Diffusion of solvent from a cast cellulose acetate solution during the formation of skinned membranes

F. W. Altena, J. Smid, J. W. A. Van den Berg, J. G. Wijmans and C. A. Smolders

Twente University of Technology, PO Box 217, 7500 AE Enschede, The Netherlands
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The transport of solvent out of a cast cellulose acetate (CA) solution into the coagulation bath during membrane formation is treated as a diffusion process. From the increase of solvent concentration in the bath with time (solvent leaching experiments) an overall solvent diffusion coefficient has been calculated. In size these coefficients compare well to mutual pseudo-binary solvent–non-solvent diffusion coefficients determined by means of a classical boundary broadening method applied to ternary solutions with fixed CA concentration, but with a gradient in solvent–nonsolvent composition. Since binary polymer–solvent interdiffusion coefficients are at least one order of magnitude lower, it is concluded that the diffusion of solvent into the coagulation bath is essentially a pseudo-binary solvent–non-solvent diffusion process. Combination of experimental results with model calculations for the effect of a thin dense skin on the diffusion of solvent out of the sublayer shows that the casting–leaching diffusion coefficient can be used to describe the out-diffusion of solvent from the layer under the skin provided that the relative skin resistance is not too high, or that the skin thickness is small.

(Keywords: cellulose acetate; diffusion coefficient; asymmetric membranes; reverse osmosis; casting–leaching technique)

INTRODUCTION

Several theories concerning the formation of skinned ('phase inversion') membranes from casting solutions immersed in a coagulation bath have been proposed during the last ten years[1-7]. In these theories an important role is played by the diffusion of non-solvent into, and solvent out of, the casting solution. Strathmann and Kock[1] and Smolders[2] explicitly state that the 'skin' will act as a barrier to these diffusion processes. These authors tacitly define a skin as a layer where, during the formation of the membrane, the diffusion coefficients are (< 100 times) lower than in the bulk of the casting solution. Cohen et al.[3] and Ataka et al.[4] both developed a diffusion model where the diffusion coefficient is assumed to be a function of polymer concentration. In this way they also account for an increased relative resistance in the skin to flow of solvent and/or non-solvent.

The object of the present study is twofold. Firstly to determine the nature of the diffusion coefficient(s) that can be used to describe the solvent outdiffusion process; are they equal to self-diffusion coefficients[6] of solvent in the polymer solution, or to mutual diffusion coefficients of the binary solvent–non-solvent system, for instance? Secondly, to investigate whether it is necessary to assume at least two diffusion coefficients for the description of the outdiffusion process; one for the skin region, and one for the solution layer under the skin, as the literature cited suggests.

The diffusion coefficients were calculated from measurements of the increase in solvent concentration in the coagulation bath as a function of time according to a formula given by Crank[8]. This procedure essentially leads to a constant mutual diffusion coefficient, independent of

concentration of the diffusing component. Frommer and coworkers[5,9] were the first to report such measurements and called the experiments 'casting–leaching experiments'[9]. However, they did not calculate diffusion coefficients.

We expect that these casting–leaching diffusion coefficients (D_f) are not equal to the self-diffusion coefficients for the binary system polymer–solvent (see ref. 6, *Figure 2*) but rather to the mutual diffusion coefficients characteristic of the ternary system polymer–solvent–non-solvent. In order to verify this hypothesis a comparison is needed between the casting–leaching diffusion coefficients and the mutual (or inter-) diffusion coefficients of the binary and the ternary systems in question. Such interdiffusion coefficients can be determined[10,11], e.g. by following the broadening of a boundary layer as a function of time in a free diffusion experiment, the boundary being formed between two mixtures of slightly different composition.

No such measurements of inter-diffusion coefficients for the ternary systems under investigation, i.e. cellulose acetate (CA)–acetone–water and CA–dioxan–water, have been reported in the literature. We therefore performed boundary broadening measurements with these systems using an analytical ultracentrifuge.

In order to meet the second goal of our study, we set up model calculations for the influence of a skin on the out-diffusion of solvent. As an approximation we calculated the flux of solvent from a solution into a coagulation bath for a two-layer model. In the bottom layer, representing the region under the skin of the membrane being formed, the diffusion process was assumed to be governed by a constant solvent–nonsolvent interdiffusion coefficient D_{fs}. For the other layer, representing the skin having a
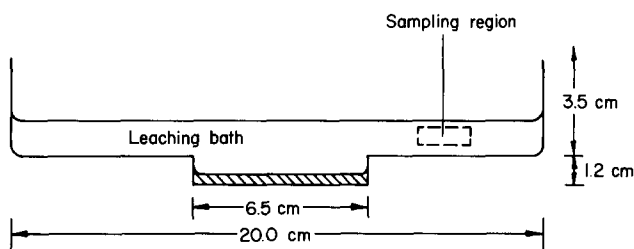
Figure 1 Casting leaching method. The outdiffusion of dioxane or acetone from the cellulose acetate casting solution is followed by drawing and analysing samples from the leaching bath

thickness l_{sk}, a much lower diffusion coefficient D_{sk} was assumed, also constant, i.e. independent of time and polymer concentration. The justification of this crude model for the formation of an asymmetric membrane is discussed below.

DETERMINATION OF DIFFUSION COEFFICIENTS

We do not expect the casting–leaching coefficients (D_f) to be equal to binary diffusion coefficients, but rather resemble mutual diffusion coefficients characteristic of diffusion in the ternary system polymer–solvent–non-solvent, since not only solvent diffuses out of but also non-solvent diffuses into the cast film. This hypothesis was verified by comparison of the casting–leaching diffusion coefficients with mutual diffusion coefficients of binary and ternary systems determined by the boundary layer broadening method.

Casting–leaching method

The casting solution is assumed to be a plane sheet of finite thickness l and volume V_f with solvent distributed uniformly through the sheet at time $t=0$. The initial concentration of solvent in the film is denoted as C_0. The film is immersed in a non-solvent bath with volume V_b $(V_b \gg V_f)$ and it is assumed that the amount of non-solvent in the bath is constant with time, while the amount of solvent in the bath may change considerably with time.

These assumptions make our problem identical to the one described by Crank (ref. 8, pp. 56–60): the outflux of a substance from a thin sheet in which it was dissolved, into a surrounding liquid in which it is soluble. This model may seem to be unrealistic for a skinned membrane being formed but it will appear (in the Materials and Methods section) that a more realistic two-layer model does not allow consistent calculations and that the model presented here approximates fairly well the two-layer model under our experimental conditions.

Crank showed that:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp(-D_f q_n^2 t/l^2) \qquad (1)$$

where:

M_t is the amount (in grams) of outdiffusing substance measured in the bath at time t

$M_\infty \equiv \lim_{t \to \infty} M_t$

$\alpha \equiv V_b/(K \cdot V_f)$
with K the partition coefficient of the outdiffusing species, its concentration (at equilibrium) in the film being K times that in the bath

D_f is the diffusion coefficient of the outdiffusing substance in the material of which the film is composed

q_n is the n-th non-zero positive root of the equation
$\tan q_n = -\alpha q_n$.

Equation (1) contains the variables M_t and M_∞ as their ratio only.

Replacing M_t and M_∞ by the concentrations (in grams of solvent per gram of non-solvent) C_t and C_∞, respectively, of the outdiffusing substance in the bath it follows, using the law of mass conservation that

$$C_\infty = \frac{M_\infty}{W_b} = \frac{C_0}{K + W_b/W_f} \qquad (2)$$

W_b and W_f are the total weights of the bath and the film, respectively.

One can calculate D_f using a curve fitting procedure to equation (1), with C_t being the dependent variable and t the independent one.

If there were no indiffusion of non-solvent, and only a small amount of solvent diffusing out, our system would be completely identical to the one described by Crank and D_f would equal the mutual diffusion coefficient of the binary polymer–solvent system at polymer concentration C_0. During the actual leaching experiment, however, two phenomena occur that may affect the value and even the physical meaning of D_f:

(i) the polymer concentration in the film (especially in the top-layer just below the interface) increases with time as the film shrinks due to the outdiffusion of solvent. The inflow of nonsolvent is smaller in magnitude than the outdiffusion of solvent[5].

(ii) non-solvent penetrates into the film.

Because of the increase in polymer concentration and because of the non-solvent penetration during membrane formation, the calculated quantity D_f has the nature of a solvent–non-solvent interdiffusion coefficient as measured in a ternary system (solvent–non-solvent–polymer) with a polymer concentration higher than that originally present in the sheet.

If we knew the polymer concentration in the membrane as a function of time and depth (within the casting solution), we would be able to calculate a more realistic
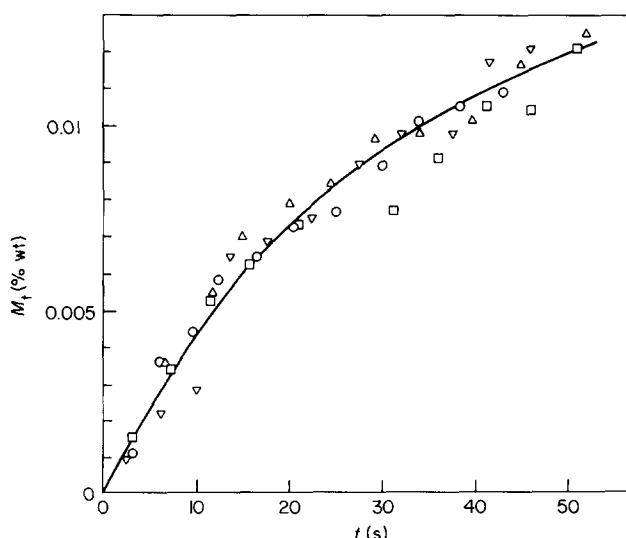

Figure 2 Typical example of 4 casting leaching experiments on a 17% cellulose acetate solution in dioxan at ambient temperature. Diffusion coefficients D_f calculated from equation (1): 1.83×10^{-6} cm^2 s^{-1} (O); 1.80×10^{-6} ($\square$); 2.16×10^{-6} ($\triangle$) and 2.00×10^{-6} ($\triangledown$). Averaged value $(1.9 \pm 0.2) \times 10^{-6}$ cm^2 s^{-1} appears in *Figure 3* and *Table 1*

concentration-dependent diffusion coefficient from a modification of equation (1) (see ref. 8, p. 239–244). For our present purpose we do not need such a detailed picture and assume the polymer concentration to be constant (and therefore D_f to be constant) within the whole casting solution. In this way we will see whether there is any relation between this averaged overall-quantity D_f, and the interdiffusion coefficients calculated from free diffusion experiments, as described in the next section.

Boundary layer broadening method

Two binary solutions differing slightly in polymer–solvent ratio (in the absence of polymer, in solvent–non-solvent ratio), or two ternary solutions having the same amount of polymer but differing slightly in solvent–non-solvent ratio, are brought in contact in the centre of an 'infinite cell'. From the broadening of the interfacial boundary as a function of time we calculate a mutual diffusion coefficient, denoted[11] by D_A and called 'the reduced height-area ratio'[10], from,

$$D_A = \frac{1}{4Y^2} \frac{\Delta r^2}{t} \qquad (3)$$

where Y is a constant from probability tables, t is the time elapsed since the creation of the boundary and Δr^2 is the squared actual distance between two previously chosen concentration levels at time t (for further details see the Materials and Methods section). In our case these levels are determined with a Rayleigh interference optical system. The use of equation (3) implies the assumption that the boundary shape is Gaussian.

An analogous method (using the so-called Gouy interferometer) has been described in detail by Cussler[10] and by Cussler and Lightfoot[11] for the ternary system polystyrene/toluene/cyclohexane. The latter performed their measurements such that they were able to split up the ternary (or rather: pseudo-binary[11]) D_A into its 4 components D_{11}, D 1985, Vol 52, No. 3, $_{12}$, D_{21} and D_{22}. Sundelöf[12] has given an expression that connects D_A to these 4 coefficients in such a way that we can envisage their significance more easily:

$$D_A \simeq D_{11}\left(1 - \frac{D_{12}D_{21}}{D_{11}D_{22}}\right) \qquad (4)$$

Thus, in our case D_{11} approaches in magnitude the value of the limiting diffusion coefficient of the solvent in a solvent/non-solvent/polymer system for vanishing polymer concentration whereas D_{22} approaches the limiting diffusion coefficient of the same system for vanishing non-solvent concentration. The main diffusion coefficients D_{11} and D_{22} as well as the cross-diffusion coefficients D_{12} and D_{21} coefficients appear in the generalized form of Fick's law[10]. They all depend on polymer concentration and on solvent–non-solvent ratio.

The order of magnitude of binary polymer–solvent diffusion coefficients is one hundredth of that of diffusion coefficients of low molecular weight compounds in binary mixtures[10]. Thus, D_{22} is about one hundredth of D_{11}. Moreover, it has been found[11,12] that D_{12} and D_{21} have the same order of magnitude as D_{22} (though not the same sign). Hence, it is mainly D_{11} that is responsible for the variation of D_A with composition (solvent–non-solvent ratio) and $D_A \simeq D_{11}$. We expect the D_A obtained from our pseudo-binary free diffusion experiments to be close to the

solvent diffusion coefficients obtained from binary solvent–non-solvent diffusion experiments.

MATERIALS AND METHODS

Materials

Cellulose acetate (Eastman, catalogue number 4644), with acetyl content of 39.8% and molecular weights, determined by gel permeation chromatography, osmometry and light scattering as described earlier[13], $M_n = 24\,000$, $M_w = 55\,000$ and $M_z = 118\,000$. 1,4-Dioxan and acetone were Baker Analyzed Reagent grades. Polymer and solvents were used as received, without further purification. Demineralized, ultrafiltered water was used throughout. Concentrations are given as % by weight.

Casting–leaching experiments

These experiments were carried out in a simple device (*Figure 1*), under non-controlled laboratory conditions (temperature 19°–23°C, relative humidity 50–70%).

The dry weight of this device was known with an accuracy of 0.01 g. The upper (leaching bath) part was made of glass, the lower part of stainless steel. After filling, the lower part, with a known amount of CA-solution (~ 20 g), was closed with a well ground lid that prevented penetration of water when a known amount of water was poured into the upper part (~ 300 g). Some tissue was fixed to the inner side of the lid and with a CA–acetone casting solution this tissue was saturated with acetone in order to decrease evaporation of acetone from the casting solution.

The whole assembly was agitated horizontally in one direction with adjustable frequency. At $t = 0$, the agitation was started and the lid removed. The polymer solution was thick enough (5 mm) and viscous enough to prevent loosening of the casting solution during the demixing ('phase inversion') process.

Dioxan or acetone concentrations in the upper part were determined by taking samples at predetermined times with a gas chromatographic syringe from the region indicated in *Figure 1*. In all cases samples were taken in the time interval $4 \leqslant t \leqslant 60$ s and injected directly into the gas chromatograph (columns filled with Carbopack C; detection method: flame ionization).

The concentration range for the CA–dioxan solutions was 13–25% and that for the CA–acetone solutions was 24–36%. The lower and higher concentration limits are set by the viscosity of the solution. At lower concentrations the surface of the film is damaged by the agitation in the bath. At higher concentrations the casting of the film is almost impossible.

Boundary layer broadening experiments

The instrument for creation of an interfacial boundary layer between two solutions of different composition and for following optically the broadening of this boundary layer was a Beckman–Spinco Model E analytical ultracentrifuge. An advantage of this instrument is that microgel particles (always present in solutions of commercial CA, according to Kamide et al.[14]) cannot disturb the measurement. The centrifugal field applied during the speeding up period of the rotor is high enough (see below) to remove microgel particles from the solution before the boundary layer is formed.

The synthetic boundary cell assembly (i.e. a 12 mm double sector cell equipped with interference window

holders, quartz windows and a capillary synthetic boundary centerpiece) was used, and the appropriate procedures for operation of the ultracentrifuge and for measurements and calculations (as recommended by Chervenka[15] and applied recently by other workers[16]) were followed throughout. The temperature of the rotor during the experiments was maintained at 25.0°C.

For viscous CA-solutions the rotor was speeded up to 15 000 r.p.m. instead of the more usual 3000–6000 r.p.m.[15,16], in order to be able to create a boundary. After the boundary was formed the rotor speed was slowed to 4000 r.p.m., at which speed the broadening of the boundary was monitored by taking photographs of the interferometric pattern. For acetone–water and dioxan–water mixtures, photographs had to be taken very quickly after each other, and the ultracentrifuge automatic photographing device could not be used.

The solution with the highest overall density always occupied the 'lower' compartment. Thus, in a typical binary experiment, the lower compartment contained a solution of 4% CA and 96% of acetone, while the upper one contained a solution of 3% CA and 97% acetone. In a typical ternary experiment, there was a solution of 5% CA in a mixture of 94% acetone and 6% of water in the lower compartment, and in a mixture of 95% acetone and 5% water in the upper one.

Thus, the concentration difference for the diffusing species was 1%, in all cases. Hence, the diffusion coefficients reported in the tables and the graphs are to be considered as the diffusion coefficients belonging to a 1% difference in concentration for the diffusing species. For these experiments too there is an upper limit to the CA concentrations. Higher concentrations gave solutions with viscosities that were too high for the experiment to be practicable: it was impossible to drive these solutions through the centerpiece's capillary in order to create the boundary. Unfortunately, the highest concentration was lower than the lowest concentration possible for the casting–leaching experiments.

Calculation procedures

D_f is obtained from the leaching bath experiments by a curve fitting method to equation (1) using program E04GAA of the NAG-library[17], with M_t the dependent variable and t the independent one. Additional input for the computer program consists of l, M_∞ and α. The l value is calculated from the dimensions of the solution compartment of the vessel shown in *Figure 1* and from weight and density of the CA-solution. The value of α was calculated from V_b and V_f, with $K = 1$. M_∞ was computed from the mass conservation equation (2). The partition coefficient K in the equations (1) and (2) has been fixed at 1, as trials with other values for K (in the range $0.02 \leqslant K \leqslant 20$) did not change the calculated value of D_f by more than 5%.

An important point to note is that the number of terms (n) in equation (1) had to be 50 or more in order to obtain a constant value of D_f, and even 80 or more for small values of D_f. The computer program needs an initial guess to start the fitting procedure. The result is insensitive to variations in the initial value within two orders of magnitude. As a guide, the D_A values determined with the ultracentrifuge were used.

Using equation (5) (see section on model calculations of the effect of a skin on solvent outdiffusion) instead of equation (1), no consistent results could be obtained by a

curve fitting procedure. The m_t versus t curves appeared to be unsuited to yield reliable values for D_{sk}, D_{fs} and l_{sk}: the results depended heavily upon the initial guesses. Hence, we used the computer program only for model calculations on the influence of a skin on m_t, or C_t, using 80 terms or more in the series expansion of equation (5).

RESULTS AND DISCUSSION

Casting–leaching diffusion coefficients

Casting–leaching curves (C_t as a function of t) were determined in at least threefold replication for the same CA-solution. A typical example is given in *Figure 2*. Our curve differs in two respects from the one reported by Rosenthal et al. (ref. 9, *Figure 5*) which was obtained in a similar experiment. Firstly, we did not reach M_∞ within the time of the leaching experiment (limited to 1 min for reasons of efficiency). Rosenthal et al.[9] used films with a total thickness of about 100 μm and reached equilibrium after only 2–3 min. Using films of ∼5 mm thickness, equilibrium was reached after ∼24 h. Secondly, the curve shown by Rosenthal et al.[9] is almost horizontal for $t \leqslant 6$ s, followed by an upward jump at $t \simeq 6$, while in our case there is no indication for such a phenomenon.

Each of the series of points obtained for one leaching experiment was subjected to the curve fitting procedure, described above. The average results for various CA concentrations are given in *Table 1*.

Boundary layer broadening diffusion coefficients

The results of the ultracentrifuge determinations are presented in *Figures 3* and *4* (open circles and squares). For comparison, some values for binary coefficients derived from the literature[18-20] are shown. For CA fractions with mean molecular weights comparable to those of our CA sample, Holmes and Smith[18] find diffusion coefficients D_0 extrapolated to zero polymer concentration in the range of 8.2 to 17.5×10^{-7} cm^2 s^{-1} as compared to our results, in the range of 9 to 12×10^{-7} cm^2 s^{-1} (*Figure 4*). Singer[19] reports D_0 to be 7.7×10^{-7} cm^2 s^{-1} for a CA with $M_n = 55\,000$.

These authors[18,19] did not obtain D_0 from a plot of D_A against concentration, but from sedimentation coefficients and second virial coefficients according to a formula checked experimentally by Singer[19]. Holmes and Smith have reported a decrease of D_A with increasing concentration at CA concentrations below 2%, followed by an upturn at about 2% CA. Hence, we did not attempt to extrapolate our D_A values to zero concentration.

Table 1 Casting–leaching experiments: diffusion coefficients D_f calculated from equation (1). Measurements: see *Figures 1* and *2*

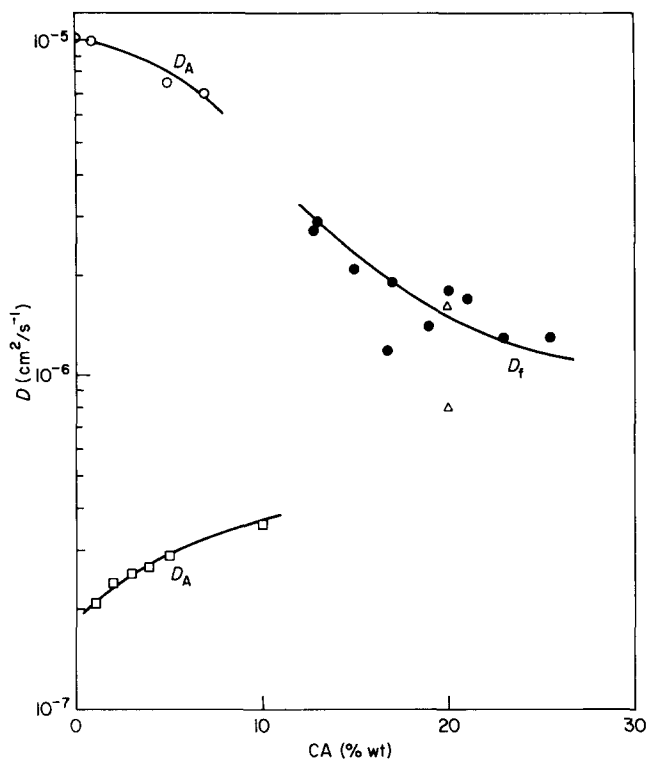| CA–dioxan casting solution		CA–acetone casting solution	
% CA	$D_f \times 10^6$ (cm^2 s^{-1})	% CA	$D_f \times 10^6$ (cm^2 s^{-1})
12.8	2.7 ± 0.3	24.0	7.2 ± 0.5
13.0	2.9 ± 0.1	26.0	6.0 ± 0.3
15.0	2.1 ± 0.2	28.1	5.1 ± 1.0
16.8	1.2 ± 0.1	30.2	4.2 ± 0.4
17.0	1.9 ± 0.2	31.6	4.1 ± 0.1
18.0	1.4 ± 0.2	32.1	3.6 ± 0.3
20.0	1.8 ± 0.2	33.9	3.3 ± 0.3
21.1	1.7 ± 0.4	36.1	3.0 ± 0.2
23.0	1.3 ± 0.2		
25.5	1.3 ± 0.2		

Figure 3 Diffusion coefficients D_f calculated according to equation (1) from casting–leaching experiments (●), compared with binary (□) and pseudo-binary (○) (for dioxan containing 5% water) diffusion coefficients D_A calculated from boundary spreading experiments (equation (2)). (△) represent D_f values calculated from literature data[8]. System: cellulose acetate–dioxan (–water). Temperature ~20°C

Another point of uncertainty is the acetyl content of the CA-samples in question which may differ.

We have found for 15% water in acetone (mole fraction of acetone is 0.64) a diffusion coefficient at 25.0°C of 1.35×10^{-5} cm^2 s^{-1} (*Figure 4*). Anderson *et al.*[20] report for a mole fraction of acetone of 0.6653 in an acetone–water mixture a value of 1.42×10^{-5} cm^2 s^{-1} for the diffusion coefficient at 25.15°C.

Cussler and Lightfoot[10] report for their system (poly-styrene–toluene–cyclohexane) the same trends for D_A as those presented in *Figures 3* and *4*. Their D_A values, for solvent as the main diffusion species, also decrease with increasing polymer concentration, and (for constant polymer concentration) with increasing amount of non-solvent (we performed such a series of measurements only for the system CA–acetone–water).

Casting–leaching results and ultracentrifuge results combined

The data are combined for comparison in *Figures 3* and *4*. In *Figure 3* also appear two D_f values at 20% CA calculated by means of our curve fitting procedure from the $M_t - t$ curve of Rosenthal *et al.*[9]. These D_f values are in the same range as ours, in spite of the difference in temperature of their measurements (1°C) and ours (19°–23°C), and in spite of our rough estimation of α from the dimensions found in their *Figure 1*, which represents the experimental device. The lowest of the two D_f values calculated from the data of Rosenthal *et al.* was based on a film thickness of 100 μm (α=450); the highest one was based on a film thickness of 150 μm (α=300). The scattering of our experimental D_f values in *Figure 3* (and

Figure 4) (closed points) stems from the scattering in the casting–leaching curves themselves (like *Figure 1*).

The main conclusion drawn from *Figure 3* is that the curve through the casting–leaching diffusion coefficients D_f when extrapolated to lower polymer concentrations almost coincides with the curve through the pseudo-binary solvent–non-solvent diffusion coefficients D_A. Unfortunately, for experimental reasons, as explained in the experimental section, there is a 'gap' between the D_A curve and the D_f curve so that one cannot be sure that the D_f curve links up with the D_A curve (and *vice versa*), within experimental error. A similar, and likewise restricted, conclusion can be drawn from *Figure 4*: the D_A curve for the 5% water mixture (or even a D_A curve for a smaller water content) appears to be continued by the D_f curve.

Keeping in mind that there is a gap between the D_f and the D_A curves, we conclude from *Figures 3* and *4* that the casting–leaching diffusion coefficients are just the pseudo-binary solvent–non-solvent interdiffusion coefficients.

Support for this conclusion comes from comparison of casting–leaching diffusion coefficients for the CA–acetone case with self-diffusion coefficients of acetone in CA given by Anderson and Ullman[6]. The reported values of the self-diffusion coefficients are about one order of magnitude higher than the casting–leaching coefficients given in this paper. Hence the diffusion of solvent out of the cast film into the coagulation bath cannot be described as self-diffusion of solvent in a binary polymer–solvent system.

Unfortunately, neither our casting–leaching experiments nor those of Frommer[5,9], enable us to conclude anything definite about the diffusion process during and directly after the formation of the skin which itself is formed within a period of microseconds after exposure of the casting solution to the non-solvent bath. The uncertainty in the location of $t = 0$ for these experiments prevents any conclusion from being made. In fact, we think
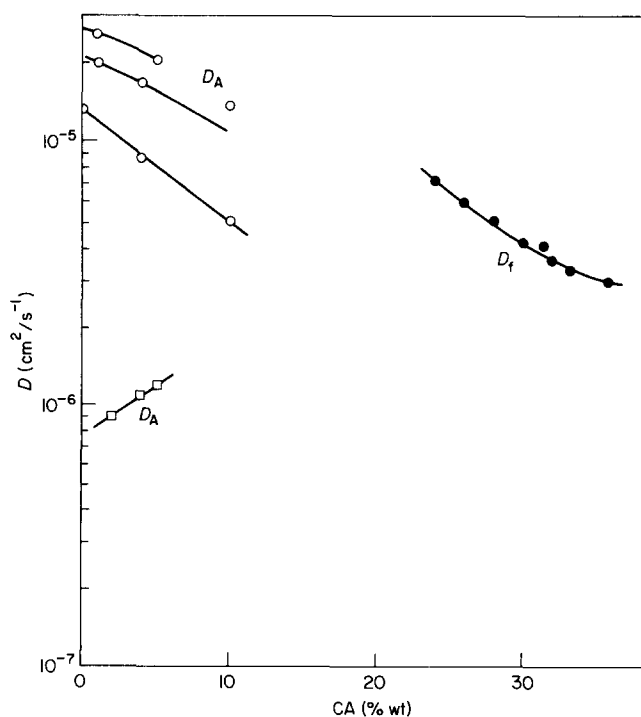

Figure 4 Same legends as *Figure 3*. System: cellulose acetate–acetone (–water). Upper pseudo-binary D_A curve: 5% water, middle curve: 10% water, lower curve: 15% water

that the almost horizontal part in the leaching curve of Rosenthal *et al.*[9] (i.e. their *Figure 5*) is an artifact: an upward bend in the leaching curve implies a temporary increase in the solvent outdiffusion, which we consider improbable.

Finally, we observe, that in *Figure 3* (CA in dioxan) the D_f curve seems to continue a D_A curve for 5% water, whereas in *Figure 4* (CA in acetone) the D_f curve seems to continue a D_A curve for less than 5% water. This could mean that water penetrates more slowly into the forming membrane in the CA–acetone case than in the CA–dioxan case. This conclusion is in agreement with the experimental data provided by Frommer[5] on the rate of penetration of the coagulation front in CA casting solutions. The smaller penetration of water in the case of a CA–acetone casting solution compared with a CA–dioxan casting solution could be in line with the more dense structure displayed by the membranes obtained from the former system[5].

Model calculations for the effect of a skin on solvent diffusion

A simple model of a skinned membrane is used to study the effect of a skin on the outdiffusion of solvent. Combination of results of model calculations and experimental data obtained with the casting–leaching technique may lead to an understanding, at least in a qualitative sense, of a possible barrier effect on the diffusion process during asymmetric membrane formation. Moreover, the model calculations help to assess the validity of the conclusions on the nature of the casting–leaching diffusion coefficients drawn in the previous part.

Considering the model of Crank (ref. 8, p. 38): a semi-infinite layer (representing the casting solution) is separated by a thin sheet of thickness l_{sk} (representing the skin) from another semi-infinite layer (the leaching bath). The initial concentration of solvent in the skin and in the casting solution is denoted by C_0 and the concentration of solvent in the leaching bath remains effectively zero throughout the diffusion process. We assume that the Crank model is applicable to our system in spite of the indiffusion of non-solvent from the bath through the skin into the casting solution and in spite of the measurable (but small) increase in solute concentration in the leaching bath. Furthermore, we assume that the skin and the casting solution under the skin remain constant in thickness and in composition.

This model seems to differ greatly from the one layer model for the calculation of D_f, described above: here we assume the casting layer to have semi-infinite thickness, whereas for the one-layer model we assumed a finite thickness (its value l even appears in equation (1)). There is no discrepancy, however, between these assumptions when the leaching times assumed in the model calculations are such that the coagulation front has proceeded over a distance smaller than l. We revert to this point shortly in the results section.

Though Crank describes only an indiffusion problem we can use his final equation for our outdiffusion problem, *viz.* :

$$\frac{m_t}{l_{sk}C_0} = 2\left(\frac{D_{sk}t}{\pi l_{sk}^2}\right)^{1/2}\left\{1 + 2\sum_{n=1}^{\infty}\beta^n \exp(-n^2 l_{sk}^2/(D_{sk}t))\right\}$$

$$-4\sum_{n=1}^{\infty} n\beta^n \operatorname{erfc}(nl_{sk}/\sqrt{D_{sk}t}) \qquad (5)$$

where:

m_t is the total amount of solvent, per unit area of skin, that has entered the leaching bath at time t

$\beta \equiv (1-k)/(1+k)$ with $k \equiv \sqrt{D_{sk}/D_{fs}}$

D_{sk} is the diffusion coefficient of the outdiffusing substance in the material of which the skin is composed

D_{fs} is the diffusion coefficient of the outdiffusing substance in the material of which the casting solution under the skin is composed.

Equation (5) is used to evaluate the influence of l_{sk}, D_{sk} and D_{fs} on m_t. As there are no data available as to which value of l_{sk} would correspond to known values of the polymer concentration (corresponding, in turn, to a certain D_{sk}), we have varied in the model calculations the ratio D_{fs}/D_{sk} at constant l_{sk}, and *vice versa*. D_{fs}, D_{sk}, l_{sk}, C_0 and t were chosen in accordance with experimental data and experimental circumstances. The ratio D_{fs}/D_{sk} is denoted as 'relative skin resistance'.

The two-layer model is clearly a crude exaggeration of reality since it assumes the diffusion coefficients to be step functions with regard to the distance in the membrane being formed. From what is known about membrane structures, the assumption of continuous functions for the calculations (corresponding to different casting conditions, cf. ref. 1, *Figure 1*) would be much more realistic. For the present purpose we consider such a detailed picture as not relevant.

The model variables for these calculations are D_{fs}/D_{sk} and l_{sk}. We have chosen D_{fs} to be equal to D_f: this enables us to calculate the l_{sk} value or the D_{fs}/D_{sk} value that causes m_t (equation (5)) to deviate appreciably from M_t (equation (1)) belonging to one single diffusion coefficient D_f.

Results of the model calculations

First we calculated from the skin model, equation (5), the concentration C_t of solvent in the bath as a function of t ($5 \leqslant t \leqslant 50$ s, cf. *Figure 2*) for a constant skin thickness of 0.2 μm, but varying relative skin resistances D_{fs}/D_{sk}. For the initial solvent concentration C_0 we took 80%, for D_{fs} a value of 2×10^{-6} cm^2 s^{-1} and for the surface area of the skin and the volume of the leaching bath 40 cm^2 and 300 cm^3, respectively. All these assumed values are typical for our leaching bath experiments. Equation (5) yields values for m_t. These values were converted to C_t values by multiplying by 40/300.

The results are presented in *Table 2*. We see that only when the diffusion coefficient of solvent in the skin is 100 or more times smaller than that in the underlying casting solution does the C_t vs. t curve differ appreciably from that calculated for an unskinned film ($D_{fs}/D_{sk}=1$). Such low values for the diffusion coefficient of solvent in the skin are realistic only when the skin is very dense, i.e. when it consists of a solution of about 90% of CA in acetone. For such a solution the binary diffusion coefficient is about 100 times lower[21] than that of the binary solutions we used for our casting–leaching experiments. Strictly speaking, ref. 21 gives self-diffusion coefficients and not interdiffusion coefficients. At vanishing concentration of diluent in the polymer, these coefficients approach each other[22].

Our second step was to calculate the influence of the skin thickness on the C_t vs. t curves for very dense skins (with $D_{fs}/D_{sk}=100$). Assuming the same values for C_0, D_{fs}, skin surface area and bath volume as above we found (cf.

Table 2 Calculated leaching curves (C_t versus time) as a function of the relative skin resistance D_{fs}/D_{sk} at constant skin thickness $l_{sk}=0.2~\mu$m. Equation (5), with $C_t=(40/300)m_t$ (see text), $D_{fs}=2\times10^{-6}$ cm^2 s^{-1} and $C_0=80.0\%$

t (s)	$D_{fs}/D_{sk}=1$	10	100	1000
5	$C_t=0.038$	0.036	0.023	0.005
10	0.054	0.052	0.038	0.009
15	0.066	0.064	0.049	0.013
20	0.076	0.074	0.059	0.017
25	0.085	0.083	0.067	0.021
30	0.093	0.091	0.075	0.025
35	0.101	0.099	0.082	0.028
40	0.108	0.106	0.089	0.032
45	0.114	0.112	0.096	0.035
50	0.120	0.118	0.102	0.038

Table 3 Calculated leaching curves as a function of skin thickness l_{sk} at constant relative skin resistance (i.e. at constant ratio $D_{fs}/D_{sk}=100$). For further data see *Table 2*

t (s)	$l_{sk}=0.1~\mu$m	0.2 μm	0.3 μm	0.5 μm	1.0 μm
5	$C_t=0.029$	0.023	0.019	0.015	0.009
10	0.045	0.038	0.025	0.016	0.032
15	0.056	0.049	0.043	0.034	0.021
20	0.066	0.059	0.052	0.043	0.029
25	0.075	0.067	0.060	0.050	0.035
30	0.083	0.075	0.068	0.057	0.040
35	0.091	0.082	0.075	0.064	0.046
40	0.098	0.089	0.082	0.070	0.051
45	0.104	0.096	0.088	0.076	0.055
50	0.110	0.102	0.094	0.081	0.060

Table 4 Calculated ratio of the 'no skin diffusion coefficient' (D_f) to the 'true diffusion coefficient' (D_{fs}) under the skin, as a function of skin thickness l_{sk} and relative skin resistance D_{fs}/D_{sk}. For further data see *Table 2*

D_{fs}/D_{sk}	1	10	100	1000
l_{sk} (μm)				
0.1	$D_f/D_{fs}=1.00$	0.98	0.80	0.19
0.2	1.00	0.96	0.65	0.07
0.3	1.00	0.94	0.54	0.03
0.5	1.00	0.91	0.38	—
1.0	1.00	0.82	0.20	—

Table 3) that for skin thicknesses larger than 0.3 μm the C_t vs. t curves differ appreciably from those calculated for a film without a skin (see the column for $D_{fs}/D_{sk}=1$ in *Table 2*). In those cases the skin is expected to influence solvent outdiffusion considerably.

The third step was to determine in which cases the curve fitting procedure according to equation (1) (assuming no skin influence) leads to values of D_f that give a realistic representation of D_{fs}. To this end, from the C_t vs. t data, generated with the aid of equation (5) and displayed in *Tables 2* and *3*, the 'no skin diffusion coefficients' D_f were computed with the help of equation (1). We compared these D_f values to the D_{fs} values for which the C_t vs. t curves were calculated (i.e. $D_{fs}=2\times10^{-6}$ cm^2 s^{-1}). Thus, the ratios D_f/D_{fs} are displayed in *Table 4* as a function of the relative skin resistance D_{fs}/D_{sk} and of the skin thickness (l_{sk}). We see, that the 'no skin diffusion coefficient' D_f differs appreciably from the diffusion coefficient of solvent

in the casting solution under the skin D_{fs} only when this skin is very thick ($>1~\mu$m) or very dense ($D_{fs}/D_{sk}>100$).

The same calculations, leading to *Table 4*, justified the validity of assuming a finite film thickness for the one layer model of equation (1) and a semi-infinite one for the two layer model of equation (5): for $t<300$ s equations (1) and (5) lead to the same C_t-t curves even when D_{fs}/D_{sk} was assumed to be 100.

It follows that, provided this skin is not too thick ($l_{sk}<0.2~\mu$m) nor too dense ($D_{fs}/D_{sk}<100$) the casting–leaching diffusion coefficients calculated from Crank's model (equation (1)) are very well in line with pseudo-binary solvent–non-solvent diffusion coefficients (in the presence of polymer), but not with mutual diffusion coefficients, nor with self-diffusion coefficients, determined for binary solvent–polymer systems.

CONCLUSIONS

The supposedly constant diffusion coefficient D_{fs} of the layer under the skin that describes the outdiffusion of solvent (acetone or dioxan) from a cast film of a CA solution into a waterbath can be approximated by a constant overall diffusion coefficient D_f calculated from the increase in solvent concentration in the coagulation bath as a function of time (leaching time >5 s) using a model by Crank for a *non-skinned* leaching film.

Model calculations of the effect of a thin dense skin on the outdiffusion of solvent show that D_f approximates D_{fs} fairly well provided that the skin is not too thick ($<0.2~\mu$m) or not too dense ($<80\%$ polymer). Under these conditions, the nascent skin does not form an appreciable barrier to solvent outflow at times >5 s.

As a function of polymer concentration, D_f appears to continue a plot of the pseudo-binary diffusion coefficient D_A, which governs the diffusion in a gradient of a solvent and non-solvent concentration at constant polymer concentration.

Hence, it is concluded that the diffusion of solvent from the casting film into the coagulation bath is essentially a pseudo-binary solvent–non-solvent diffusion process and not a binary polymer–solvent diffusion. The outdiffusion process should not be described by polymer–solvent self- or (binary) interdiffusion coefficients.

On the basis of comparison of values for D_s and D_A for CA–acetone and CA–dioxan casting solutions, the indiffusion of non-solvent into the CA–acetone solution is expected to be smaller than that for CA–dioxan solutions, in accordance with observations of other investigators.

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SYMBOL LIST

$\%$ concentration, see Materials and Methods section for definition

α partition coefficient, corrected for the difference in volume between leaching film (V_f) and leaching bath (V_b); see equation (1). (Dimensionless)

β dimensionless parameter that accounts for the difference between D_{sk} and D_{fs} in equation (5). (Dimensionless)

C_0 initial concentration of solvent in the casting solution, in the leaching film model (equation (1)) as well as in the skinned film model (equation (5)). (%)

C_t concentration of solvent in the leaching bath at time t. (%)

C_∞ concentration of solvent in the leaching bath in the limit $t \rightarrow \infty$ (equation (2)). (%)

D_A diffusion coefficient calculated from boundary layer broadening in a free diffusion experiment (equation (3)); for a ternary mixture D_A is a pseudo-binary diffusion coefficient). (cm^2 s^{-1})

D_f diffusion coefficient of solvent in the leaching film (equation (1); leaching film model, no skin). (cm^2 s^{-1})

D_{fs} diffusion coefficient of solvent in the material of which the casting solution, under the skin, is composed (equation (5), skinned film model). (cm^2 s^{-1})

D_{sk} diffusion coefficient of solvent in the material of which the skin is composed (equation (5), skinned film model). (cm^2 s^{-1})

D_{11},   main diffusion coefficients in a ternary mixture
D_{22} appearing in an expression (equation (4)) for the pseudo-binary diffusion coefficient D_A; see text immediately following equation (4). (cm^2 s^{-1})

D_{12},   cross-diffusion coefficients appearing in D_A; cf.
D_{21} D_{11} and D_{22}

k dimensionless parameter that accounts for the difference between D_{sk} and D_{fs} in equation (5). (Dimensionless)

K partition coefficient, appearing in equation (1) through the corrected partition coefficient, α. (Dimensionless)

l thickness of the casting solution (equation (1)). (μm)

l_{sk} thickness of the skin of the membrane being formed from the casting solution (equation (5)). (μm)

m_t total amount of solvent diffused at time t into the leaching bath per unit area of the skin (equation (5)). (g cm^{-2})

M_t total amount of solvent diffused into the leaching bath at time t (equation (1)). (g)

M_∞ amount of solvent diffused into the leaching bath in the limit $t \rightarrow \infty$ (equation (1)). (g)

n number of terms in summations (equations (1) and (5)). (Dimensionless)

q_n angle, appearing in equation (1). (Radians)

Δr^2 boundary broadening parameter (cf. text following equation (3)). (cm^2)

t time. (s)

V_b volume of the leaching bath (equation (1)). (cm^3)

V_f volume of the leaching film (equation (1)). (cm^3)

W_b total weight of leaching bath (equation (2)). (g)

W_f total weight of leaching film (equation (2)). (g)

Y probability constant (equation (3)). (Dimensionless)