terms of the polymer volume fraction $u_3 = (1 - u_1 - u_2)$. The above equation is solved along with the governing equations of the model (Eqs. (32)–(35)) to give the concentration profiles of acetone and formamide along with the temperature of the solution and the support and the position of the moving boundary as a function of time.

3.2. The model parameters

The density, the specific heat capacity and the thermal conductivity of the polymer solution were calculated by a simple addition rule, assuming constant partial properties [42–55]. The thermophysical properties of the polymer solution constituents and the glass support are given as a function of the solution temperature in standard references [56–58]. The heat transfer and the mass transfer rates at the polymer–solution gas interface were calculated from appropriate semi-empirical correlations [54]. Flory–Huggins thermodynamics was used to describe the variation of chemical potential with respect to process conditions [59]. The acetone–CA Flory–Huggins interaction parameter is given elsewere [59]. The other Flory–Huggins interaction parameters were calculated from vapor pressure data over the binary formamide–acetone [60] (χ_{12}) and ternary solutions [40] (χ_{13}):

$$\chi_{13} = 0.855; \quad \chi_{12} = 0.993 - 0.383 H_2 + 1.2 H_2^2; \\ H_2 = \frac{u_2}{(u_1 + u_2)} \tag{45}$$

According to Vrentas-Duda and co-workers [20,61] the solvents free volume parameters could be estimated from pure substances data. The free volume parameters (Eqs. (27)–(29)) for acetone and CA are given in full detail elsewhere [54]. Regarding the pro-exponential factor of the formamide self-diffusion equation (D_{01}, Eq. (27)) was found to be equal to 1.73×10^{-7} m^2/s by using the Dullien correlation [61,62]. The formamide specific critical hole free volume V_1^* was estimated by using group contribution methods [63] equal to 0.86×10^{-3} m^3/kg. The formamide free volume parameter ($K_{21} - T_{g1}$, Eqs. (27)–(29)) was directly estimated to be equal to -74.2 K by using the Doolittle equation [64] and the Goletz-Tassios correlation [65] for the prediction of liquid viscosity vs. temperature data combined with the Vrentas-Duda equation [32]. The parameter (K_{11}/γ) was calculated equal to 6.9×10^{-7} m^3/kg.K by fitting formamide viscosity-temperature data [58]. Finally, the parameter ξ is defined as the ratio of the critical molar volume of the solvent jumping unit to that of the polymer jumping unit [20]. Ju et al. [66] proposed a linear relationship between ξ and the solvent molar volume at 0 K estimated from group contribution methods [63]:

$$\xi = aV(0) \tag{46}$$

where a is a constant which has been determined from the polymer–solvent diffusion data. Once a is known for a particular polymer, the value of ξ for any solvent in this polymer can be estimated assuming that the solvent moves as a single unit. The $\xi_{23} V_3^*$ parameter for the acetone–CA solution is equal to 0.64×10^{-3} m^3/kg, according to our previous work [35,54]. The specific critical hole free volume of CA is equal to 0.61×10^{-3} m^3/kg [54]. Therefore, the value of a for this polymer is equal to 0.0192×10^{-6} g mol/m^3. Consequently, ξ_{13} was found equal to be equal to 0.74 by using Eq. (46) and the previously determined molar volume of formamide at 0 K.

3.3. Finite element formulation

The resulting system of the governing equations (Eqs. (32)–(35)) augmented by the moving boundary equation (Eq. (44)) along with the initial and boundary conditions is solved with the Galerkin finite element method. According to this method the final formulation of the weighted residuals R^i (after expanding the unknown variables in quadratic basis functions (ϕ^i), introducing convective terms in the governing equations, due to the transformation of partial to total time derivatives and applying the divergence theorem) becomes:

$$R^i_{M1} = \int_0^s \left[\frac{\partial u_1}{\partial \tau}\varphi^i - \frac{d\eta}{d\tau}\frac{\partial u_1}{\partial \eta}\varphi^i + \frac{\partial \varphi^i}{\partial \eta}\left(C_1\frac{\partial u_1}{\partial \eta}\right) + \frac{\partial \varphi^i}{\partial \eta}\left(C_2\frac{\partial u_2}{\partial \eta}\right)\right]\mathrm{d}\eta - \left(C_1\frac{\partial u_1}{\partial \eta} + C_2\frac{\partial u_2}{\partial \eta}\right)\varphi^i\Big|_{\eta=0}^{\eta=s} \tag{47}$$

$$R^i_{M2} = \int_0^s \left[\frac{\partial u_2}{\partial \tau}\varphi^i - \frac{\mathrm{d}\eta}{\mathrm{d}\tau}\frac{\partial u_2}{\partial \eta}\varphi^i + \frac{\partial \varphi^i}{\partial \eta}\left(C_3\frac{\partial u_1}{\partial \eta}\right) + \frac{\partial \varphi^i}{\partial \eta}\left(C_4\frac{\partial u_2}{\partial \eta}\right)\right]d\eta - \left(C_3\frac{\partial u_1}{\partial \eta} + C_4\frac{\partial u_2}{\partial \eta}\right)\varphi^i\Big|_{\eta=0}^{\eta=s} \tag{48}$$

$$R^i_{\mathrm{E,sol}} = \int_0^s \left[C_5\frac{\partial \Theta}{\partial \tau}\varphi^i - \frac{\mathrm{d}\eta}{\mathrm{d}\tau}\frac{\partial \Theta}{\partial \eta}C_5\varphi^i + \frac{\partial \varphi^i}{\partial \eta}\left(C_6\frac{\partial \Theta}{\partial \eta}\right)\right]\mathrm{d}\eta - C_6\frac{\partial \Theta}{\partial \eta}\varphi^i\Big|_{\eta=0}^{\eta=s} \tag{49}$$

$$R^i_{\mathrm{E,sup}} = \int_{-L/L_{\mathrm{sup}}}^{0} \left[C_7\frac{\partial \Theta_{\mathrm{sup}}}{\partial \tau}\varphi^i + \frac{\partial \varphi^i}{\partial \eta}\left(C_8\frac{\partial \Theta_{\mathrm{sup}}}{\partial \eta}\right)\right]\mathrm{d}\eta - C_8\frac{\partial \Theta_{\mathrm{sup}}}{\partial \eta}\varphi^i\Big|_{\eta=-L_{\mathrm{sup}}/L_0}^{\eta=0} \tag{50}$$

The computational domain was discretized in 70 elements. The residuals are numerically evaluated by using three point Gaussian integration. The time integration follows the Euler backward scheme. A system of non-linear algebraic equations results which is solved with the Newton–Raphson iterative method according to scheme $q^{(n+1)} = q^{(n)} - J^{-1}R(q^{(n)})$, where $q^{(n)}$ is the vector of unknowns of the nth iteration and J is the Jacobian matrix of residuals R with respect to the nodal unknowns $q^{(n)}$. The time step was equal to 10^{-4}. The computer program exhibits quadratic convergence in 4–6 iterations at each time step. Any additional mesh refinement or time step decrease has an improvement of less than 10^{-6} in the accuracy of the solution. A detailed presentation of the finite element technique that enables the simultaneous solution of the primary unknowns of the problem (volume fractions and temperature) with the moving boundary can be found elsewhere [54,67].

4. Results and discussion

In Figs. 2 and 3 the model predictions are compared with experimental data for polymer solution weight and surface temperature vs. evaporation time. It was found convenient to represent polymer solution weight as the ratio of the acetone plus formamide weight to the cellulose acetate weight presented in the polymer solution. The experimental data and conditions of Ohya and Sourirajan [40] were used in our numerical experiments. The initial conditions are summarized in Table 2. Only acetone was assumed to evaporate due to the high boiling point of formamide compared to that of acetone. Please note that in our numerical experiments there are no adjustable parameters and all model parameters were estimated from literature data. In Figs. 2 and 3 a satisfactory agreement between model predictions and experimental data [40] is depicted thus validating the present theory. The observed discrepancy at the surface temperature profiles after 200s is attributed to errors in the semi-empirical correlations used

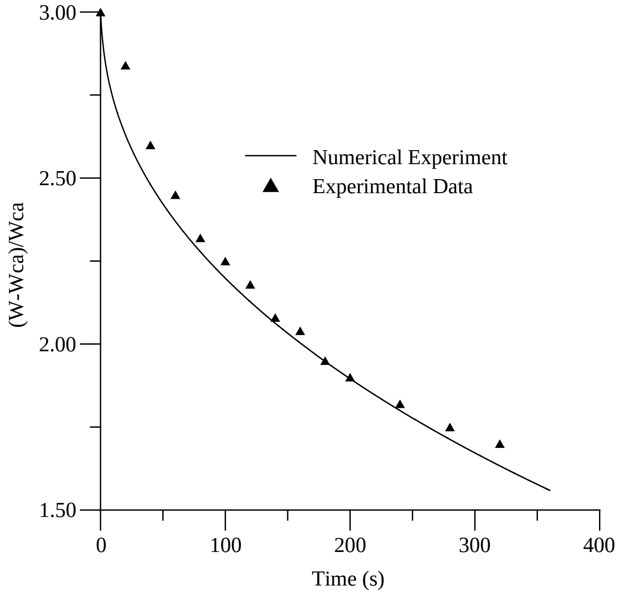

Fig. 2. Comparison of model predictions for polymer solution weight with experimental data [40].

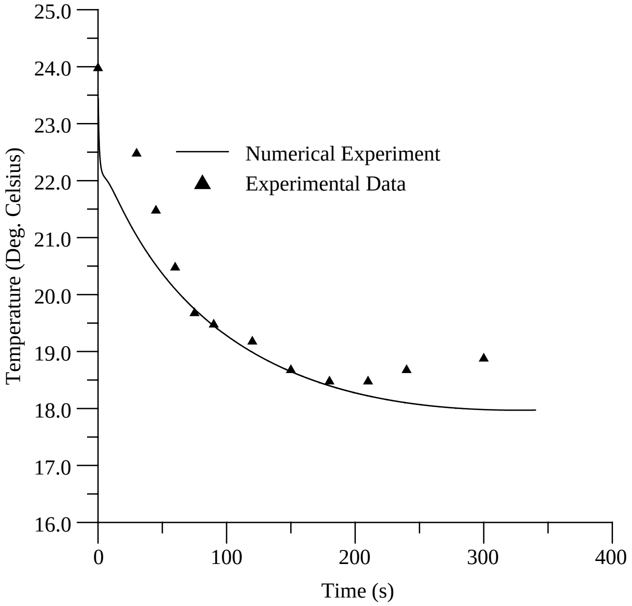

Fig. 3. Model predictions for polymer solution surface temperature vs. experimental data [40].

Table 2
Initial experimental conditions [40]

Quantity	Value	Units
Initial temperature, T_0	297	K
Glass support thickness[a], L_{sup}	2×10^{-3}	m
Initial acetone weight fraction	0.45	
Initial formamide weight fraction	0.25	
Initial solution weight	2.4	gr
Casting surface	64.2	cm^2
Initial solution thickness, L_0	Calculated from the initial conditions	

[a] Assumed

for the heat transfer and mass transfer at the gas–liquid interface.

Satisfactory results using the previously described methodology for the calculation of the friction coefficients were also obtained for the diffusing system water–acetone–CA [68]. The authors are aware that further validation of their theory may be required by comparing model predictions with the available data not only from open literature but also from industry. Since, this is not possible due to the large amount of data, the source codes of this work are at the disposal of our colleagues from both academia and industry if they wish to further validate this theory. The source codes can be obtained by directly contacting the authors.

In Fig. 4 the concentration profiles in the ternary diagram formamide–acetone–CA are plotted for two different times along with the experimental gel curve [69] and the calculated binodal. Unlike to the water–acetone–CA system [54,68] smooth profiles were observed in this work. This is attributed to the higher affinity of formamide with respect to acetone and CA compared to the small affinity of water in the acetone–water–CA system. It is also shown that a considerable amount of the solution is in the gel state and no phase separation occurs due to liquid–liquid de-mixing for the conditions used in our numerical experiments. This observation is in accordance with SEM experimental data [39] for gel formation under the same experimental conditions.

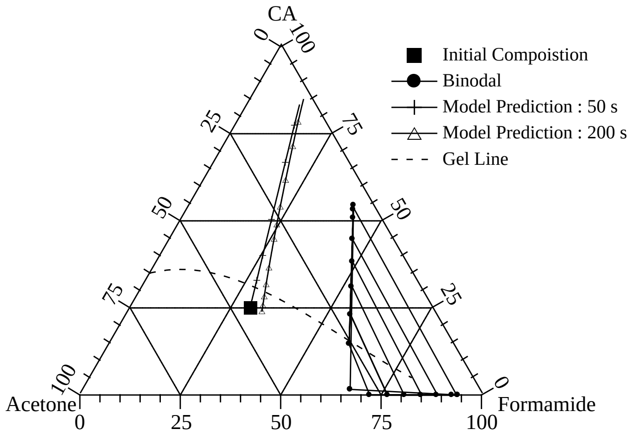

Fig. 4. Typical ternary concentration profiles.

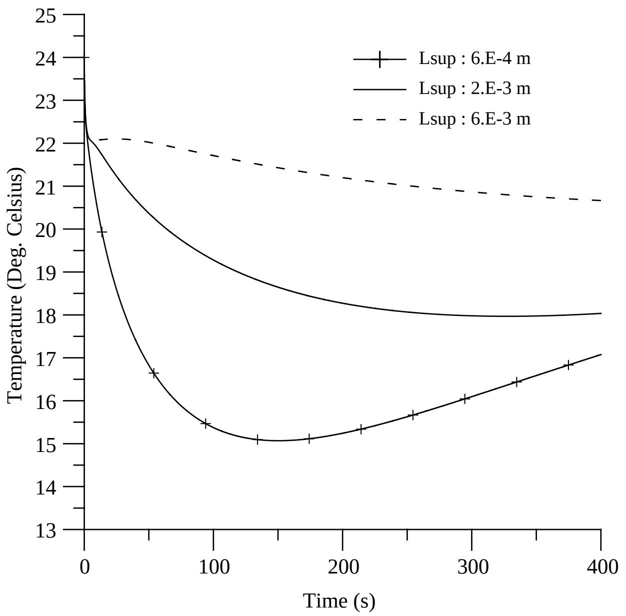

Fig. 5. Effect of support thickness on polymer solution surface temperature.

A parametric analysis was carried out to justify the results due to the uncertainty in the heat transfer characteristics of the support (insulation, thickness) which are assumed in the present work. Although the heat transfer characteristics of the support or the used semi-empirical correlations for the heat transfer and mass transfer at the gas–liquid interface influence polymer solution surface temperature (Fig. 5) they have little effect on gravimetric results (Fig. 6). This is attributed to the fact that diffusion is mainly controlled by the transport phenomena inside the polymer film [42–55]. Consequently, this analysis further justifies the results as the

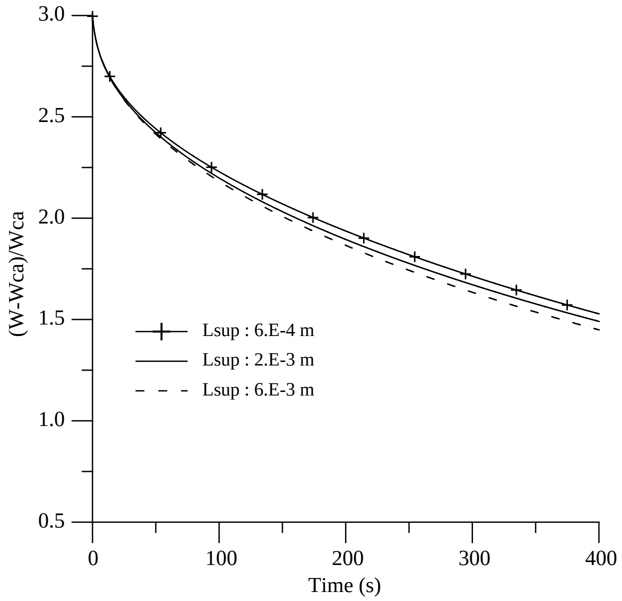

Fig. 6. Effect of support thickness on polymer solution weight.

error introduced in the gravimetric results, due to uncertainty in the heat and mass transfer coefficients, is quite small.

5. Conclusions

In the present work a novel theory for multi-component diffusion in polymer solutions is proposed. This theory is based on well-established principles such as the Gibbs-Duhem equations for diffusing systems. It is shown that application of the Gibbs-Duhem theorem along with the simple geometric rule to a ternary system solvent (1)–solvent(2)–polymer(3) 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. It is believed that this theory could be generalized to other multi-component systems having more than three constituents.

Finally, the above theory was validated against established experimental data for acetone evaporation from the ternary formamide–acetone–cellulose acetate system which is used 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, drying of coatings and reverse osmosis that exhibit similar multi-component diffusion phenomena thus leading to a more rational design of processes and products.

Acknowledgements

This work has been sponsored by the Archimedes grant of the Hellenic Science Foundation. George Verros thanks Ms Kate Somerscales for her help in preparing the manuscript.

Appendix A

One can directly show the geometric rule by eliminating the concentrations in the Gibbs-Duhem equations for a binary system. In a ternary diffusing system the Gibbs-Duhem equations are written as:

$$\begin{aligned} &c_1\zeta_{11}+c_2\zeta_{12}+c_3\zeta_{13}=0,\\ &c_2\zeta_{22}+c_1\zeta_{12}+c_3\zeta_{23}=0,\\ &c_3\zeta_{33}+c_2\zeta_{23}+c_3\zeta_{13}=0 \end{aligned} \tag{A1}$$

We define the arbitrary functions λ_{ij} as:

$$\begin{aligned} &\zeta_{12}=\lambda_{12}\sqrt{\zeta_{11}\zeta_{22}}, \quad \zeta_{13}=\lambda_{13}\sqrt{\zeta_{11}\zeta_{33}},\\ &\zeta_{23}=\lambda_{23}\sqrt{\zeta_{22}\zeta_{33}} \end{aligned} \tag{A2}$$

By eliminating the concentrations c_1 or c_2 in Eq. (A1) and by introducing the λ_{ij} functions the following equations are derived:

$$\begin{aligned} &c_2^2\zeta_{22}(\lambda_{12}^2-1)=c_3^2\zeta_{33}(\lambda_{13}^2-1), c_3^2\zeta_{33}(\lambda_{23}^2-1)\\ &\quad =c_1^2\zeta_{11}(\lambda_{12}^2-1) \end{aligned} \tag{A3}$$

In other words, the Gibbs-Duhem equation states that if one λ_{ij} is equal to unity, all the other λ are equal to unity. For example by assuming $\lambda_{12}=1$ then $\lambda_{12}=\lambda_{13}=1$ due to the Gibbs-Duhem theorem (Eq. (A3)). Please notice, that for a ternary system the following equation holds [22]:

$$c_1v_1+c_2v_2+c_3v_3=1 \tag{A4}$$

where v_i is the molar volume of the ith substance. By (i) solving Eqs. (A1) and (A4) with respect to c_1 (ii) introducing the functions λ_{ij} (iii) dividing the ith equation of the system by $(\zeta_{ii})^{0.5}$ the above system (Eqs. (A1) and (A4)) is written in a matrix form as:

$AC=B$;

$$A=\begin{pmatrix} \lambda_{12}\zeta_{22}^{0.5}-(v_2/v_1)\zeta_{11}^{0.5} & \lambda_{13}\zeta_{33}^{0.5}-(v_2/v_1)\zeta_{11}^{0.5}\\ (\zeta_{22})^{0.5}-\lambda_{12}(v_2/v_1)\zeta_{11}^{0.5} & \lambda_{23}\zeta_{33}^{0.5}-(v_2/v_1)\lambda_{12}\zeta_{11}^{0.5}\\ (\zeta_{22})^{0.5}-\lambda_{13}(v_2/v_1)\zeta_{11}^{0.5} & \zeta_{33}^{0.5}-(v_2/v_1)\lambda_{13}\zeta_{11}^{0.5} \end{pmatrix} \tag{A5}$$

$$C=\begin{pmatrix} c_2\\ c_3 \end{pmatrix}; \quad B=\begin{pmatrix} -\zeta_{11}^{0.5}/v_1\\ -\lambda_{12}\zeta_{11}^{0.5}/v_1\\ -\lambda_{13}\zeta_{11}^{0.5}/v_1 \end{pmatrix}$$

As the Gibbs-Duhem theorem holds for arbitrary friction coefficients as well as molar concentrations and not for specific values, one could safely conclude that the rank of matrices A and B is equal to unity and at least one λ_{ij} is equal to unity. Consequently, all the λ_{ij} are equal to unity due to Eq. (A3). Therefore, for a ternary system the mean geometric rule holds:

$$\zeta_{12}=\sqrt{\zeta_{11}\zeta_{22}}, \quad \zeta_{13}=\sqrt{\zeta_{11}\zeta_{33}}, \quad \zeta_{23}=\sqrt{\zeta_{22}\zeta_{33}} \tag{A6}$$

By using a similar methodology the mean geometric rule can be proved for a quaternary system and so forth.

References

[1] Loeb S, Sourirajan S. Adv Chem Ser 1962;38:117–32.
[2] Riley RL, Gardner JO, Merten V. Science 1964;143:801–3.
[3] Kunst B, Sourirajan S. J Appl Polym Sci 1970;14:1983–96.
[4] Pinnau I, Koros WJ. J Appl Polym Sci 1991;43:1491–502.
[5] Kesting RE. Synthetic polymeric membrane A structural perspective. New York: Wiley; 1985.
[6] Paul DR, Yampol'skii YP, editors. Polymeric gas separation membranes. Boca Raton: CRC Press; 1994.
[7] Stoye D, Freitag W, editors. Paints, coatings and solvents. Weinheim: Wiley-VCH; 1998.
[8] Albalak RJ, editor. Polymer devolatilization. New York: Marcel Dekker; 1996.
[9] Russell GT, Napper DH, Gilbert RG. Macromolecules 1988;21(7): 2133–40.

[10] Russell GT, Napper DH, Gilbert RG. Macromolecules 1988;21(7): 2141–8.

[11] Achilias DS, Kiparissides C. Macromolecules 1992;25(14):3739–50.

[12] O'Neil GA, Wisnudel MB, Torkelson JM. Macromolecules 1996;29(23): 7477–90.

[13] O'Neil GA, Torkelson JM. Macromolecules 1999;32(2):411–22.

[14] Verros GD, Latsos T, Achilias DS. Polymer 2005;46:539–52.

[15] Curtiss CF, Bird B. Proc Natl Acad Sci, USA 1996;93:7440–5.

[16] Alsoy S, Duda JL. AIChE J 1999;45(4):896–905.

[17] Zielinski JM, Hanley BF. AIChE J 1999;45(1):1–12.

[18] Nauman EB, Savoca J. AIChE J 2001;47(5):1016–21.

[19] Dabral M, Francis LF, Scriven LE. AIChE J 2002;48(1):25–37.

[20] Vrentas JS, Duda JL, Ling HC. J Polym Sci, Part B: Polym Phys 1984;22: 459–69.

[21] Cussler EL. Multicomponent diffusion. Amsterdam: Elsevier; 1976.

[22] Tyrrell HJV, Harris KR. Diffusion in liquids A theoretical and experimental study. London: Butterworths; 1984.

[23] Cussler EL. Diffusion mass transfer in fluid systems. Cambridge: Cambridge University Press; 1997.

[24] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.

[25] Onsager L. Proc Natl Acad Sci, USA 1945;46:241–65.

[26] Bird RB, Stewart R, Lightfoot EN. Transport phenomena. New York: Wiley; 1960.

[27] Bearman RJ. J Phys Chem 1961;65:1961–8.

[28] Vrentas JS, Duda JL, Ling HC. J Appl Polym Sci 1985;30:4499–516.

[29] Price Jr PE, Romdhane IH. AIChE J 2003;49(2):309–22.

[30] Bearman RJ. J Chem Phys 1960;32:1308–13.

[31] Crank J. The mathematics of diffusion. Oxford: Clarendon Press; 1975.

[32] Vrentas JS, Vrentas CM. Macromolecules 1993;26:6129–31.

[33] Vrentas JS, Duda JL. J Polym Sci, Polym Phys Ed 1977;15:403–16.

[34] Zielinski JM. J Polym Sci, Part B: Polym Phys 1996;34:2759–66.

[35] Verros GD, Malamataris NA. Ind Eng Chem Res 1999;38:3572–80.

[36] Zielinski JM, Alsoy S. J Polym Sci, Part B: Polym Phys 2001;39: 1496–504.

[37] Miller DG. J Phys Chem 1966;70:2639–59.

[38] Manjikian S. Ind Eng Chem Prod Res Dev 1967;6:23–32.

[39] Frommer MA, Lancet D. In: Lonsdale HK, Podal HE, editors. Reverse osmosis membrane research. New York: Penum Press; 1972.

[40] Ohya H, Sourirajan S. J Appl Polym Sci 1971;15:705–13.

[41] Pilon R, Kunst B, Sourirajan S. J Appl Polym Sci 1971;15:1317–34.

[42] Cohen C, Tanny GB, Prager S. J Polym Sci, Part B: Polym Phys 1979;17: 477–89.

[43] Reuvers AJ, Van den Berg JWA, Smolders CA. J Membr Sci 1987;34: 45–65.

[44] Tsay CS, McHugh AJ. J Polym Sci, Part B: Polym Phys 1990;28: 1327–65.

[45] Radovanovic P, Thiel SW, Hwang STJ. Membr Sci 1992;65:231–46.

[46] Shojaie SS, Polymeric dense films and membranes via the dry-cast phase inversion process. Modeling, casting and morphological studies, PhD Thesis, Boulder, Colorado; 1992.

[47] Shojaie SS, Krantz WB, Greenberg ARJ. J Membr Sci 1994;94:255–80.

[48] Vrentas JS, Vrentas CM. J Polym Sci, Part B: Polym Phys 1994;32: 187–94.

[49] Cheng LP, Soh YS, Dwan AH, Gryte CC. J Polym Sci, Part B: Polym Phys 1994;32:1413.

[50] Cairncross RA, Jeyadef EN, Dunham RF, Evans KL, Francis F, Scriven LE. J Appl Polym Sci 1995;58:1279–90.

[51] Matsuyama H, Teramoto M, Uesaka T. J Membr Sci 1997;135:271–88.

[52] Guerrier B, Bouchard C, Allain C, Benard C. AIChE J 1998;44(4):791–8.

[53] Verros GD, Malamataris NA. Comput Mech 2001;27:332–40.

[54] Verros GD, Malamataris NA. Macromol Theory Simul 2001;10:737–49.

[55] Alsoy-Altinkaya SA, Ozbas B. J Membr Sci 2004;230:71–89.

[56] Dean JA.. 11th ed Lange's handbook of chemistry. New York: McGraw-Hill; 1973.

[57] Perry RH, Green D.. 6th ed Perry's chemical engineers' handbook. New York: McGraw Hill; 1984.

[58] Verein Deutscher Ingenieure. VDI-Warmeatlas. Dusseldorf: VDI-Verlag GmbH; 1974.

[59] Yilmaz L, McHugh AJ. J Appl Polym Sci 1986;31:997–1018.

[60] Quitzsch K, Hofmann HP, Pfestorf R, Geiseler G. Z Phys Chem (Leipsig) 1967;235:99–109.

[61] Zielinski JM, Duda JL. AIChE J 1992;38:405–15.

[62] Dullien FAL. AIChE J 1972;18:62–70.

[63] Haward RN. J Macromol Sci Rev Macromol Chem 1970;C4:191–242.

[64] Doolittle AK. J Appl Phys 1951;22:1471–5.

[65] Goletz E, Tassios D. Ind Eng Chem Process Des Dev 1977;16:75–9.

[66] Ju ST, Duda JL, Vrentas JS. Ind Eng Chem Prod Res Dev 1981;20:330–5.

[67] Kistler SF, Scriven LE. In: Pearson JRA, Richardson SM, editors. Computational analysis of polymer processing. London: Applied Science Publication; 1983. p. 243–99.

[68] Verros GD, Malamataris NA. Paper presented in the International Conference of Computational Methods in Science and Engineering 2005 (ICCMSE 2005), 21-26 October 2005, Loutraki Korinthos, Greece. In: Simos TE, Maroulis G, editors. Paper published in the proceedings of the conference: In Lecture series on computer and computational sciences. In the frontiers of computational science, vol. 3. Leiden: Brill Academic Publishers; 2005. p. 360–83.

[69] Fahey PM, Grethlein HE. Desalination 1971;9:297–313.