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FORMATION OF MEMBRANES BY MEANS OF IMMERSION PRECIPITATION

PART I. A MODEL TO DESCRIBE MASS TRANSFER DURING IMMERSION PRECIPITATION

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Summary

Equations and boundary conditions are derived for the isothermal diffusion processes in the coagulation bath and in the polymer solution after immersion of a cast (ternary) polymer solution into a (binary) coagulation bath. The mass transfer is expressed in terms of thermodynamic driving forces and frictional coefficients. The frictional coefficients in the ternary system are assumed to be interrelated through the Onsager reciprocal relations and to be related to the measurable frictional coefficients defined in the three limiting binary composition ranges. In combination with knowledge about the demixing processes which can take place in the polymer solution (liquid-liquid phase separation or solid-like aggregate formation), this model makes it possible to calculate the polymer concentration profile in the immersed film at the moment of demixing of the polymer solution as a function of several process parameters. The calculated concentration profile and its relation to the asymmetric structure of the ultimate membrane are presented in Part II*.

Introduction

The preparation of asymmetric polymeric membranes by means of immersion precipitation of a casting solution started with the development of reverse-osmosis membranes by Loeb and Sourirajan [1] in 1962. Since then different kinds of asymmetric membranes have been prepared by means of immersion precipitation. The immersion precipitation process is also used to prepare the supporting layer of composite membranes.

It is possible to vary the membrane properties to a great extent, from typical reverse-osmosis behavior to microfiltration behavior, by changing the process parameters during membrane formation or by adding extra components to the casting solution or to the coagulation bath.

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The basic process of immersion precipitation can be carried out with three components. Solvent and polymer are used to prepare the casting solution and nonsolvent is used as the coagulation bath.

The formation process of the membrane can be split up into three parts:

1. Composition changes in the polymer solution before immersion into a coagulation bath, by evaporation;
2. Composition changes in the polymer solution after immersion into a coagulation bath prior to possible demixing processes;
3. Demixing processes which take place when the composition of the polymer solution becomes metastable.

Binary diffusion during the time in between casting and immersion of the polymer solution (the evaporation step) has been investigated by a number of authors [2–5]. In general they conclude that the asymmetric structure in case of Loeb–Sourirajan-type CA (cellulose acetate) membranes is caused by the evaporation of acetone, which leads to an increase of the polymer concentration in the top layer of the polymer solution. We agree that the duration of the evaporation step influences the membrane structure when volatile solvents are used. However, when nonvolatile solvents are used or when no evaporation step is carried out (which is the case for the innerside of a wet-spun hollow-fiber membrane) asymmetric membranes can also be obtained. This means that the ternary diffusion process which starts after immersion of the polymer solution into a nonsolvent bath mainly determines the asymmetric structure of the membrane.

The mass transfer in the still homogeneous polymer solution, after immersion into a nonsolvent bath, has not been a subject of much investigation until now. The most far-reaching theoretical investigation has been carried out by Cohen, Tanny and Prager [6]. They showed that after immersion of the casting solution in a coagulation bath the polymer concentration at the interface of the casting solution and the coagulation bath increases strongly. With their diffusion model they also examined whether the exchange of solvent and nonsolvent could lead to instable compositions in the polymer solution. Only if this is the case, according to Cohen and coauthors, porous membranes can be formed as a result of liquid–liquid demixing.

The third important feature of the membrane formation process is the type of demixing processes that can occur in the immersed polymer solution after diffusion has led to a metastable composition. These demixing processes create the pores in the sublayer and determine the structure of the top layer of the membrane.

Much research has been done into the demixing processes that occur in Loeb–Sourirajan-type CA membranes. The results of these investigations have been summarized by Lonsdale [7]. The general conclusion is that the polymer precipitates in the nonsolvent and that gelation occurs by coagulation. We prefer to call this demixing process ‘aggregate formation’. Within our group we have found that aggregate formation takes place in several membrane-forming systems [8,9] and that this can lead to very different structures. This demixing process can be discriminated from liquid–liquid phase separation. It has been shown that both demixing processes occur in membrane-forming systems and that they can be distinguished by examining the kinetics of demixing [9]. Especially at a low degree of supersaturation, aggregate formation is a slow process compared with liquid–liquid phase separation, probably because some orientation of the polymer molecules is required for the formation of aggregates.

In order to understand how these demixing processes influence the membrane structure it is necessary to examine experimentally the structure induced by demixing as a function of composition, and it is necessary to know the composition profile in the polymer film as a function of time after immersion of the film into the coagulation bath prior to the demixing processes. In this paper it will be shown how the composition change in the film prior to demixing can be described as a function of several process parameters. The present work has been inspired by the model of Cohen et al. [6].

The diffusion model: Correspondence to and difference from the model of Cohen et al.

Following Cohen, Tanny and Prager [6] we will describe the ternary diffusion process in the immersed polymer solution by means of two phenomenological diffusion equations. Chemical potential gradients are taken as the driving forces and phenomenological coefficients relate the driving forces to the diffusion fluxes.

We do not use the generalized form of Fick's law to describe the ternary diffusion process because ternary diffusion coefficients are not available and hardly measurable within the composition range of interest. For ternary phenomenological coefficients and thermodynamic nonideality parameters, however, reasonable assumptions can be adopted which relate these coefficients (and parameters) to their more easily measurable values in the three limiting binary composition ranges.

It is assumed that the compositions at both sides of the interface between the polymer solution and the coagulation bath are always at equilibrium. In order to simplify the moving boundary problem the diffusion equations are described using polymer-fixed position coordinates and the phenomenological coefficients are defined in a polymer-fixed frame of reference. So far we will copy the model of Cohen et al. To simplify their model Cohen et al. adopted a few assumptions. It will be briefly discussed why these simplifications were omitted from our model or why different assumptions were adopted.

Wijmans et al. [10] clearly showed that it is not allowed to use the steady-state approximation of Cohen et al. to describe the diffusion during membrane formation. Therefore, the steady-state assumption will not be adopted; the exact solution of the diffusion equations will be given.

Furthermore, Cohen et al. neglected the frictional forces acting between solvent and nonsolvent by omitting the cross terms in the diffusion equations. We will not omit them; it will be shown that their omission can lead to erroneous results.

The two above-mentioned simplifications enabled Cohen et al. to calculate composition paths without knowing the influence of the polymer concentration on the frictional forces acting between polymer and solvent and between polymer and nonsolvent. However, in the present model the dependence of these frictional forces on polymer concentration has to be known.

Cohen et al. used constant thermodynamic interaction parameters in their expressions for the chemical potentials. From results of Altena and Smolders [11] it can be concluded that the Flory–Huggins interaction parameter shows a strong concentration dependence for many solvent–water mixtures. Therefore, concentration-dependent binary interaction parameters will be used in the expressions for the chemical potentials.

Cohen et al. assumed that the composition of the coagulant at the boundary of the casting solution remains equal to the bulk composition of the original bath. However, even if the coagulation bath is well stirred, there will be a stagnant layer in the vicinity of the interface. Here it is assumed that only diffusion takes place in the coagulation bath. When the coagulation bath is stirred this assumption is still valid during the very important first seconds after immersion of the polymer solution.

Cohen et al. assumed that liquid–liquid demixing can occur only when an instable spinodal composition has been reached. In our opinion liquid–liquid demixing takes place when the binodal has been passed and a metastable composition with even a very low degree of supersaturation has been reached.

The phenomenological equations describing the diffusion in the polymer solution

In this section we will derive the phenomenological equations describing the diffusion in the polymer solution. It will be shown that the diffusion equations of Cohen et al. lack a factor (the polymer volume fraction) and that the recent criticism of McHugh and Yilmaz [12] on the continuity equations used by Cohen is unfounded.

The components are indexed as follows: nonsolvent (1), solvent (2) and polymer (3). For a complete list of symbols the reader is referred to the end of this paper.

De Groot and Mazur [13] derived the following relation between fluxes J_i^c and thermodynamic driving forces X_j in a ternary system:

$$J_i^c = \sum_{j=1}^{2} L_{ij} X_j, \qquad i=1,2 \tag{1}$$

The superscript 'c' refers to a mass flux [kg/m^2-sec]. Because of the exchange of solvent and nonsolvent after immersion of the film, the interface between the polymer solution and the coagulation bath will move. Hartley and Crank [14] suggest that this moving-boundary problem can be simplified by defining the fluxes relative to a polymer-fixed frame of reference:

$$J_i^c = c_i(\bar{v}_i - \bar{v}_3), \tag{2}$$

where c_i is the concentration of component i [kg/m^3]. For these fluxes the thermodynamic driving forces in eqn. (1) are given by [13]:

$$X_j = -\delta \mu_j / \delta x, \tag{3}$$

where μ_j is the chemical potential of component j per kilogram j and x is the Cartesian spatial position coordinate perpendicular to the membrane surface. We assume that the phenomenological coefficients, L_{ij}, obey the Onsager reciprocal relations [13]:

$$L_{12} = L_{21} \tag{4}$$

In order to obtain differential equations describing the ternary diffusion process the flux equations (1) have to be combined with the continuity equations.

Assuming that the partical specific volume, $\bar{V}_i$, does not (appreciably) depend on concentration, it can be derived [13, p. 256] that the volume-average velocity relative to the cell is zero:

$$\sum_{j=1}^{3} c_i \bar{V}_i \bar{v}_i = 0,$$

where $\bar{v}_i$ is the velocity of component i relative to the cell (in our case the glass plate). The assumption that the $\bar{V}$s are constant also implies that the continuity equations in terms of volume fluxes [m/sec] relative to the cell are given by [13]

$$\frac{\delta \tilde{J}_i^\phi}{\delta x} = -\frac{\delta \phi_i}{\delta t}, \qquad i=1,2 \tag{5}$$

where ϕ_i ($= c_i \bar{V}_i$) is the volume fraction of component i. The tilde (~) denotes that $\tilde{J}_i$ is a flux relative to the cell

$$\tilde{J}_i^\phi = \phi_i \bar{v}_i (= c_i \bar{V}_i \bar{v}_i) \tag{6}$$

The desired differential equations describing the mass transport relative to the polymer-fixed frame of reference can be obtained from eqns. (1) and (5), only after rewriting eqn. (5) in terms of fluxes relative to the polymer-fixed

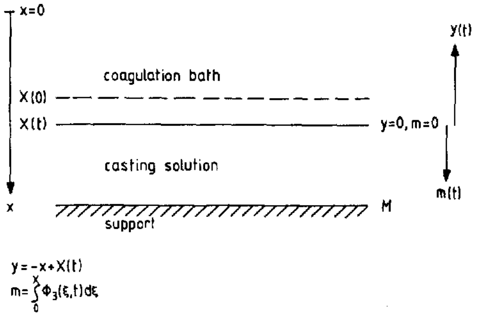

Fig. 1. Schematic representation of the cast polymer solution layer, the coagulation bath and the position coordinates used.

frame of reference. This is achieved in the following manner. From eqns. (2) and (6) it can be derived that $J_i^\phi\,[=\phi_i(\bar{v}_i-\bar{v}_3)]$ and $\tilde{J}_i^\phi$ are related as

$$J_i^\phi=\tilde{J}_i^\phi-(\phi_i/\phi_3)\tilde{J}_3^\phi, \qquad i=1,2 \tag{7}$$

where J_i^ϕ refers to a volume flux relative to the polymer-fixed frame of reference. Combination of eqns. (5) and (7) yields

$$\frac{\delta J_i^\phi}{\delta x}=-\phi_3\frac{\delta(\phi_i/\phi_3)}{\delta t}-\tilde{J}_3^\phi\frac{\delta(\phi_i/\phi_3)}{\delta x}, \qquad i=1,2 \tag{8}$$

As suggested by Hartley and Crank [14] we introduce a new position coordinate, m (see Fig. 1), in order to eliminate $\tilde{J}_3^\phi$ from eqn. (8):

$$m(x,t)=\int_0^x \phi_3(\xi,t)\,\mathrm{d}\xi \tag{9}$$

$$\delta m(t=\text{constant})=\phi_3\delta x(t=\text{constant}).$$

A detailed description will be given of the way in which eqn. (8) is transformed by the transition from x to m position coordinates. In our opinion, McHugh et al. [12] perform this transformation in a wrong way, which leads to their erroneous continuity equations.

In the following equations the subscripts to the derivatives refer to constant parameters.

$$\phi_3\left(\frac{\delta(\phi_i/\phi_3)}{\delta t}\right)_m=\phi_3\left(\frac{\delta(\phi_i/\phi_3)}{\delta t}\right)_x+\phi_3\left(\frac{\delta(\phi_i/\phi_3)}{\delta x}\right)_t\times\left(\frac{\delta x}{\delta t}\right)_m \tag{10}$$

$$\phi_3\left(\frac{\delta x}{\delta t}\right)_m=\tilde{J}_3^\phi \tag{11}$$

$$\left(\frac{\delta J_i^{\phi}}{\delta x}\right)_t = \phi_3 \left(\frac{\delta J_i^{\phi}}{\delta m}\right)_t \tag{12}$$

By substituting eqns. (10), (11) and (12) in eqn. (8) we finally obtain

$$\left(\frac{\delta J_i^{\phi}}{\delta m}\right)_t = -\left(\frac{\delta(\phi_i/\phi_3)}{\delta t}\right)_m, \qquad i=1,2 \tag{13}$$

These continuity equations are in agreement with the equations of Wijmans et al. [10] who examined the mass balance in a 'polymer-fixed' volume element. They are also in agreement with the equations proposed by Hartley and Crank [14] to simplify a moving boundary problem.

In order to combine the flux equation (1) with the continuity equation (13) so as to eliminate the fluxes, first the mass fluxes J_i^c in eqn. (1) have to be substituted by volume fluxes J_i^{ϕ}:

$$J_i^{\phi} = -\sum_{j=1}^{2} \bar{V}_i L_{ij} \frac{\delta \mu_j}{\delta x}, \qquad i=1,2 \tag{14}$$

The transition to m position coordinates according to eqn. (9) transforms eqn. (14) into

$$J_i^{\phi} = -\sum_{j=1}^{2} \bar{V}_i \phi_3 L_{ij} \frac{\delta \mu_j}{\delta m}, \qquad i=1,2 \tag{15}$$

It may be observed that this transformation leads to the appearance of ϕ_3 in the flux equations, the term that is missing in the flux equations of Cohen et al.

Now, the flux equation (15) and the continuity equation (13) can be combined:

$$\frac{\delta(\phi_i/\phi_3)}{\delta t} = \frac{\delta}{\delta m}\left\{\sum_{j=1}^{2} \bar{V}_i \phi_3 L_{ij}(\phi_1,\phi_2) \frac{\delta \mu_j}{\delta m}\right\}, \qquad i=1,2 \tag{16}$$

These ternary diffusion equations describe the concentration changes as a function of time and place in the immersed polymer solution, if the appropriate boundary and initial conditions are used.

The phenomenological coefficients L_{ij} (defined in the polymer-fixed frame of reference) are concentration dependent. These ternary coefficients can be related to binary frictional coefficients which in turn can be related to measurable diffusion and sedimentation coefficients, as will be shown.

The expressions for the chemical potentials as a function of the composition are given in Appendix A.

The equations describing the binary diffusion in the coagulation bath

The presence of polymer in the coagulation bath, after immersion of the polymer solution is neglected, although a very small amount of polymer may dissolve in the coagulation bath in the presence of an excess amount of solvent in the coagulation bath.

As a consequence of neglecting the concentration dependence of the partial specific volumes, the binary diffusion process in the coagulation bath — relative to the cell (the glass plate) — is described by Fick's second law:

$$\frac{\delta\phi_i}{\delta t}=\frac{\delta}{\delta x}\left\{D(\phi_i)\,\frac{\delta\phi_i}{\delta x}\right\} \tag{17}$$

where $D(\phi_i)$ is the mutual diffusion coefficient.

In the preceding section it has been shown that through the introduction of the position coordinate m in the polymer solution, the moving boundary between the coagulation bath and the solution can be fixed to the position $m=0$. By introducing a new position coordinate, y, the diffusion process in the coagulation bath relative to the moving interfacial boundary will be described, in order to transform this moving-boundary problem to a fixed-boundary problem as well (see Fig. 1):

$$y=-x+X(t) \tag{18}$$

where $X(t)$ is the position of the boundary between the polymer solution and the coagulation bath, measured in position coordinates x.

The transformation to position coordinates y, according to eqn. (18), converts eqn. (17) into

$$\frac{\delta\phi_i}{\delta t}=\frac{\delta}{\delta y}\left\{D(\phi_i)\,\frac{\delta\phi_i}{\delta y}\right\}-\frac{\delta\phi_i}{\delta y}\times\frac{\delta X(t)}{\delta t} \tag{19}$$

$$\frac{\delta X(t)}{\delta t}=J_1^\phi(y=0)+J_2^\phi(y=0) \tag{19a}$$

These equations will be used to describe the diffusion in the unstirred coagulation bath.

The initial and boundary conditions

At the very moment of immersion of the cast film into the coagulation bath, the film and the bath are considered to be completely homogeneous. This leads to the following initial conditions.

$$\begin{array}{lll} y>0: & \phi_i^{(c)}(y,0)=\phi_i^{(c)} & i=1,2 \\ 0\leqslant m\leqslant M: & \phi_i^{(s)}(m,0)=\phi_i^{(s)} & i=1,2,3 \end{array} \tag{20}$$

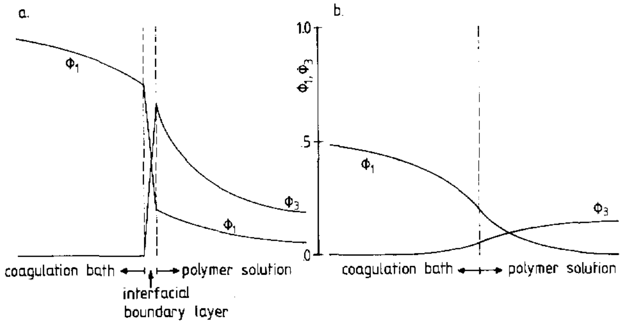

Fig. 2. Schematic representation of the two possible types of concentration profiles in the contact area between the bath and the solution after immersion of a polymer solution into a coagulation bath; (a) Concentration profile with an interfacial boundary layer between the two liquid phases. (b) Concentration profile without an interfacial boundary layer.

The superscripts (c) and (s) refer to the coagulation bath and the polymer solution, respectively. M is the total volume of polymer per unit area of casting solution.

From the moment of contact between the film and the bath, in principle two different kinds of concentration profiles are possible in the area of contact between the bath and the film:

(a) A concentration profile consisting of an interfacial boundary layer between two liquid phases and on both sides of this interfacial boundary layer steep concentration gradients which become smoother in the course of time.

(b) A concentration profile consisting of one concentration gradient which becomes smoother in the course of time.

Both types of concentration profiles are shown in Fig. 2.

Whether a real interfacial boundary will be formed (situation a) mainly depends on the initial solvent concentration in the coagulation bath. When the solvent concentration in the vicinity of the surface of the polymer solution remains below a certain limiting value, the local Gibbs free energy can be minimized by the formation of an interfacial boundary (i.e. the high local nonsolvent concentration prevents the polymer solution to be miscible with the coagulation bath). Situation (a) will be assumed to correctly describe the actual concentration profile during membrane formation. In Part II of this paper a method of verification of this assumption is described.

It is assumed that the thickness of the interfacial boundary layer is equal to zero.

One of the assumptions of irreversible thermodynamics is the existence of a state of local equilibrium even when no equilibrium exists on a macroscopic scale. This means that at the boundary of the two phases considered (the coagulation bath and the polymer solution) the following boundary conditions exist:

$$\mu_i^{(c)}(y=0,t)=\mu_i^{(s)}(m=0,t), \quad i=1,2,3 \tag{21}$$

When the ternary phase diagram is considered, eqn. (21) implies that at any time the boundary compositions in the film and in the coagulation bath are situated on the binodal and are connected by a tie line. The boundary conditions (21) make it necessary to calculate the tie lines using expressions for μ_i as a function of composition. It will be shown that $\phi_3^{(c)}(y=0,t)$ can be neglected if $\phi_2^{(c)}$ does not exceed a certain limiting value.

The other conditions at the boundary of the two phases are

$$J_i^{\phi}(y=0,t)=-J_i^{\phi}(m=0,t), \quad i=1,2 \tag{22}$$

At $m=M$ the boundary conditions are given by

$$\frac{\delta\phi_i}{\delta m}=0, \quad i=1,2 \tag{23}$$

The coagulation bath is considered to be infinitely thick.

Our calculations are only valid as long as the diffusion gradients in the film and in the bath are not disturbed by demixing processes or by convection.

$mt^{-1/2}$ Dependent solutions

In this section it will be shown that the solution of the equations describing the diffusion in the polymer film is a function of $mt^{-1/2}$ and that the interfacial boundary compositions are constant during a certain period after immersion of the polymer film.

To start assume that the interfacial boundary compositions are constant as long as the polymer film can be treated as infinitely thick and the convection in the coagulation bath can be neglected. It will be shown that these assumptions yield the one and only solution of the equations, obeying the boundary conditions.

The introduction of a new variable $l=mt^{-1/2}$ enables transformation of eqn. (16) into

$$\frac{\delta(\phi_i/\phi_3)}{\delta l}=-\frac{2}{l}\frac{\delta}{\delta l}\left\{\sum_{j=1}^{2}\bar{V}_i\phi_3 L_{ij}(\phi_1,\phi_2)\frac{\delta\mu_j}{\delta l}\right\}, \quad i=1,2 \tag{24}$$

Regarding the boundary and initial conditions it follows that the composition in the polymer solution is a function of l, if the above-mentioned assumptions hold. Under the same circumstances it can be shown that

$$J_i^\phi(m=0,t)=\frac{\delta}{\delta t}\int_0^M\left\{\frac{\phi_i(m,t)}{\phi_3(m,t)}-\frac{\phi_i(m,0)}{\phi_3(m,0)}\right\}\mathrm{d}m$$
$$=\frac{1}{2}t^{-1/2}C_i,\qquad i=1,2 \tag{25}$$

the constant C_i being given by

$$C_i=t^{-1/2}\int_0^M\left\{\frac{\phi_i(m,t)}{\phi_3(m,t)}-\frac{\phi_i(m,0)}{\phi_3(m,0)}\right\}\mathrm{d}m$$

The rate of movement of the boundary (19a) is given by

$$\frac{\delta X(t)}{\delta t}=-J_1^\phi(m=0,t)-J_2^\phi(m=0,t)=-\frac{1}{2}t^{-1/2}(C_1+C_2) \tag{26}$$

Rewriting the diffusion equation for the coagulation bath by introducing the new variable $l'=yt^{-1/2}$ yields:

$$\frac{\delta\phi_i}{\delta l'}=\frac{2}{l'}\left\{(C_1+C_2)\frac{\delta\phi_i}{\delta l'}-\frac{\delta}{\delta l'}\left[D(\phi_i)\frac{\delta\phi_i}{\delta l'}\right]\right\} \tag{27}$$

It follows that the composition in the coagulation bath is a function of l' as long as the assumption holds that no convection takes place and the boundary composition is constant. This implies that

$$J_i^\phi(y=0,t)=\frac{\delta}{\delta t}\int_0^Y\phi_i(y,t)-\phi_i(y,0)\,\mathrm{d}y+\frac{\delta X(t)}{\delta t}\phi_i(t=0)$$
$$=\frac{1}{2}t^{-1/2}C_i',\quad i=1,2 \tag{28}$$

where C_i' is given by

$$C_i'=t^{-1/2}\int_0^Y\phi_i(y,t)-\phi_i(y,0)\,\mathrm{d}y-(C_1+C_2)\phi_i(t=0),$$

and Y is a position in the coagulation bath on a constant distance from the interfacial boundary, where the original composition remains unchanged. If the solvent concentration in the coagulation bath is not too high it is always possible to find a pair of constant boundary compositions obeying condition (21) which yield such C_i and C_i' values that boundary condition (22) is obeyed.

Thus, it has been shown that the assumption mentioned at the beginning of this section yields a solution of the diffusion equations that obeys the boundary conditions mentioned in the previous section. Because these boundary conditions restrict the number of solutions of the diffusion equations to only one solution, it can be concluded that this unique solution yields constant interfacial boundary compositions under the special circumstances mentioned in the assumption. Besides it has been shown that the composition in the film is a function of $mt^{-1/2}$ as long as the composition at $m=M$ remains unchanged and no convection takes place in the coagulation bath. These conclusions simplify the solution of our diffusion problem considerably.*

Ternary phenomenological coefficients L_{ij} simplified to functions of binary frictional coefficients R_{ij}

For the solution of eqn. (16) expressions are needed for the phenomenological coefficients L_{ij}. As has been pointed out before, some assumptions will be adopted which relate the hardly measurable ternary coefficients L_{ij} to their values in the three limiting binary composition ranges. These binary L_{ij} values are related to binary diffusion or sedimentation coefficients, which can be obtained easily.

For the derivation of expressions for L_{ij} as a function of these binary coefficients it is helpful to introduce frictional coefficients R_{ij} which are defined by the Stefan–Maxwell flux equations [16,17]:

$$\frac{\delta\mu_i}{\delta x}=-\sum_{j=1}^{3} R_{ij}c_j(\bar{v}_i-\bar{v}_j), \quad i=1,2,3 \tag{29}$$

$\bar{v}_i$ and $\bar{v}_j$ are the average velocities of components i and j with respect to the cell-fixed frame of reference. Unlike L_{ij} the frictional coefficients R_{ij} do not depend on the choice of frame of reference.

Dunlop [16] showed that eqn. (29) can be reduced to the following form:

$$\frac{\delta\mu_1}{\delta x}=-R_{13}c_3(\bar{v}_1-\bar{v}_3)-R_{12}c_2(\bar{v}_1-\bar{v}_2) \tag{30}$$

$$\frac{\delta\mu_2}{\delta x}=-R_{21}c_1(\bar{v}_2-\bar{v}_1)-R_{23}c_3(\bar{v}_2-\bar{v}_3) \tag{31}$$

We assume that $R_{12}=R_{21}$ [16,17]. Because $\delta\mu_i/\delta x$ is the driving force per kilogram i, $R_{ij}c_j(\bar{v}_i-\bar{v}_j)$ is the frictional force acting between component i and j per kilogram i.

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*The square-root relationship would not have been found when relaxation-type diffusion equations were used. However, relaxation times associated with structural changes in rubbery polymers are too short to cause diffusion anomalies [15]. For the compositions present in the freshly immersed casting solution it is very reasonable to assume that the glass temperature has not yet been reached.

In references [16,17] moles are used where we use kilograms. This means that their R_{ij} values differ a factor $M_i \times M_j \times 10^{-6}$ from the R_{ij} values as defined above. (M_i = molecular weight of component i [g-mol^{-1}].)

First, the relation between the L_{ij} and the R_{ij} values will be derived. Rearrangement of eqn. (30) yields the following expression:

$$c_i(\bar{v}_i - \bar{v}_3) = -\sum_{j=1}^{2} \frac{\beta_{ij}}{\alpha} \frac{\delta \mu_j}{\delta x}, \quad i=1,2 \tag{32}$$

where

$$\beta_{12} = \beta_{21} = c_1 c_2 R_{12}$$

$$\beta_{11} = c_1 (c_1 R_{12} + c_3 R_{23})$$

$$\beta_{22} = c_2 (c_2 R_{12} + c_3 R_{13})$$

$$\alpha = c_3 (c_2 R_{12} R_{23} + c_1 R_{12} R_{13} + c_3 R_{13} R_{23})$$

When we compare eqn. (32) with eqns. (1) to (3):

$$c_i(\bar{v}_i - \bar{v}_3) = -\sum_{j=1}^{2} L_{ij} \frac{\delta \mu_j}{\delta x}, \quad i=1,2$$

it is clear that the relation between the phenomenological and the frictional coefficients is given by

$$L_{ij} = \beta_{ij}/\alpha, \quad i=1,2, j=1,2 \tag{33}$$

This result is in agreement with the expression derived by Spiegler [18].

In the three limiting binary composition ranges eqn. (30) yields the following relations for $\phi_i + \phi_j = 1$:

$$\frac{\delta \mu_i}{\delta x} = -c_j R_{ij}(\phi_j)(\bar{v}_i - \bar{v}_j), \quad i=1, j=2 \text{ or } 3;\ i=2, j=1 \text{ or } 3. \tag{34}$$

In the next section it will be shown how the binary frictional coefficients in eqn. (34) are related to binary diffusion or sedimentation coefficients. However, the ternary frictional coefficients will first be expressed as a function of the binary coefficients $R_{ij}(\phi_j)$. This can be done by adopting a few assumptions concerning the concentration dependence of the ternary frictional coefficients.

For $R_{12}(\phi_1,\phi_2)$ the assumption is adopted that this coefficient is a function of the ratio $\phi_1/(\phi_1+\phi_2)$. We assume that the presence of the polymer influences the frictional force per cubic meter acting between components 1 and 2. However, the magnitude of the frictional force per kilogram 1 remains proportional to c_2 at constant ratio $\phi_1/(\phi_1+\phi_2)$ and varying ϕ_3:

$$R_{12}(\phi_1,\phi_2) = R_{12}(\phi_1')(\phi_3 = 0) \tag{35}$$

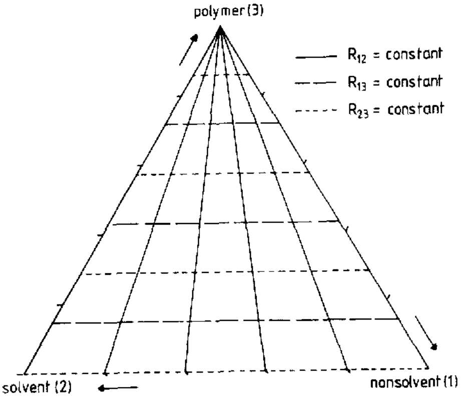

Fig. 3. Lines connecting compositions with equal ternary frictional coefficients R_{ij} according to eqns. (35) and (36).

where $\phi_1' = \phi_1/(\phi_1+\phi_2)$.

Because of the reciprocal relation (31),

$$R_{21}(\phi_1,\phi_2) = R_{12}(\phi_1,\phi_2) \tag{35a}$$

For the concentration dependence of R_{13} and R_{23} a different assumption is adopted in that these frictional coefficients are assumed to depend on the polymer volume fraction only. The polymer is considered to act as a porous plug whose permeability for component 1 or 2 is not influenced by the presence of the other low molecular weight component; thus, assuming that the permeability of the plug is only influenced by the polymer volume fraction.

$$R_{i3}(\phi_i,\phi_3) = R_{i3}(\phi_3)(\phi_i+\phi_3=1) \tag{36}$$

In Fig. 3 assumptions (35) and (36) are visualized in a ternary diagram.

Binary frictional coefficients $R_{ij}(\phi_j)$ as a function of binary diffusion or sedimentation coefficients

In this section the binary coefficients R_{ij}, occurring in mass transport equation (16) via eqns. (33), (35) and (36), are expressed as a function of parameters which can be determined experimentally.

The binary frictional coefficient R_{ij} can be related to the binary phenomenological coefficient $(L_i)_j$ defined as follows:

$$J_i^c = c_i(\bar{v}_i - \bar{v}_j) = -(L_i)_j \frac{\delta \mu_i}{\delta x} \tag{37}$$

Combination of eqns. (37) and (34) yields the following relation:

$$R_{ij}(\phi_i+\phi_j=1) = \bar{V}_j\phi_i/\bar{V}_i\phi_j(L_i)_j \tag{38}$$

In Appendix B the following relation between the binary diffusion coefficient D and $(L_j)_j$ is derived:

$$(L_i)_j = D\Big/\left(\phi_j \frac{\delta\mu_i}{\delta c_i}\right)$$

Substitution of this expression in eqn. (38) yields the following expression for the binary frictional coefficient:

$$R_{ij}(\phi_i + \phi_j = 1) = \frac{\bar{V}_j \phi_i}{D} \times \frac{\delta\mu_i}{\delta\phi_i} \tag{39}$$

In Part II of this paper this expression will be used for the calculation of the binary coefficient R_{12}.

The binary coefficient $(L_i)_j$ can also be expressed as a function of the sedimentation coefficient s_j. This relation is derived for the coefficients $(L_2)_3$ and s_3 in Appendix C:

$$(L_2)_3 = \frac{1}{\bar{V}_2(\rho\bar{V}_2 - 1)} \times s_3(\phi_3) \tag{40}$$

When substituted in eqn. (38), this expression yields the following expression for the binary coefficient R_{23}:

$$R_{23}(\phi_1 = 0) = \frac{\phi_2 \bar{V}_3(\rho\bar{V}_2 - 1)}{\phi_3} \times \frac{1}{s_3(\phi_3)} \tag{41}$$

Thus the binary coefficient R_{23} can be obtained by measuring the sedimentation coefficient of the polymer in the solvent as a function of the concentration. In Part II of this paper results for the system CA–acetone will be presented.

It is very difficult to determine R_{13} by means of diffusion or sedimentation measurements because the polymer can be dissolved in the nonsolvent only within a very small concentration range. Even if we could determine R_{13} it is doubtful whether this quantity would describe the friction between nonsolvent and polymer correctly in the presence of an excess amount of solvent. It will appear that mainly in this composition range the ternary diffusion process in a membrane-forming system takes place. Thus R_{13} has to be estimated. $R_{13}(\phi_3)$ will be estimated by relating this coefficient to $R_{23}(\phi_3)$. For a proper estimation of $R_{13}(\phi_3)$ it is helpful to derive a relation between R_{13} and R_{23} in the hypothetical case that, for a binary polymer solution with a certain volume fraction of polymer, the resistance force per cubic meter exerted by the polymer on the solvent is equal whether using solvent 2 or 'solvent' 1 (the nonsolvent). The binary flux equations are then given by (see eqn. 37):

$$J_i^\phi = -\bar{V}_i^2(L_i)_3 \times \left\{\frac{1}{\bar{V}_i} \frac{\delta\mu_i}{\delta x}\right\}, \quad i = 1,2 \tag{42}$$

where μ_i denotes the chemical potential per kilogram of i and $(1/\bar{V}_i)(\delta\mu_i/\delta x)$ the driving force per cubic meter. It can be concluded that in our hypothetical case

$$\bar{V}_1^2(L_1)_3 = \bar{V}_2^2(L_2)_3 \tag{43}$$

From eqns. (38) and (43) it follows that

$$R_{13} = \frac{\bar{V}_1}{\bar{V}_2} R_{23} \tag{44}$$

In reality the resistance forces exerted by the polymer on the solvent and the nonsolvent will differ, especially because the sizes of the two low-molecular weight components differ. Therefore we will use the following expression for R_{13} in our model calculations:

$$R_{13} = C \times \frac{\bar{V}_1}{\bar{V}_2} R_{23}, \tag{45}$$

where C may either be constant, or depending on ϕ_3.

Conclusions

A set of general diffusion equations (eqn. 16) and boundary conditions have been derived for the mass transport in a ternary polymer solution after immersion into a coagulation bath and prior to possible demixing processes.

In addition, expressions for the binary diffusion in the coagulation bath, relative to the moving boundary between the polymer film and the coagulation bath, have been derived (eqns. 19 and 19a).

As long as the composition at the bottom of the polymer solution remains unchanged, the composition changes in the polymer solution are a function of $mt^{-1/2}$ only. This means that during this period, all compositions existing in the polymer solution can be described by a constant composition trajectory.

The relation between the ternary phenomenological coefficients L_{ij} and the ternary frictional coefficients R_{ij} is given by eqn. (33). We have simplified the ternary frictional coefficients to functions of binary frictional coefficients, eqns. (35) and (36). The frictional coefficient describing the interaction between solvent and nonsolvent is related to the binary diffusion coefficient, eqn. (39). The frictional coefficient describing the interaction between solvent and polymer is related to the sedimentation coefficient, eqn. (41). The frictional coefficient describing the interaction between nonsolvent and polymer must be estimated.

In Part II of this paper the composition profiles will be calculated in a cellulose acetate–acetone solution after immersion into water. Experimental, concentration-dependent sedimentation and diffusion coefficients will be used in the expressions for R_{ij}. In the expressions for the chemical potentials, eqns.

(A2–A4), experimental, concentration-dependent Flory–Huggins parameters will be used.

An experimental method will be presented to verify the results of the calculations and to estimate the value of R_{13}.

List of symbols

c_i	Concentration of component i (kg-m^{-3})
C	Constant defined in eqn. (45)
C_i	Constant defined in eqn. (25)
C'_i	Constant defined in eqn. (28)
D	Binary mutual diffusion coefficient, defined in volume- or cell-fixed frame of reference, eqn. (B1)
χ_{ij}	Flory–Huggins interaction parameter
g_{ij}	Concentration-dependent Flory–Huggins interaction parameter
J_i	Flux of component i relative to the polymer-fixed frame of reference
$\tilde{J}_i$	Flux of component i relative to the volume- or cell-fixed frame of reference
$\overset{*}{J}_i$	Flux of component i relative to the mass-fixed frame of reference
J_i^{φ}	Volume flux of component i (m-sec^{-1})
J_i^c	Mass flux of component i (kg-m^{-2}-sec^{-1})
L_{ij}	Ternary phenomenological coefficient, defined in polymer-fixed frame of reference, eqns. (1–3)
$(L_i)_j$	Binary phenomenological coefficient, defined in component j-fixed frame of reference, eqn. (37)
$\tilde{L}_i$	Binary phenomenological coefficient, defined in volume- or cell-fixed frame of reference, eqn. (B1)
l	$mt^{-1/2}$
l'	$yt^{-1/2}$
m	Position coordinate of the polymer-fixed reference frame, defined in eqn. (9) (m)
M	Total volume of polymer per unit area of polymer film (m)
M_i	Molecular weight of component i (g-mol^{-1})
Q	Binary phenomenological coefficient, defined in mass-fixed frame of reference, eqn. (C2)
R	Gas constant (J-K^{-1}kmol^{-1})
R_{ij}	Frictional coefficient describing the interaction between the components i and j (defined in eqn. 29)
r	$\bar{V}_1M_1/\bar{V}_3M_3$
s	$\bar{V}_1M_1/\bar{V}_2M_2$
s_i	Sedimentation coefficient of component i

$\bar{v}_i$	Average velocity of component i relative to the volume- or cell-fixed frame of reference
$\bar{V}_i$	Partial specific volume of component i (m^3-kg^{-1})
x	Cartesian spatial position coordinate perpendicular to the membrane surface (m)
X	Position of the interface between the film and the coagulation bath (m)
y	Position coordinate relative to $X(t)$ (m)
μ_i^+	Chemical potential of component i (J-$kmol^{-1}$)
μ_i	Chemical potential of component i (J-kg^{-1})
ρ	Solution density $= \Sigma_i c_i$ (kg m^{-3})
ϕ_i	Volume fraction of component i

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Appendix A

Equilibrium thermodynamics for a three-component system

For the expression of the Gibbs free energy of mixing we use the Flory–Huggins theory for polymer solutions [19], extended to systems with three components by Tompa [20]

$$\frac{\Delta G_{\mathrm{m}}}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_2) n_1 \phi_2 + \chi_{13} n_1 \phi_3 + g_{23}(v_2) n_2 \phi_3 \qquad (\mathrm{A1})$$

where n_i is the number of moles of i and χ_{13} is the nonsolvent–polymer interaction parameter; g_{12} is the solvent–nonsolvent interaction parameter, which is assumed to be a function of u_2, with $u_2 = \phi_2/(\phi_2 + \phi_1)$; g_{23} is the solvent–polymer interaction parameter which is assumed to be a function of $v_2 = \phi_2/(\phi_2 + \phi_3)$.

In eqn. (A1) the — strictly speaking — ternary nonideality parameters $g_i(\phi_i, \phi_j)$ are related to their more easily measurable values in the three limiting binary composition ranges. For practical reasons $g_{13}(\phi_1, \phi_3)$ is even assumed to be constant and equal to χ_{13}, measured at the saturation composition of the nonsolvent-swollen polymer.

In fact eqn. (A1) is valid only in the case of vanishing concentration gradients. By using eqn. (A1) the influence on the local free energy of the steep concentration gradients at the boundary between the polymer solution and the coagulation bath is neglected. This means that, for extremely short time intervals immediately after immersion of the polymer solution, the diffusion model gives an approximation of real diffusion behavior.

From eqn. (A1) the following equations for the chemical potentials of the components in the mixture are derived:

$$\Delta \mu_1^+ / RT = \ln \phi_1 - s\phi_2 - r\phi_3 + (1 + g_{12}\phi_2 + \chi_{13}\phi_3)(1 - \phi_1) - s g_{23}\phi_2\phi_3 - \phi_2 u_2 (1 - u_2) \frac{\mathrm{d}g_{12}}{\mathrm{d}u_2} \qquad (\mathrm{A2})$$

$$s\Delta\mu_2^+/RT = s\ln\phi_2 - \phi_1 - r\phi_3 + (s + g_{12}\phi_1 + sg_{23}\phi_3)(1-\phi_2) - \chi_{13}\phi_1\phi_3 + \phi_1 u_2(1-u_2)\frac{dg_{12}}{du_2} + s\phi_3 v_2(1-v_2)\frac{dg_{23}}{dv_2} \quad \text{(A3)}$$

$$r\Delta\mu_3^+/RT = r\ln\phi_3 - \phi_1 - s\phi_2 + (r + g_{23}s\phi_2 + \chi_{13}\phi_1)(1 - \phi_3) - g_{12}\phi_1\phi_2 - s\phi_2 v_2(1-v_2)\frac{dg_{23}}{dv_2} \quad \text{(A4)}$$

The chemical potentials are expressed per kilomole of segments of component 1; s and r are the ratios of the molar volumina:

$$s = \bar{V}_1 M_1/\bar{V}_2 M_2, \qquad r = \bar{V}_1 M_1/\bar{V}_3 M_3$$

The expressions (A2) and (A3) are used in the diffusion equations for the polymer solution. For the boundary condition all three expressions for the chemical potentials have to be evaluated. The conditions for liquid–liquid equilibrium (at the boundary) are:

$$\Delta\mu_i^+ \text{ (diluted phase)} = \Delta\mu_i^+ \text{ (concentrated phase)} \qquad (i=1,2,3) \quad \text{(A5)}$$

Altena et al. [11] described how the binodal and the tie lines, connecting the coexisting phases in a ternary diagram can be calculated.

Appendix B

The relation between the binary coefficients $(L_i)_j$ *and* D

The binary diffusion coefficient D is measured relative to the cell-fixed frame of reference, which is equal to the volume-fixed frame of reference in the case of constant partial volumes $\bar{V}_i$ [13].

The relation between D and $\tilde{L}_i$ is given by

$$J_i^c = c_i\bar{v}_i = -D\frac{\delta c_i}{\delta x} = -\tilde{L}_i\frac{\delta\mu_i}{\delta x} \quad \text{(B1)}$$

where $\tilde{L}_i$ is the phenomenological coefficient defined in the volume-fixed frame of reference.

From eqn. (B1) it can be derived that

$$\frac{D}{\delta\mu_i/\delta c_i} = \tilde{L}_i \quad \text{(B2)}$$

The relation between the coefficient $(L_i)_j$, defined in the component j-fixed frame of reference, and D is derived as follows:

$$-(L_i)_j\frac{\delta\mu_i}{\delta x}=c_i(\bar{v}_i-\bar{v}_j)=\frac{c_i}{\phi_j}\,[(1-\phi_i)\bar{v}_i-\tilde{J}_j^{\phi}]$$

$$=\frac{c_i}{\phi_j}\,[(1-\phi_i)\bar{v}_i+\tilde{J}_i^{\phi}]=\frac{c_i\bar{v}_i}{\phi_j}=-\frac{\tilde{L}_i}{\phi_j}\frac{\delta\mu_i}{\delta x} \qquad \text{(B3)}$$

From eqns. (B2) and (B3) it follows that

$$(L_i)_j=D\Big/\left(\phi_j\frac{\delta\mu_i}{\delta c_i}\right) \qquad \text{(B4)}$$

Appendix C

The relation between the binary coefficient $(\mathrm{L}_2)_3$ *and the sedimentation coefficient* s_3

s_3 is related to a phenomenological coefficient Q, defined below [21]:

$$s_3=Q\frac{\rho\bar{V}_2}{c_3}\,(1+c_3/c_2)(1-\rho\bar{V}_3) \qquad \text{(C1)}$$

where $s_3=\bar{v}_3/g$, with $\bar{v}_3$ the average velocity of component 3 relative to the cell-fixed frame of reference, and g the centrifugal field strength; $\rho=c_2+c_3$, the solution density.

In the absence of a centrifugal field Q is defined as follows [21]:

$$\overset{*}{J}{}_3^{c}=-Q(1+c_3/c_2)\,\frac{\delta\mu_3}{\delta x} \qquad \text{(C2)}$$

where $\overset{*}{J}{}_3^{c}$ is the mass flux of component 3 relative to the mass-fixed frame of reference.

Conversion of Q from the mass-fixed frame of reference to the polymer-fixed frame of reference yields the following relation between Q and $(L_2)_3$:

$$(L_2)_3=\frac{\rho c_2(1-c_3/c_2)}{c_3^2}Q$$

When we substitute this relation in expression (C1) we obtain

$$(L_2)_3=\frac{1}{\bar{V}_2(\rho\bar{V}_2-1)}s_3(\phi_3) \qquad \text{(C3)}$$