NRC Publications Archive Archives des publications du CNRC

Formation of polymeric membranes by immersion precipitation: an improved algorithm for mass transfer calculations

Karode, Sandeep K.; Kumar, Ashwani

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

[https://doi.org/10.1016/S0376-7388\(01\)00358-1](https://doi.org/10.1016/S0376-7388(01)00358-1)

Journal of Membrane Science, 18, June, pp. 287-296, 2001

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=89857009-56b0-4a88-9bc2-54741d0e8841>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=89857009-56b0-4a88-9bc2-54741d0e8841>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Formation of polymeric membranes by immersion precipitation: an improved algorithm for mass transfer calculations[☆]

Sandeep K. Karode, Ashwani Kumar*

*Institute for Chemical Processing and Environmental Technology, National Research Council of Canada,
Montreal Road Campus, Ottawa, Ont., Canada K1A 0R6*

Received 16 October 2000; received in revised form 22 January 2001; accepted 24 January 2001

Abstract

This note describes an improved algorithm for the solution of the governing equations describing ternary mass transfer during the quench-period in the formation of immersion precipitation membranes. The algorithm is applied to the model developed by Reuvers et al. (J. Membr. Sci. 34 (1987) 45) for the water–acetone–cellulose acetate system. The improved algorithm developed in this work numerically simulates the multi component unsteady state diffusion process in immersion precipitation membrane formation without the necessity of user intervention in terms of initial guesses for the interfacial composition. Phase separation is assumed to take place at the spinodal. The algorithm is presented in detail for three component systems, however, it is easily extendable to four component systems. Numerical simulations using the improved algorithm are in good agreement with those of Reuvers et al. (J. Membr. Sci. 34 (1987) 45), however, experimental studies are required to validate some of the assumptions relating to the polymer phase separation. Published by Elsevier Science B.V.

Keywords: Mass transfer; Immersion precipitation; Phase inversion; Membrane

1. Introduction

Membrane formation by immersion precipitation has been extensively modeled in the literature [1–7,13,14]. In order to predict phase separation, the interfacial composition of the precipitating polymer film needs to be calculated. All the literature models assume the following: (i) instantaneous local equilibrium, (ii) no polymer dissolution in coagulation bath, (iii) equality of solvent flux across the interface, (iv) equality of non-solvent flux across the interface. The net difference between the solvent flux leaving

the polymer film and the non-solvent flux entering it gives the rate of movement of the interface.

For a three component system, there are three unknowns: (a) volume fraction of non solvent in the coagulation bath side of the interface, (b) volume fraction of solvent in polymer film side and (c) volume fraction of non solvent in the polymer film side of the interface. Assumption of local equilibrium leads to two equations for equality of solvent and non-solvent chemical potentials. Equality of (solvent/non-solvent) flux assumptions result in additional two equations. The system, therefore, becomes over-constrained and an iterative procedure is required for estimation of the interfacial compositions. In this work, the algorithm of Reuvers and coworkers [1,3] is modified to eliminate the iterative procedure required for estimation of interfacial compositions. Interfacial compositions are

[☆] NRC number 42017.

* Corresponding author. Tel.: +1-613-998-0498;

fax: +1-613-941 2529.

E-mail address: ashwani.kumar@nrc.ca (A. Kumar).

Nomenclature

C	constant defined in Eq. (B.2e)
D	diffusivity ($L^2 T^{-1}$)
D_0	reference diffusivity ($L^2 T^{-1}$)
g_{ij}	binary interaction parameter
G	defined by Eq. (9)
G_{ij}	$= \partial^2 G / \partial \phi_i \partial \phi_j$
J	volumetric flux ($L T^{-1}$)
L_{ij}	phenomenological coefficient ($L^{-3} T \text{ mol}$)
m	spatial coordinate from interface into polymer film (L)
M	grid point defining location of boundary between polymer film and coagulation bath
M'	grid point defining coagulation bath side interface after phase separation
M''	grid point defining polymer film side interface after phase separation
MW	molecular weight (Mmol^{-1})
t	time (T^{-1})
$\bar{V}_i$	partial specific volume of species i ($\text{M}^{-1} L^3$)
X	location of interface (L)
y	spatial coordinate from interface into coagulation bath (L)

Greek letters

ϕ_i	volume fraction of species i
$\phi_i^{k,t}$	volume fraction of species i at grid point k at time t
μ_i	chemical potential ($\text{ML}^2 T^{-2} \text{ mol}^{-1}$)

Superscripts

'	polymer lean phase
''	polymer rich phase
*	non-dimensional quantity

Subscripts

1	non-solvent
2	solvent
3	polymer

A method of solving the governing equations without iterative solution for the interfacial composition and some simulation results are presented.

2. Model of Reuvers and coworkers [1,3]

The equations that describe ternary diffusion in the polymer solution during the quench period in the formation of phase inversion membranes are given by

$$\frac{\partial(\phi_i/\phi_3)}{\partial t} = \frac{\partial}{\partial m} \left\{ \sum_{j=1}^2 \bar{V}_i \phi_3 L_{ij} \frac{\partial \mu_i}{\partial m} \right\}, \quad i = 1, 2 \quad (1)$$

where $\bar{V}_i$ and ϕ_i are the partial specific volume and volume fraction of component i , respectively; μ_j is the chemical potential of component j , and m is a special position coordinate given by

$$m(x, t) = \int_0^x \phi_3(\xi, t) d\xi \quad (2)$$

The phenomenological coefficients L_{ij} are related to the frictional coefficients as given in Appendix B.

The binary diffusion in the coagulation bath is described by

$$\frac{\partial \phi_i}{\partial t} = \frac{\partial}{\partial y} \left\{ D(\phi_i) \frac{\partial \phi_i}{\partial y} \right\} - \frac{\partial \phi_i}{\partial y} \frac{dX}{dt} \quad (3)$$

$$\frac{dX}{dt} = J_1^\phi(y=0) + J_2^\phi(y=0) \quad (4)$$

where y is a special coordinate relative to the moving interface between the coagulation bath and the polymer film, and $X(t)$ the position of this interface. J_i^ϕ is the volumetric flux of species i relative to the polymer fixed frame of reference (see [1] for further details).

The following initial conditions describe the start-up volume fraction profiles:

$$y > 0 : \quad \phi_i'(y, 0) = \phi_{i,0}', \quad i = 1, 2 \quad (5a)$$

$$0 \leq m \leq M : \quad \phi_i''(m, 0) = \phi_{i,0}'', \quad i = 1, 2, 3 \quad (5b)$$

where ' and '' refer to the polymer lean (coagulation bath) and polymer rich (casting solution) phases, respectively.

calculated from a set of simultaneous equations that result after appropriate discretization of the governing equations.

In subsequent sections, the governing equations for the Reuvers model [1,3] are listed for completeness.

The boundary conditions are as follows:

$$\mu'_i(y=0, t) = \mu''_i(m=0, t), \quad i = 1, 2 \quad (6a)$$

$$J_i^\phi(y=0, t) = -J_i^\phi(m=0, t), \quad i = 1, 2 \quad (6b)$$

$$\left. \frac{\partial \phi_i''}{\partial m} \right|_{m=M} = 0, \quad i = 1, 2 \quad (6c)$$

$$\phi'_i|_{y \rightarrow \infty} = \phi'_{i,0}, \quad i = 1, 2 \quad (6d)$$

Eqs. (1)–(4) along with initial/boundary conditions (5)–(6) describe the mass transfer process in phase inversion membranes with one polymer, one solvent and one non-solvent. The solution algorithm for the above equations has been described in detail by Reuvers and coworkers [1,3].

In the next section, an alternate method of solving the governing Eqs. (1)–(4) along with the initial and boundary conditions (Eqs. (5) and (6)) is presented. Phase separation is assumed to be delayed till the spinodal has been crossed. This assumption has been previously made by Cheng et al. [6] where the diffusion equations were integrated beyond the binodal, and the spinodal was taken as a barrier where phase separation could not be neglected any further.

3. Improved algorithm to calculate diffusion profiles

Eqs. (1)–(6) can be non-dimensionalized by defining the following non-dimensional variables:

$$m^* = \frac{m}{X(0)} \quad (7a)$$

$$y^* = \frac{y}{X(0)} \quad (7b)$$

$$t^* = \frac{D_0 t}{X(0)^2} \quad (7c)$$

$$\mu_i^* = \frac{\mu_i}{RT} \quad (7d)$$

where D_0 is a scaling factor having the units of diffusivity. From here onwards, the equations presented are in non-dimensional form, with the asterisks dropped for convenience.

In order to implement the algorithm, Eqs. (1) and (3) are discretized using the second-order

discretization for the spatial coordinate and a first-order discretization for time. These discretized equations are given in Appendix A for completeness.

As discussed by Flory [8] and Tompa [9], the equation for the spinodal for a three component mixture is given by

$$G_{22}G_{33} - G_{23}^2 = 0 \quad (8)$$

where G_{ij} are the appropriate second-order derivatives of the following expression with respect to ϕ_2 and ϕ_3 :

$$G = \sum_i \frac{\phi_i}{v_i} \ln \phi_i + \sum_{i \neq j} g_{ij} \phi_i \phi_j \quad (9)$$

For example, $G_{23} = \partial^2 G / \partial \phi_2 \partial \phi_3$. In taking the derivatives, ϕ_1 is set equal to $1 - \phi_2 - \phi_3$.

Consider two points in phase space, points “a” and “b” located very near each other. Eq. (8) can be used to determine whether the spinodal surface has been crossed when moving from point “a” to point “b” by keeping track of the sign of the expression on the LHS.

In order to solve for diffusion profiles, Eqs. (1) and (3) are discretized using a second-order discretization procedure [10] (see Appendix A). The grid used is shown in Fig. 1a. In Fig. 1a, grid points 0– M represent the polymer film while grid points $M+1$, $M+2$, $\dots$, N represent the coagulation bath. A variable number of grid points are used in the coagulation bath (N is a function of time) so as to enforce boundary condition 6d. This is discussed in Appendix A.

From here onward, $\phi_i^{k,t}$ is used to represent the value of ϕ_i at grid position k and time t .

The algorithm to calculate the diffusion profiles can now be explained as follows:

1. ϕ_i ($i = 1, 2, 3$) at all grid points are initialized to the appropriate value corresponding to the initial conditions (Eqs. (5a) and (5b)). This corresponds to time $t = 0$.
2. The LHS of Eq. (8) at grid point M is calculated.
3. Eqs. (A.7) and (A.8) (given in Appendix A) are used to simultaneously solve for $\phi_1^{M,t}$ and $\phi_2^{M,t}$ using the current values for volume fractions at other grid points. This, in effect, is the implicit enforcement of boundary condition 6b at a time step $t + \Delta t$ (or $t = \Delta t$ for the first time integration).
4. The LHS of Eq. (8) at these updated values is again calculated. If the sign is the same as that calculated

Fig. 1. Schematic of grid employed for discretization of governing equations (a) before phase separation, (b) after phase separation and formation of an interface.

in step 2, the spinodal has not been crossed and hence, it is assumed that the system is still homogeneous.

5. The diffusion profiles are then numerically updated using Eqs. (A.1) and (A.3)–(A.5) (given in Appendix A). This generates the updated profile at time step $t + \Delta t$. The number of grid points in the coagulation bath was increased if the updated volume fractions at point N differed by $>10^{-6}$ from the initial values. This ensures that boundary condition 6d was always satisfied (see Appendix A for details).
6. Steps 3–5 are repeated until the spinodal boundary is crossed.

It should be noted that the boundary condition corresponding to the equality of chemical potentials (Eq. (6a)) is implicitly satisfied at the grid point M .

Following steps 3–6, the exact time at which the polymer film interface enters the unstable region can

be calculated. As soon as the spinodal is crossed, the spatial grid is re-arranged to accommodate the formation of an interface. This is shown in Fig. 1b, where, grid point M'' is the polymer rich boundary of the interface, while point M' is the polymer lean branch.

Once an interface is formed, we need to solve for the following three variables: $\phi_1^{M'',t}$, $\phi_2^{M'',t}$ (which define the polymer rich branch of the binodal) and $\phi_1^{M',t}$ (which defines the polymer lean branch, assuming that the polymer does not dissolve in the coagulation bath).

The requisite three equations are, (1) chemical potential equality for non-solvent (Eq. (A.8)), (2) chemical potential equality for solvent (Eq. (A.9)) and (3) flux equality for non-solvent (Eq. (A.6)) appropriately modified to account for the formation of the interface). These three are extremely non-linear equations that require a very good initial guess for successful convergence. In this case, the values at grid point M just prior to the spinodal being crossed are extremely good guesses. Using these initial guesses, the three equations mentioned above can be solved using the Newton–Raphson method [11] to calculate $\phi_1^{M',t}$, $\phi_1^{M'',t}$ and $\phi_2^{M'',t}$.

Once these are calculated, the diffusion profiles can be updated as in step 5 above. After diffusion profiles are updated, it was verified that the flux equality of the solvent (Eq. (A.7)) appropriately modified to account for the formation of the interface) was always satisfied.

However, now that an interface has been formed, the governing Eqs. (1)–(7) are no longer valid since the polymer film does not remain a continuum [12]. Therefore, in the present work, once the spinodal was crossed, the interface compositions were calculated, the diffusion profiles updated and the simulation stopped. Some results of implementation of the above algorithm to the water–acetone–cellulose acetate system will now be presented.

4. Results and discussion

In implementing the algorithm, the non-dimensional thickness of the polymer film was divided into 50 intervals. Initially, 500 equally spaced intervals were used for the coagulation bath. This number was increased as the simulation proceeded as and when required so as to satisfy boundary condition 6d at all

times. The reference diffusivity (D_0) was taken as $10^{-5} \text{ cm}^2/\text{s}$. The initial thickness of the polymer film ($X(0)$) was taken to be $220 \mu\text{m}$. The stability of the solution was ensured by following the analysis presented by Tsay and Mchugh [4]. Cheng et al. [6] have reported typical computational times of 15 h using Reuvers' algorithm implemented on a 60 MHz/80486 computer. Using the improved algorithm the average computation time for a set of initial conditions was about 1 h on a P-III, 600 MHz machine. By comparison, Reuvers' algorithm when implemented on the same machine took between 3–4 h depending on initial guesses.

The improved algorithm discussed in the previous section was applied to the well-analyzed membrane forming system: water–acetone–cellulose acetate. Various model parameters used in this work are taken from Reuvers and coworkers [1,3] and are listed in Table 1 for easy reference. In order to cross check the location of the diffusion profile with respect to the phase diagram, the binodal curve was calculated

Table 1

Model parameters

$D(\phi_1)$	$=1.25 \times 10^{-5} (\bar{V}_2 MW_2 \phi_1 / \bar{V}_1 RT) (\partial \mu_1 / \partial \phi_1) (\text{cm}^2/\text{s})$
v_1	$18 \text{ cm}^3/\text{g-mol}$
v_2	$74 \text{ cm}^3/\text{g-mol}$
v_3	$27000 \text{ cm}^3/\text{g-mol}$
g_{12}	$0.979 + 1.127 \exp(-2.306\phi_1) + 0.292 \exp(-12.564\phi_1)$
g_{13}	1.4
g_{23}	$0.645 - 0.11\phi_2$
$\bar{V}_1$	$1.0 \text{ cm}^3/\text{g}$
$\bar{V}_2$	$1.27 \text{ cm}^3/\text{g}$

using the method suggested by Altena and Smolders [13] and the parameters listed in Table 1. Fig. 2 shows the calculated binodal. Good agreement is seen with Fig. 2 of Reuvers and Smolders [3] thereby validating the numerical routine.

Fig. 3 shows the interfacial polymer film volume fraction after phase separation ($\phi_3^{M''}$), calculated by solving Eqs. (A.8) and (A.9) and the modified Eq. (A.6) for various values of the parameter C . The

Fig. 2. Three phase diagram for the water–acetone–cellulose acetate system showing the calculated binodal curve, tie lines and the initial polymer solution composition for which precipitation times reduce rapidly.

Fig. 3. Interfacial polymer-film volume fraction calculated in this work (for two different values of C) for different initial composition of the coagulation bath. Symbols are the results calculated by Reuvers and Smolders [3] using their algorithm.

X-axis shows the initial coagulation bath composition. The calculated values reported by Reuvers and Smolders [3] are also shown in the figure as symbols. Good agreement is seen between the values calculated using the improved algorithm presented in this work with that calculated by Reuvers and Smolders [3].

Fig. 4 shows the precipitation times in pure non-solvent for various values of the parameter C (see Appendix B and Reuvers and coworkers [1,3] for details) for different values of (ϕ_1/ϕ_2) in the polymer solution along with experimental data [3]. As can be seen, the numerical algorithm presented in this work effectively picks up the experimentally observed trend. Agreement with $C = 0.5$ is much better than that with $C = 1$. This was also observed by Reuvers and Smolders [3] in their work where they calculated precipitation times of around 40 and 22 s, respectively, for $C = 1$ and $C = 0.5$. The precipitation times calculated numerically in this work are slightly higher than those experimentally measured

by Reuvers and Smolders [3] using light transmission. One possible reason could be that in reality, nucleation of the polymer lean phase could cause a drop in light transmission intensity. Hence, light transmission experiments would pick up any changes due to nucleation while this is ignored in the present model. These results also indicate that though the polymer film interface does indeed proceed rapidly to near the spinodal, some nucleation does indeed take place. Hence, in any realistic model for prediction of structure of phase inversion membranes, nucleation needs to be necessarily included as a possible phase separation mechanism.

Fig. 3 also shows that the precipitation time decreases sharply after a ϕ_1/ϕ_2 ratio of 0.12. This is consistent with the experimental data reported by Reuvers and Smolders [3]. For a polymer volume fraction of 0.1, this corresponds to a non-solvent volume fraction of 0.096. On a three phase plot (see Fig. 2), it can be seen that the initial point is quite far away from the binodal. The interfacial polymer

Fig. 4. Precipitation times into pure water calculated for different ratios ϕ_1/ϕ_2 calculated in this work. Symbols are experimental values reported by Reuvers and Smolders [3] for initial polymer film thickness of 220 μm .

concentration for this initial polymer film composition is calculated to be 0.43 for $C = 0.5$. However, a faster precipitation of the polymer film need not necessarily lead to a better membrane. A potentially interesting case would be if, by tailoring the casting conditions, the polymer film interfacial composition could be taken directly to the so called Berghmans' point, without it ever crossing the binodal/spinodal envelops. In such a situation, a defect free membrane would be expected since the polymer matrix would be frozen in a glassy state as soon as phase separation occurs. Kools [14] has recently presented an excellent method for locating Berghmans' point.

The algorithm presented in this work is easily extendable to quaternary mixtures, whereas, the iterative algorithm of Reuvers and coworkers [1,3] would be difficult to implement without a pseudo-three component assumption (i.e. two of the four components being treated as a single third component). However, there is a large gap in available experimental data that does

not permit the estimation of all the model parameters to a reasonable degree of accuracy.

5. Conclusions

In this work, an improved algorithm is presented that allows numerical integration of the diffusion profiles in a ternary membrane forming system, without the iterative procedure described by Reuvers and coworkers [1,3]. In the present algorithm, no user intervention in terms of repeated initial guesses for the interfacial composition are required; the interfacial compositions are calculated from a set of simultaneous equations. This algorithm is tested against literature data for the system water–acetone–cellulose acetate. The simulations run using the improved algorithm show good agreement between the calculations of Reuvers and Smolders [3] and also with experimental data.

This algorithm would allow apriori prediction of the effectiveness of additives to polymer dope solutions in forming defect free membranes. This is because, the system is left to “evolve” from its initial state. Experimental data required to make reliable estimates of model parameters required, such as the frictional coefficients, is however lacking in the literature.

Appendix A

Eq. (1) after discretization and normalization becomes

$$\frac{\phi_i^{k,t} - \phi_i^{k,t-\Delta t}}{\Delta t} = \frac{\Delta}{\Delta m} \left\{ \frac{(\phi_3^{k,t})^2 RT \bar{V}_i}{D_0} \left[L_{11} \frac{\Delta \mu_1}{\Delta m} \Big|_t + L_{12} \frac{\Delta \mu_2}{\Delta m} \Big|_t \right] \right\},$$

$$k = 1, \dots, M-1, i = 1, 2 \quad (\text{A.1})$$

The spatial gradients are discretized using the second-order central difference scheme

$$\frac{\Delta f^k}{\Delta m} = \frac{f^{k+1} - f^{k-1}}{2\Delta m} \quad (\text{A.2a})$$

$$\frac{\Delta^2 f^k}{\Delta m^2} = \frac{f^{k+1} - 2f^k + f^{k-1}}{(\Delta m)^2} \quad (\text{A.2b})$$

In Eq. (A.1), since L_{ij} and μ_i are functions of volume fractions, they also are indirect functions of the spatial coordinate m . Therefore, the operator $\Delta/\Delta m$ has to be operated on the RHS of Eq. (A.1) in order to finally arrive at first/second-order spatial derivatives for the volume fractions ϕ_i . Discretized first and second-order derivatives are calculated as given in Eqs. (A.2a) and (A.2b), respectively.

Similarly, Eq. (3) after discretization and normalization becomes

$$\frac{\phi_i^{k,t} - \phi_i^{k,t-\Delta t}}{\Delta t} = \frac{\Delta}{\Delta y} \left\{ \frac{D(\phi_i^{k,t})}{D_0} \frac{\Delta \phi_i}{\Delta y} \Big|_t \right\} - \frac{\Delta \phi_i}{\Delta y} \Big|_t \left\{ \sum_j - \frac{D(\phi_j^{k,t})}{D_0} \frac{\Delta \phi_j}{\Delta y} \Big|_t \right\},$$

$$k = M+1, \dots, N, i = 1, 2 \quad (\text{A.3})$$

In Eq. (A.3) too, the diffusivity is a function of volume fraction (hence spatial coordinate). The final discretized spatial coordinates are calculated as indicated above.

It must be noted that in Eqs. (A.1) and (A.3), the RHS contains volume fractions at time t . Using these equations recursively, the volume fractions at each grid point k at a time t can be calculated from the values at time $t - \Delta t$.

To calculate values at grid point 0 (corresponding to the lower boundary of the polymer film), Eq. (6c) is used. This equation is discretized to give

$$\frac{\Delta \phi_i}{\Delta m} \Big|_{k=0,t} = \frac{4\phi_i^{1,t} - \phi_i^{2,t} - 3\phi_i^{0,t}}{2\Delta m} = 0, \quad i = 1, 2 \quad (\text{A.4})$$

Using Eq. (A.4), the volume fractions at grid point 0 (at time t) can be updated, once all the other grid points have been updated using Eq. (A.1).

In order to implement Eq. (6d), the following procedure is adopted. The volume fractions at grid point N are calculated using the following equation:

$$\frac{\phi_i^{N-2,t} - 4\phi_i^{N-1,t} + 3\phi_i^{N,t}}{2\Delta y} = 0, \quad i = 1, 2 \quad (\text{A.5})$$

This equation is the discretized version of a zero gradient condition. Far enough away from the interface into the bulk coagulation bath, the first-order spatial gradients of the volume fractions would tend to zero. However, one still needs to determine how far, is far enough. In order to do this, Eq. (A.5) is employed to calculate $\phi_i^{N,t}$. If the calculated value differs from the initial values by more than 10^{-6} , the number of grid points in the coagulation bath (N) is increased till the volume fractions calculated from Eq. (A.5) are within 10^{-6} of the initial values. This in effect enforces boundary condition 6d.

In order to calculate the volume fractions at grid point M before phase separation takes place, Eq. (6b) is discretized. This leads to the following equations:

$$\begin{aligned}
& -D(\phi_1^{M,t}) \left[\frac{4\phi_1^{M+1,t} - \phi_1^{M+2,t} - 3\phi_1^{M,t}}{2\Delta y} \right] \\
& = \bar{V}_1 \phi_3^{M,t} \left\{ L_{12} RT \left[\left(\frac{1}{\phi_2^{M,t}} - 1 + \frac{v_2}{v_3} - \left(g_{12} \frac{v_2}{v_1} \phi_1^{M,t} + g_{23} \phi_3^{M,t} \right) - g_{23}(1 - \phi_2^{M,t}) + g_{13} \frac{v_2}{v_1} \phi_1^{M,t} \right) \right. \right. \\
& \quad \left. \left. + L_{11} RT \left(-\frac{v_1}{v_2} + \frac{v_1}{v_3} + (1 - \phi_1^{M,t})(g_{12} - g_{13}) + g_{23} \frac{v_1}{v_2} (\phi_2^{M,t} - \phi_3^{M,t}) \right) \right] \right. \\
& \quad \left. \times \left(\frac{\phi_2^{M-2,t} - 4\phi_2^{M-1,t} + 3\phi_2^{M,t}}{2\Delta m} \right) \right. \\
& \quad \left. + L_{11} RT \left[\left(\frac{1}{\phi_1^{M,t}} - 1 + \frac{v_1}{v_3} - (g_{12} \phi_2^{M,t} + g_{13} \phi_3^{M,t}) - g_{13}(1 - \phi_1^{M,t}) + g_{23} \frac{v_1}{v_2} \phi_2^{M,t} \right) \right. \right. \\
& \quad \left. \left. + L_{12} RT \left(-\frac{v_2}{v_1} + \frac{v_2}{v_3} + (1 - \phi_2^{M,t}) \left(g_{12} \frac{v_2}{v_1} - g_{23} \right) + g_{13} \frac{v_2}{v_1} (\phi_1^{M,t} - \phi_3^{M,t}) \right) \right] \right. \\
& \quad \left. \times \left(\frac{\phi_1^{M-2,t} - 4\phi_1^{M-1,t} + 3\phi_1^{M,t}}{2\Delta m} \right) \right\} \tag{A.6}
\end{aligned}$$

$$\begin{aligned}
& -D(\phi_2^{M,t}) \left[\frac{4\phi_2^{M+1,t} - \phi_2^{M+2,t} - 3\phi_2^{M,t}}{2\Delta y} \right] \\
& = \bar{V}_2 \phi_3^{M,t} \left\{ \left[L_{22} RT \left(\frac{1}{\phi_2^{M,t}} - 1 + \frac{v_2}{v_3} - \left(g_{12} \frac{v_2}{v_1} \phi_1^{M,t} + g_{23} \phi_3^{M,t} \right) - g_{23}(1 - \phi_2^{M,t}) + g_{13} \frac{v_2}{v_1} \phi_1^{M,t} \right) \right. \right. \\
& \quad \left. \left. + L_{21} RT \left(-\frac{v_1}{v_2} + \frac{v_1}{v_3} + (1 - \phi_1^{M,t})(g_{12} - g_{13}) + g_{23} \frac{v_1}{v_2} (\phi_2^{M,t} - \phi_3^{M,t}) \right) \right] \right. \\
& \quad \left. \times \left[\frac{\phi_2^{M-2,t} - 4\phi_2^{M-1,t} + 3\phi_2^{M,t}}{2\Delta m} \right] \right. \\
& \quad \left. + \left[L_{21} RT \left(\frac{1}{\phi_1^{M,t}} - 1 + \frac{v_1}{v_3} - (g_{12} \phi_2^{M,t} + g_{13} \phi_3^{M,t}) - g_{13}(1 - \phi_1^{M,t}) + g_{23} \frac{v_1}{v_2} \phi_2^{M,t} \right) \right. \right. \\
& \quad \left. \left. + L_{22} RT \left(-\frac{v_2}{v_1} + \frac{v_2}{v_3} + (1 - \phi_2^{M,t}) \left(g_{12} \frac{v_2}{v_1} - g_{23} \right) + g_{13} \frac{v_2}{v_1} (\phi_1^{M,t} - \phi_3^{M,t}) \right) \right] \right. \\
& \quad \left. \times \left[\frac{\phi_1^{M-2,t} - 4\phi_1^{M-1,t} + 3\phi_1^{M,t}}{2\Delta m} \right] \right\} \tag{A.7}
\end{aligned}$$

In deriving Eqs. (A.6) and (A.7), the concentration dependence of g_{ij} is neglected. Further, $\phi_3^{M,t} = 1 - \phi_1^{M,t} - \phi_2^{M,t}$. Eqs. (A.6) and (A.7) are two equations in two independent variables ($\phi_i^{M,t}$, $i = 1, 2$). Solution of these two equations lead to the values of the volume fraction of non-solvent and solvent at grid point M for time t . Once these values are updated, the entire

diffusion profile can be updated using Eqs. (A.1) and (A.3)–(A.5).

All the above analysis holds provided the spinodal boundary has not been crossed.

Once the spinodal is crossed, an interface is formed between the polymer rich film and the polymer lean coagulation bath (corresponding to Fig. 2a in Reuvers

et al. [1]). Chemical potential equality of non-solvent and solvent across this interface leads to the following two equations:

$$\mu'_1(\phi_1^{M',t}) = \mu''_1(\phi_1^{M'',t}, \phi_2^{M'',t}) \quad (\text{A.8})$$

$$\mu'_2(\phi_1^{M',t}) = \mu''_2(\phi_1^{M'',t}, \phi_2^{M'',t}) \quad (\text{A.9})$$

The chemical potentials are given by

$$\begin{aligned} \mu_1 = & \ln \phi_1 + (1 - \phi_1) - \frac{v_1}{v_2} \phi_2 - \frac{v_1}{v_3} \phi_3 \\ & + (1 - \phi_1) (g_{12} \phi_2 + g_{13} \phi_3) - g_{23} \frac{v_1}{v_2} \phi_2 \phi_3 \\ & - \phi_2 u_2 (1 - u_2) \frac{dg_{12}}{du_2} \end{aligned} \quad (\text{A.10})$$

$$\begin{aligned} \mu_2 = & \ln \phi_2 + (1 - \phi_2) - \frac{v_2}{v_1} \phi_1 - \frac{v_2}{v_3} \phi_3 \\ & + (1 - \phi_2) \left(g_{12} \frac{v_2}{v_1} \phi_1 + g_{23} \phi_3 \right) \\ & - g_{13} \frac{v_2}{v_1} \phi_1 \phi_3 + \frac{v_2}{v_1} \phi_1 u_2 (1 - u_2) \frac{dg_{12}}{du_2} \\ & + \phi_3 w_2 (1 - w_2) \frac{dg_{23}}{dw_2} \end{aligned} \quad (\text{A.11})$$

where

$$u_2 = \frac{\phi_2}{\phi_2 + \phi_1} \quad (\text{A.12})$$

$$w_2 = \frac{\phi_2}{\phi_2 + \phi_3} \quad (\text{A.13})$$

Appendix B

The phenomenological coefficients L_{ij} are expressed as a function of the ternary frictional coefficients R_{ij} as [3]

$$L_{ij} = \frac{\beta_{ij}}{\alpha} \quad (\text{B.1})$$

where

$$\beta_{12} = \beta_{21} = \phi_1 \bar{V}_1^{-1} \phi_2 \bar{V}_2^{-1} R_{12} \quad (\text{B.2a})$$

$$\beta_{11} = \phi_1 \bar{V}_1^{-1} (\phi_1 \bar{V}_1^{-1} R_{12} + \phi_3 \bar{V}_3^{-1} R_{23}) \quad (\text{B.2b})$$

$$\beta_{22} = \phi_2 \bar{V}_2^{-1} (\phi_2 \bar{V}_2^{-1} R_{12} + \phi_3 \bar{V}_3^{-1} R_{13}) \quad (\text{B.2c})$$

$$\begin{aligned} \alpha = & \phi_3 \bar{V}_3^{-1} (\phi_2 \bar{V}_2^{-1} R_{12} R_{23} + \phi_1 \bar{V}_1^{-1} R_{12} R_{13} \\ & + \phi_3 \bar{V}_3^{-1} R_{13} R_{23}) \end{aligned} \quad (\text{B.2d})$$

$$R_{13} = C \left(\frac{\bar{V}_1}{\bar{V}_2} \right) R_{23} \quad (\text{B.2e})$$

References

- [1] A.J. Reuvers, J.A.W. van den Berg, C.A. Smolders, Formation of membranes by means of immersion precipitation, Part I. A model to describe mass transfer during immersion precipitation, *J. Membr. Sci.* 34 (1987) 45.
- [2] C. Cohen, G.B. Tanny, S. Prager, Diffusion-controlled formation of porous structures in ternary polymer systems, *J. Polym. Sci., Polym. Phys.* 17 (1979) 477.
- [3] A.J. Reuvers, C.A. Smolders, Formation of membranes by means of immersion precipitation Part II. The mechanism of formation of membranes prepared from the system cellulose acetate-water, *J. Membr. Sci.* 34 (1987) 67.
- [4] C.S. Tsay, A.J. McHugh, Mass transfer modeling of asymmetric membrane formation by phase inversion, *J. Polym. Sci., Polym. Phys.* 28 (1990) 1327.
- [5] C.S. Tsay, A.J. McHugh, An improved numerical algorithm for ternary diffusion with a moving boundary, *Chem. Eng. Sci.* 46 (1991) 1179.
- [6] L.P. Cheng, Y.S. Soh, A.H. Dwan, C.C. Gryte, An improved model for mass transfer during the formation of polymeric membranes by the immersion-precipitation process, *J. Polym. Sci., Polym. Phys.* 32 (1994) 1413.
- [7] R.M. Boom, T. van den Boomgaard, C.A. Smolders, Mass transfer and thermodynamics during immersion precipitation for a two-polymer system: evaluation with the system PES-PVP-NMP-water, *J. Membr. Sci.* 90 (1994) 231.
- [8] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953.
- [9] H. Tompa, *Polymer Solutions*, Academic Press Inc., New York, 1956.
- [10] B. Carnahan, H.A. Luther, J.O. Wilkes, *Applied Numerical Methods*, Wiley, New York, 1969.
- [11] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, *Numerical Recipes: The Art of Scientific Computing (FORTRAN Version)*, Cambridge University Press, Cambridge, 1990.
- [12] K. Kamide, H. Ijima, S. Matsuda, Thermodynamics of formation of porous polymeric membrane by phase separation method I. Nucleation and growth of nuclei, *Polym. J.* 25 (11) (1993) 1113.
- [13] F.W. Altena, A. Smolders, Calculation of liquid-liquid phase separation in a ternary system of a polymer in a mixture of a solvent and nonsolvent, *Macromolecules* 15 (1982) 1491.
- [14] W.F.C. Kools, *Membrane Formation by Phase Inversion in Multicomponent Polymer Systems*, Ph.D. Dissertation, University of Twente, The Netherlands, 1998.