Diffusion During the Coagulation Step of Wet-Spinning

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Synopsis

The coagulation of viscous polymer solutions by diffusional interchange with a liquid bath is the key step to fiber formation by wet-spinning. Model experiments were performed on gelled solutions of an acrylic polymer in dimethylacetamide, to determine the mass-transfer rates of solvent and nonsolvent (water) during coagulation, the rate of movement of a boundary associated with coagulation, and the final equilibrium between the coagulated phase and the bath. Each is given as a function of bath composition and temperature. The data are analyzed by means of various diffusion models, one of them giving quite good agreement. The data and the models are used in conjunction with each other for the elucidation of the mechanism of the processes involved in coagulation.

INTRODUCTION

Fiber formation by wet-spinning accounts for a significant fraction of the production of today's man-made fibers. In this process a very viscous polymer solution is extruded through the small holes of a spinnerette immersed in a liquid bath. A diffusional interchange between the freshly formed fluid filaments and this bath causes the polymer to solidify. This process is called coagulation. During coagulation one or more of the bath components diffuse into the filament, while the solvent diffuses out of it. The polymer precipitates or crystallizes as a consequence of this exchange, because it is rendered insoluble by chemical reaction of the polymer or by an excessive buildup of nonsolvent or by both. In viscose spinning both phenomena can occur.[1,2] The coupled diffusion and chemical reaction can be adequately analyzed by a method given by Hermans.[3] In acrylic fiber formation, as in many other systems, coagulation is brought about by the exchange of solvent and nonsolvent only. This problem of diffusion during coagulation has received some attention in the past, but the mechanism and details of this problem have not been studied enough.

In this work the coagulation of an acrylic fiber system was studied with the intention of defining the mechanism of the processes occurring during fiber formation by wet-spinning. A copolymer of acrylonitrile and vinyl acetate (7.7% VA by weight) was used with dimethylacetamide (DMAc) as solvent for the polymer. The coagulation bath consisted of various mixtures of DMAc and water (a nonsolvent). The actual spinning pro-

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cedure would be very difficult to study with the idea of obtaining funda-
mental information, so only model experiments were used.   They consisted
of coagulating large specimens of the spinning solution in static experiments.
This eliminates the rheological phenomenon associated with extrusion
through the spinnerette holes and the attenuation of the filaments in the
bath.   Further, the diffusion to the filament within the bath liquid[6] can be
eliminated by rapid stirring.   Both of these are important problems, but
they should be eliminated if diffusion within the filament is to be studied
effectively.

All experiments were performed with gelled rods[7] of a 26% solution (by
weight) of the polymer mentioned above in DMAc.   The solutions were
gelled into the form of rods by being poured into test tubes (0.935 by 12
cm.) and then chilling overnight in a Dry ice and acetone bath.[7]   This
gives the specimens to be studied a convenient and fixed geometrical form.
A definite geometry is necessary for mathematical analysis of the diffusion.
The gelation in this way should not appreciably affect the diffusion mecha-
nism or the final equilibrium attained.   The gelation eliminated the void-
formation problem noted earlier.[8,9]   It was necessary to prevent void
formation since this would render the gravimetric techniques employed
useless.   The large size of the samples lengthened the diffusion time scale
to a range convenient for measurement.

It will be worth while to point out briefly the various uses of the word
"gel."   In some cases the coagulated filament leaving the bath is referred
to as a gel; however, this is not the type of material that is meant here.
The term "gel" in this case refers to a very soft, elastic material, very
similar to a gelatin gel.[7]

COAGULATION EQUILIBRIUM

When a spinning solution is brought into contact with a coagulation
bath (a mixture of solvent and nonsolvent), a diffusional interchange
occurs between the two phases.   Solvent leaves, while nonsolvent enters,
the polymer phase.   After a sufficient length of time no more exchange
takes place: hence, a state of equilibrium is achieved between the two
phases.   In view of the nature of the polymer this is probably not a true
thermodynamic equilibrium, and the final state may depend on the path
to a certain extent.   For a given spinning solution, however, the final
state should be adequately described by the composition of the coagulant
and the temperature at which coagulation occurs.

In this section experiments that give information about this equilibrium
are discussed.   All equilibrium measurements were made by immersing
specimens of the gelled solution into relatively large volumes of various
mixtures of DMAc and water for at least 24 hr. while the temperature
was held constant.   The size of the sample was shown to have no effect
on the equilibrium state.   All bath compositions were analyzed by measur-
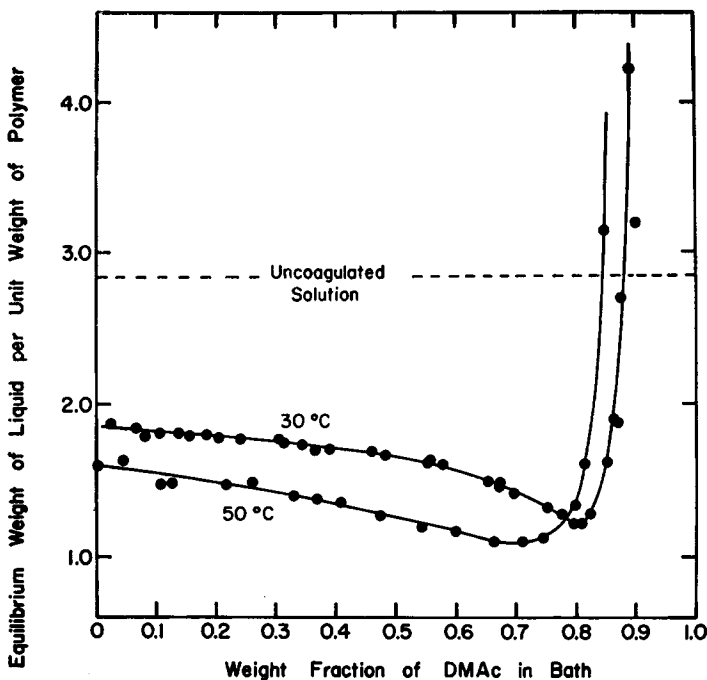ing its refractive index at 30°C.

Fig. 1. Coagulation equilibrium: degree of swelling.

The first experiment was very simple, but it gave quite interesting results. Samples of the gel were weighed before and after equilibration in baths of different concentrations.   From the change in weight and the initial solids level the amount of liquid in the solid phase per unit weight of polymer at equilibrium could be calculated.   This quantity is essentially a degree of swelling.   The results for 30 and 50°C. are shown in Figure 1 as a function of the DMAc content of the bath.   These results show that the degree of swelling after coagulation in a 100% water bath is less than the original degree of swelling (2.85; see dotted line) which indicates the DMAc loss by diffusion is greater than the water gain.   As the DMAc content of the bath increases from zero, the degree of swelling initially decreases slightly, then goes through a minimum, and finally rises very steeply.   The original degree of swelling is surpassed, as the DMAc content of the bath reaches 85 to 90% by weight.   In other words, the gel is actually being swollen by the bath in this region, and just a small increase in DMAc would result in the bath's actually dissolving the polymer (an infinite degree of swelling). This behavior should be expected, since water is a nonsolvent and DMAc is a solvent; hence, some mixture should be on the borderline of being a solvent and a coagulant.   This happens at a lower DMAc level at 50°C. than at 30°C.; this is to be expected, since DMAc becomes a better solvent at higher temperatures.[7]

A second experiment was used for determining the concentration of the liquid contained in the coagulated phase.   This was done by dissolving

known weights of the undried coagulated phase into given amounts of DMAc, to form a solution containing about 2% polymer. The amount of water in this solution was determined by an accurate Karl Fischer titration. From this the composition of the liquid could be computed. The results are shown in Figure 2 as the weight fraction of DMAc (on a polymer-free basis) in the entrapped liquid versus the concentration of the bath. Clearly, this liquid has the same composition as the bath. The result is something of a surprise, since one might expect some kind of preference to be shown by the polymer for one of the components, presumably the solvent. It can be explained, however, by the fact shown by electron
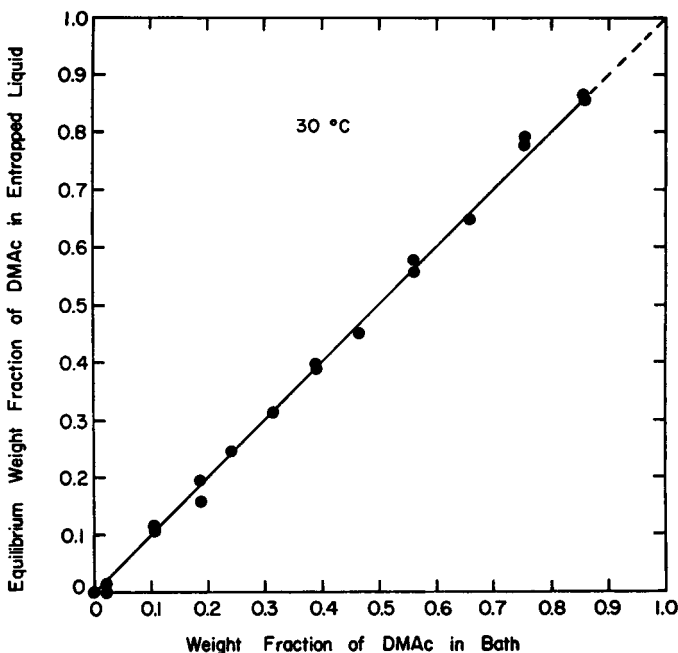

Fig. 2. Coagulation equilibrium: liquid composition.

photomicrographs that the structure of freeze-dried fiber is a porous, fibrillar network.[8,9] Now, if we consider the same network to exist in the undried mass, then it is clear that nearly all of the liquid is merely entrapped inside the small voids or pores (not to be confused with macrovoids), and it is reasonable that this mechanically held liquid should have the same composition as the bath. Perhaps some liquid is associated with the polymer in the fibrils, and this may be of a different composition; however, the amount so absorbed is not sufficient to change the overall composition significantly. This suggests that the polymer is rather inert to the bulk of the entrapped liquid and that the amount of this liquid present is really an indication of the pore volume formed by a given set of coagulation conditions. This is discussed in another section.
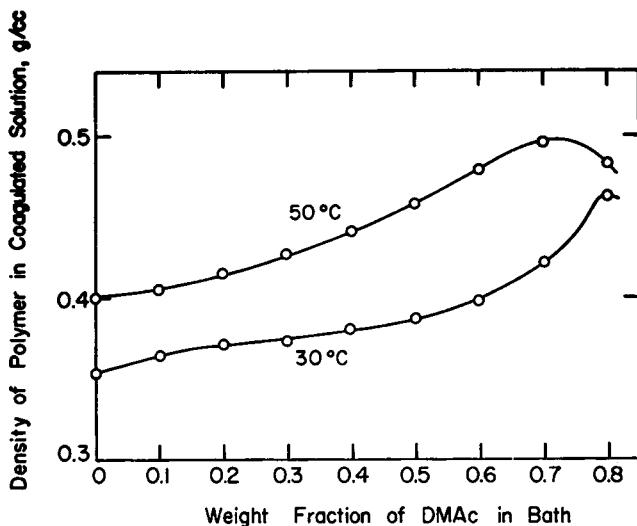
Fig. 3. Equilibrium polymer density.

In a third experiment the total density ρ_∞ of the coagulated phase was measured by a pycnometer liquid-displacement technique. Paraffin oil was the liquid. The densities were measured at 25°C. for samples coagulated at both 30°C. and 50°C. At both temperatures ρ_∞ was independent of bath composition. This density was found to be 1.026 g./cm.[3] at 30°C. and 1.036 g./cm.[3] at 50°C. Calculations involving the bath and polymer densities showed small deviations from volume additivity, suggesting that perhaps there is a small preferential absorption of the liquid by the fibrils.

The data in Figure 1 can be used for calculating the weight fraction of the polymer in the coagulated phase. This weight fraction multiplied by ρ_∞ gives the density of the polymer in this phase, i.e. the weight of polymer per unit volume of liquid plus polymer at a reference temperature of 25°C. As indicated above, this is a morphological parameter giving information about the fibrillar structure of the polymer. It is related to the bulk density of the freeze-dried fiber.[9] Figure 3 shows this density as a function of bath composition for the two temperatures. Fiber morphology is clearly related to coagulation conditions.

DIFFUSION DURING COAGULATION: EXPERIMENTAL

The experiments described in this section give information regarding the diffusion rates associated with coagulation. Such knowledge can be useful both for practical applications and for elucidating the mechanisms of coagulation. Only the latter will be emphasized here. Two devices were employed that circumvented difficulties that have been major barriers to obtaining such data. The first was to use larger specimens than fibers. This extends the time scale and mass-transfer rates into measurable regions.

The second was to use gelled solutions for eliminating the major problem of macrovoid formation. All evidence indicates that the diffusion rates in these lightly gelled solutions are essentially the same as in ungelled ones.

In all the following experiments a 26 wt.-% solution of the polymer in DMAc was used in the form of gelled rods (diameter 0.935 cm., length 9 to 10 cm.) prepared by the method mentioned earlier. The tubes were stored (closed) at room temperature until ready for use. The gel was easily removed from the tube by pulling with tweezers. Care was exercised to prevent moisture from the air or hands from contacting the gel. No evidence was ever seen to suggest that gelation time or age had any effect on the results.

Mass Transfer Rates

During coagulation DMAc (component 1) is removed from the spinning solution (polymer is component 2), while water (component 3) is added. If coagulation is carried out in a bath of limited size, the result will be an increase in DMAc content of the bath and a change in weight of the polymer phase, if species 1 and 3 do not diffuse at equal and opposite rates. This change in weight happens to be a decrease for this system in the regions of interest, as has already been shown. By following the composition of the bath and the weight of the polymer phase one can determine the amounts of 1 removed and 3 added at any given time. These amounts are given by the following material balances:

$$M_{1t}/M_0 = (W_0/M_0)(w_{1t} - w_{10}) + (1 - M_t/M_0)w_{1t} \tag{1}$$
$$M_{3t}/M_0 = (W_0/M_0)(w_{1t} - w_{10}) - (1 - M_t/M_0)(1 - w_{1t}) \tag{2}$$

where the symbols have the following meanings:

M_{1t} = weight of DMA removed by time t
M_{3t} = weight of H$_2$O added by time t
M_0 = initial weight of gel
M_t = weight of gel phase at time t
W_0 = initial weight of coagulation bath
w_{10} = initial weight fraction of DMAc in bath
w_{1t} = weight fraction of DMAc in bath at time t

The bath composition w_1 was obtained by measuring the refractive index of the bath, and the weight changes were followed simply by weighing different samples that had been in separate baths for various lengths of time. The ratio of bath to sample weight, W_0/M_0, was normally set at about 10, since this gave measurable responses without the bath's undergoing a significant composition change. The gel and the bath were brought to the same temperature before the experiment was started. The process was started by immersing the gel in the bath. Adequate mixing was provided by magnetic stirrers. The temperature was held constant by jacketing the bath by another bath at a controlled temperature. The measurements were, then, the refractive index of the bath and the percent

weight loss of the rod as a function of time for each set of coagulation conditions. Each of these gave a plot that is initially linear in the square root of time, as shown by the example in Figure 4. The relation of refractive index versus concentration for DMAc and water can be accurately approximated by two straight lines, whose slopes are 0.00131 (refractive index units per percent DMAc) for mixtures less than 57% DMAc and 0.001125 for those more than 52% but less than 68% DmAc. Because of these large slopes one can accurately follow small changes in bath concentration.

From the data in Figure 4 one has the w_{1t} and M_t/M_0 information needed for eqs. (1) and (2). Evaluation of M_{1t}/M_0 and M_{3t}/M_0 as a function of time showed that both were proportional to $t^{1/2}$ during the early stages of
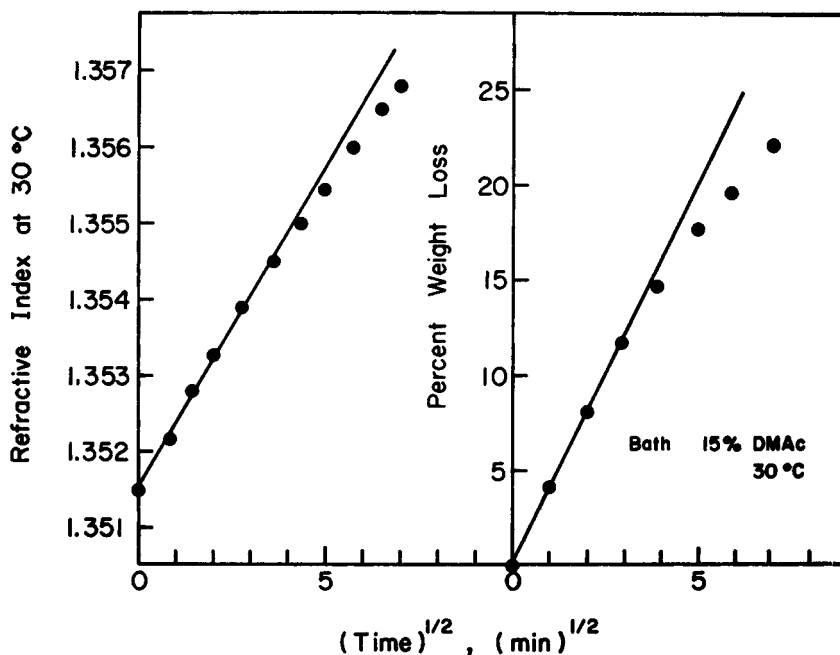

Fig. 4. Typical experimental data.

diffusion for all coagulation conditions. That this would be so is obvious from Figure 4. The data are summarized in Figure 5 by plotting the slope of this initial linear region [i.e., $(M_{2t}/M_o) t^{-1/2}$] for each species at two temperatures against the concentration of the coagulation bath. The data show increased transfer rates at higher temperatures, as one would expect; however, the DMAc rate is affected to a much larger degree than the H_2O rate. The rates of transfer for both species decrease as the DMAc content of the bath increases. The large difference in the relative rates of DMAc and H_2O diffusion is very significant. Since the rates of both components 1 and 3 are related to time in the same way during the initial stages, then the ratio of the two rates is a constant so long as this relationship is obeyed.
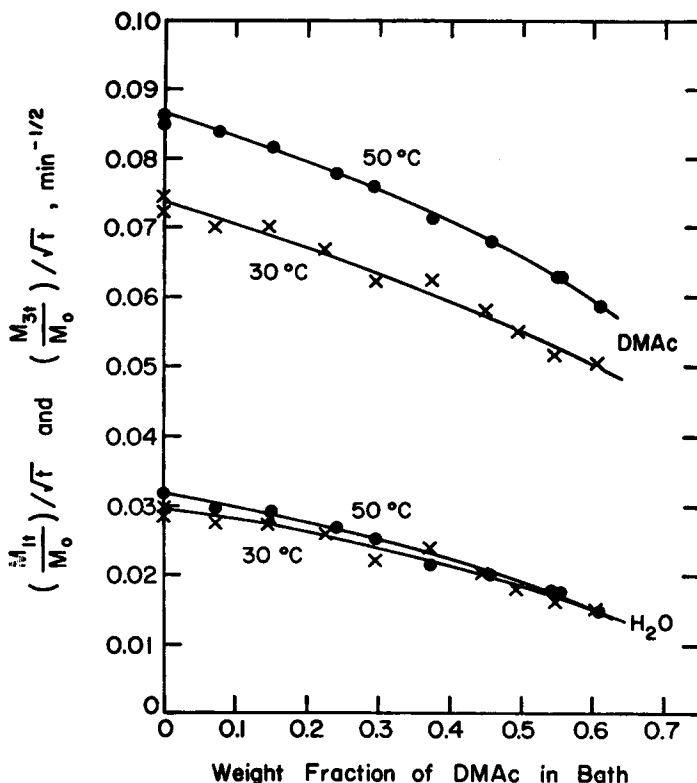
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Fig. 5. Mass transfer rates during coagulation.

Figures 6 and 7 show the ratio of the amount of DMAc transferred to that of H_2O. The ratio for the initial period mentioned earlier is denoted by k'. This was calculated from the data of Figure 5. The final ratio, i.e. at equilibrium, is denoted $M_{1\infty}/M_{3\infty}$ and was calculated from the data in Figures 1 and 2. Both ratios increase as the DMAc content of the bath increases. Under most conditions the final ratio is lower than the initial one. In part this decrease is associated with the finite sample diameter, as discussed next.

The square-root-of-time relationship is a consequence of Fick's law for binary systems in either infinite or semi-infinite geometry.[10] It exists for systems of finite size for the early stages of diffusion, because during this time the sample really appears infinite. Actual geometry is only important in the later stages. Thus, later deviations from the square-root of time law may be interpreted as influences of the geometry. Since it was observed that the ratio M_{1t}/M_{3t} is constant during this initial stage, one can argue that it would always be constant if the samples were really infinite.

It should be noted that the mass-transfer data contain an end effect due to the finite length of the test specimens. That is, we do not truly have the amount of diffusion per unit length of rod when the rod length is infinite,
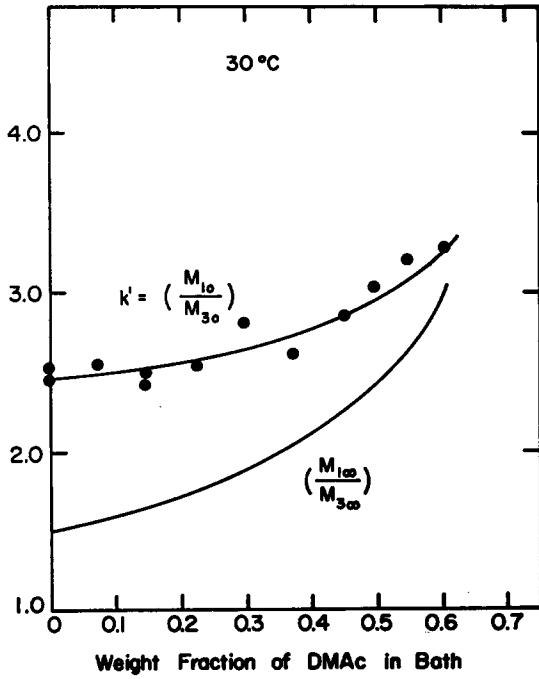
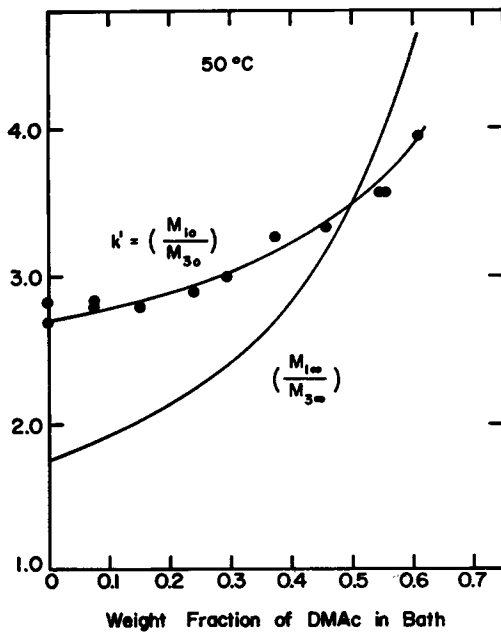Fig. 6. Ratio of transferred solvent to transferred nonsolvent.

Fig. 7. Ratio of transferred solvent to transferred nonsolvent.

since the ends add additional surface area.   This can be corrected approximately by multiplying all the values from eqs. (1) and (2) by the factor $L/(L + R_0)$, where L and R_0 are the sample length and initial radius, respectively.   This correction (always less than 5%) was applied before any data analysis.

The data in Figures 6 and 7 show that DMAc leaves the sample at a faster mass rate than water enters, since the densities are nearly the same; then a similar statement can be made regarding the volumetric transfer rates. Since the molecular weights of DMAc and water differ by a factor of 4.84, however, the same cannot be said of the molar or molecular transfer rates. In fact, under most conditions the number of water molecules transferred is greater than the number of DMAc molecules transferred within the same time period.   The mass flux ratio will be used hereafter, because diffusion theory is most conveniently expressed in mass units for liquids.

Boundary Movement

Observations have shown that a very distinct moving boundary is associated with coagulation.   One side of the boundary is hard, coagulated polymer (plus retained liquid), while the other side is the soft original gel. Therefore, this boundary can be seen visually or located by some mechanical hardness test if desired.   The boundary begins at the sample surface and moves inward with time.   Coagulation may be considered essentially complete when the boundary reaches the center.

This boundary motion was followed by immersing gelled rods of polymer solution in coagulant baths for various lengths of time.   At the prescribed time the sample was removed from the bath and cross-sectioned by a razor
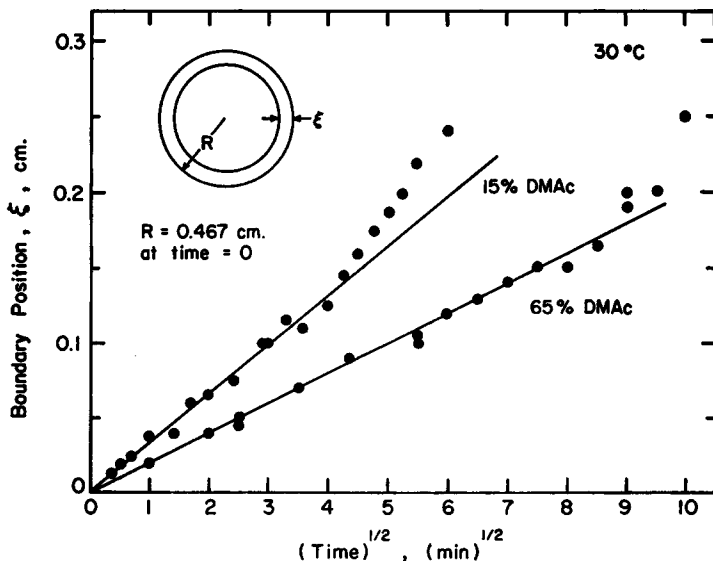

Fig. 8. Rate of boundary motion.

blade. The cross section was viewed through a low-powered stereo-microscope fitted with a calibrated scale used for measuring the depth of penetration of the boundary. The depth of penetration ξ was measured at various points along the periphery of the cross section and was found to be uniform even in cases in which the cross-sectional shape had changed from round to oval. The sample diameter departed very little from the initial value of 0.935 cm. for the early stages of diffusion. The shape was essentially round during this time. Penetration greater than 40 to 50% could not be measured reliably.

Typical data are shown in Figure 8. Up to about 30% the penetration ξ is proportional to the square root of time for all conditions. The data for
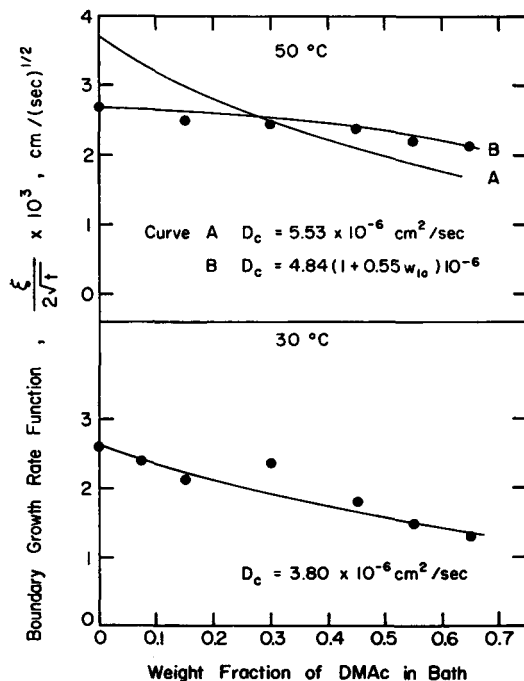

Fig. 9. Boundary growth rates.

other coagulation conditions are given in Fig. 9 by plotting the slope of the linear region, i.e. $\xi/2\,t^{1/2}$ versus the bath composition at 30 and 50°C. In Figure 9 the dots are experimental data and the curves are analytical expressions (developed later). Similar results were obtained by Booth[4] for model acrylic fibers spun by using salt solutions for the solvent and coagulant.

The square-root of time relationship appeared earlier in the mass-transfer results; thus, it seems necessary at this point to elaborate further the reasons for this behavior. For normal Fickean diffusion in a system of infinite depth or during the initial stages of a finite system the distance and time

variables, x and t, in the diffusion equations can be combined into a single variable, η, by the Boltzmann transformation.[10]

$$\eta = x/2t^{1/2} \tag{3}$$

This has the consequence that concentrations and fluxes depend only on this combination of x and t, no matter how the diffusion coefficient varies with concentration. For finite systems this will be true only in the initial stages. This implies that the concentration at the moving boundary observed must be constant, since $\xi/2\ t^{1/2}$ is a constant. In the following section various diffusion models will be considered in the light of the data given here.

MATHEMATICAL MODELS FOR DIFFUSION DURING COAGULATION

By this time it should be realized that coagulation is a complex process, and a rigorous and formal mathematical description does not seem very likely to be developed, in view of the limited number of problems that can be successfully analyzed by present diffusion theory. Each item listed below alone causes serious complications for any diffusion analysis; however, all of them are involved in coagulation of polymer solutions.

1. A ternary system with possible coupling effects.
2. One of the components is a polymer.
3. The polymer undergoes some type of phase change.
4. Thermal effects due to heat of mixing of solvent and nonsolvent.
5. A possible latent heat associated with the polymer phase change.
6. The boundaries and volume of the sample are not fixed.

It does seem, however, that it would be very enlightening to construct approximate theories, of various degrees of sophistication, to see how well the data given here can be described by them. This is an indirect way of arriving at the details of the mechanism of the processes involved. The list given above should merely detract from the clarity and fineness of the details that can be deduced but not obscure them completely.

In the following developments items 4 and 5 will be completely ignored. Item 6 should not be important during the early stages of diffusion. A very great simplification and, perhaps, an equal limitation will be made with regard to item 1 by treating it as a pseudobinary system. This is done by considering explicitly only the diffusion of components 1 and 3, DMAc and water. The justification for this follows. The diffusion of DMAc results in a net removal of it from the sample, just as the diffusion of water results in its net addition. The polymer, component 2, does neither and, indeed, at equilibrium it is still essentially distributed uniformly throughout the sample, as it was in the beginning. The density of polymer at the end is higher than at the start but still more or less uniform. As the polymer changes phase, it goes from a molecularly dispersed solution (lightly

crosslinked in the gel) to a porous, fibrillar network. This means that on one side of the boundary discussed earlier the molecules of DMAc and water diffuse through a molecular network of polymer chains, while on the other side they diffuse through a fibrillar network of coagulated polymer. Local diffusion of polymer is necessary to accomplish this change of morphology, but it is believed that this does not have to be considered to give a macroscopic description of the process.

Next we consider the phase change of the polymer. From the data presented earlier it is clear that within a given volume element of coagulating solution the water content is increasing while the DMAc level is decreasing. Moreover, since the DMAc leaves faster than the water enters, the amount of liquid in this element of volume decreases, or the solids level increases. This eventually creates a thermodynamic situation that causes the phase change. Earlier studies[11] showed the phase change to be a rate process. It was indicated above that the composition at this boundary must be constant. This idea will be incorporated into the models to follow. The water composition (on a polymer-free basis) at the boundary will be denoted w_3^*. A certain solids level higher than 26% will exist there. The easiest way to handle the phase change is to consider it to happen instantaneously, when the critical composition is reached, even though the change is a progressive one. A very simple model that utilizes this approach will be given. A second model takes a more sophisticated approach by considering the densification of the polymer just ahead of the boundary, where it is finally immobilized completely. Again, the weight fraction of water at the boundary is considered to be w_3^*.

Since the problem is being considered a pseudobinary system, it will be convenient to express the composition of the liquid on a polymer-free basis by using the weight fractions w_1 and w_3, where the sum $w_1 + w_3$ is equal to 1. In Fick's law of diffusion the density of the liquid (not including the polymer) should be used rather than the total density. The liquid density will be variable, since the solids level changes. Fick's law can be written for species 3 as the vector equation

$$\mathbf{n}_3 = -\rho D \nabla w_3 + w_3(\mathbf{n}_1 + \mathbf{n}_3) \tag{4}$$

where D is not a simple binary diffusion coefficient, because of the presence of the polymer in either molecular or fibrillar form.

An Equal-Flux Model

In many diffusion problems either one of the fluxes is zero or the two are equal and opposite. The case is neither here, but it will be informative to consider the latter for the moment. That is, let us assume that the inward flux of water is equal to the flux of DMAc out, so that everywhere $\mathbf{n}_1 + \mathbf{n}_3 = 0$. Next, assume that the diffusion coefficient is constant and equal on both sides of the boundary and that the phase change occurs instantaneously at a weight fraction of water of w_3^*, i.e. the composition at the moving boundary. The composition of water at the surface, w_{30}, is

just the bath composition, as shown by Figure 2.   Solutions to Fick's law
for this problem are given by Jost.[10]   It is not possible to compare the
mass-transfer data with this model, since it predicts $M_{1t} = M_{3t}$.   It does
predict, of course, that the amount transferred is proportional to $t^{1/2}$.
Perhaps more interesting is the rate of boundary movement predicted by
this simple model.   This is shown in Figure 10.   The similarity to the data
in Figure 8 is clear.   The curves in Figure 10 (at two values of $w_3{}^*/w_{30}$) were
calculated for cylindrical geometry, whereas the straight lines were cal-
culated for an infinite system.   Note that for the initial diffusion the two
are coincident; however, the cylindrical system indicates a later upward
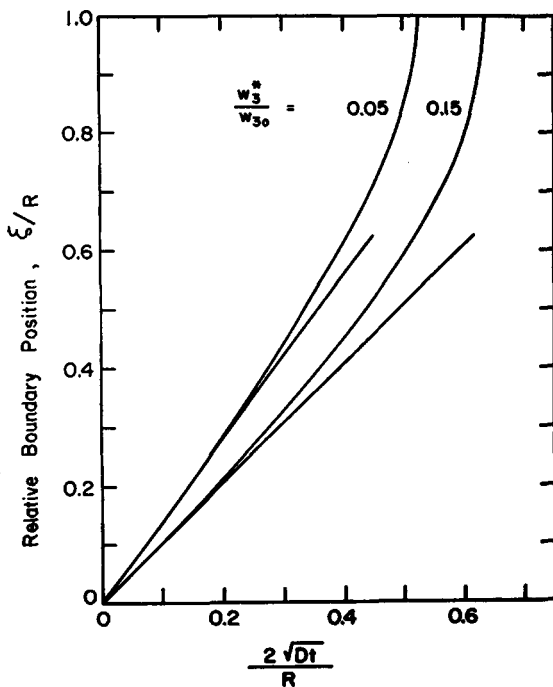curvature, which is a consequence of geometrical factors imposed on the

Fig. 10. Simple model calculation of boundary motion.

diffusion.   As long as the plots in Figure 10 are linear, ξ is proportional to
$t^{1/2}$ and independent of R.

   This model predicts that, as the DMAc content of the bath increases,
i.e. an increasing ratio $w_3{}^*/w_{30}$, the rate of boundary motion slows down,
or $\xi/2\,t^{1/2}$ decreases.   The data of Figures 8 and 9 are certainly in qualitative
agreement with this.

   Such a simple model is obviously not sophisticated enough, since it does
not account for changes in weight of the system.   It does qualitatively
predict several features of the actual system, as was just pointed out.   It
also provides a conceptual basis on which to build more descriptive models.

The model here given has been the primary basis used in the past for interpreting the coagulation process.[5]

A Constant-Flux Ratio Model

In this section one way of accounting for unequal fluxes will be given. Since the mathematics are more complex in cylindrical coordinates, we shall develop the model in rectangular coordinates for an infinite system. During the early stages of diffusion the solution will be the same as that for the cylindrical geometry, as illustrated in Figure 10. The experimental data reported apply only to this region anyway.

During the early stages the ratio of fluxes at the surface was found to be a constant k'. Equilibrium data showed that the ratio of fluxes did eventually change, but it is believed that this ratio would be invariant for a truly infinite system. This becomes reasonable when one considers that for a finite cylindrical rod the moving boundary eventually reaches the center of the rod (thus, all the polymer is precipitated), and further diffusion serves merely to equalize the composition in the rod to the level in the bath. This final step is considered responsible for the fact that $M_{1\infty}/M_{3\infty} \neq k'$. It never occurs for an infinite system. So in this model we shall build in a constant-flux ratio at the surface. The easiest way to do this is to consider the flux ratio constant throughout the entire specimen for all positions and time; that is,

$$k' = -\mathbf{n}_1/\mathbf{n}_3 \tag{5}$$

To build a proper mathematical basis for a diffusion model we must start with the following continuity equations:

$$\partial\rho/\partial t = -[\nabla \cdot (\mathbf{n}_1 + \mathbf{n}_3)] \tag{6}$$

$$\partial\rho_3/\partial t = -(\nabla \cdot \mathbf{n}_3) \tag{7}$$

where ρ_3 is the density of component 3, and $\rho = \rho_1 + \rho_3$, or the density of the liquid. Fick's first law of diffusion can be combined with these two equations to give the following general form of Fick's second law for binary diffusion:

$$\rho(\partial w_3/\partial t) = (\nabla \cdot \rho D \nabla w_3) - [(\mathbf{n}_1 + n_3) \cdot \nabla w_3] \tag{8}$$

Fick's first law, eq. (4), can be written as

$$\mathbf{n}_3 = -[\rho D/(1 + kw_3)]\nabla w_3 \tag{9}$$

where $k = k' - 1$. By these equations it can be shown that

$$\partial\rho/\partial w_3 = -k\rho/(1 + kw_3) \tag{10}$$

indicating the relationship between density changes and concentration changes. This equation can be easily integrated to give

$$\rho/\rho_u = 1/(1 + kw_3) \tag{11}$$

where ρ_u is the density of liquid (DMAc) in the sample before any coagulation has occurred, i.e. when $w_3 = 0$. Because of the condition n_1/n_3 equal to a constant the density and composition are uniquely related. Equation (11) shows that, as the water content at a point increases, the solids level increases. Both of these factors decrease the solubility of the polymer in the surrounding liquid.[7,11] The fibrillar network structure is being formed during this period of densification just ahead of the moving boundary. The polymer must be able to move locally for the liquid density to decrease (i.e. for the solids level to increase); however, owing to the network formation, the densification must end at some point because of complete immobilization of the polymer. This point should correspond to the observed boundary, where the water content is w_3^* and the liquid density ρ_c is given by eq. (11):

$$\rho_c/\rho_u = 1/(1 + kw_3^*) \tag{12}$$

In terms of these ideas the coagulation mechanism is as follows. The bath and polymer solution meet at an interface at position $x = 0$. There is a moving boundary at $x = \xi$, where $\xi \propto t^{1/2}$. The water concentration is w_3^* at ξ and w_{30} (bath composition) at the surface. Ahead of the moving boundary the liquid density changes according to eq. (11), whereas it remains constant at ρ_c in the region $x = 0$ to $x = \xi$. The total continuity relation, eq. (6), dictates that *both* ρ and k', where $k' \neq 1$, cannot be constant in this region. This inconsistency in the model will be ignored for the moment. A solution will now be found, which satisfies all of the requirements except eq. (6).

Solutions will be sought for both regions by assuming constant but unequal diffusion coefficients for each region owing to different influences of the polymer. The two regions will be referred to as "coagulated" and "uncoagulated"; hence the subscripts u and c. Ahead of the boundary, where $x > \xi$, the liquid density is given by eq. (11), so eqs. (8) and (9) can be combined to give

$$\partial f/\partial t = D_u \frac{\partial^2 f}{\partial x^2} \tag{13}$$

where $f = kw_3/(1 + kw_3)$. Behind the boundary, $0 < x < \xi$, the liquid density is assumed constant, so eqs. (8) and (9) can be reduced to

$$\partial u/\partial t = D_c \frac{\partial^2 u}{\partial x^2} \tag{14}$$

where $u = \ln (1 + kw_3)$. The solutions to eqs. (13) and (14) are

$$f = f^*[1 - \text{erf } (x - \zeta)]/(D_u t)^{1/2} \tag{15}$$

$$u = u_0 - (u_0 - u^*)[\text{erf } x/2(D_c t)^{1/2}]/[\text{erf } (\beta_c)] \tag{16}$$

where the subscript 0 indicates conditions at $x = 0$, the asterisk denotes conditions at $x = \xi$, and β_c is a constant equal to $\xi/2(D_c t)^{1/2}$.
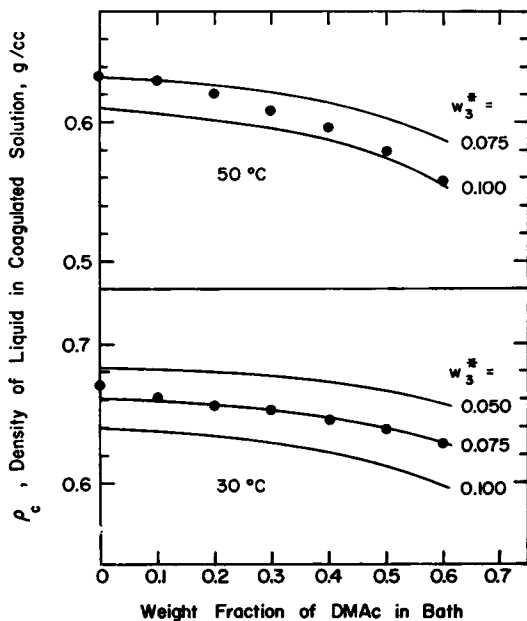
Fig. 11. Equilibrium liquid density.

With these solutions to Fick's second law for this problem in semi-infinite geometry it can be shown that the amount of water added in time t to a rod of initial weight M_0 for the initial period of diffusion is

$$M_{3t}/M_0 = 4/\pi(1 - w_{20})([1/k(1 + kw_3^*)]$$

$$\times \{(u_0 - u^*)/[\text{erf } (\beta_c)]\})(D_c t/R_0^2)^{1/2} \quad (17)$$

where w_{20} is the initial weight fraction of the polymer, i.e. 0.26, and $u_0 - u^*$ $= \ln [(1 + kw_{30})/(1 + kw_3^*)]$. An additional relationship,

$$(D_c/D_u)^{1/2}[(u_0 - u^*)/kw_3^*] = \exp \beta_c^2 \text{ erf } (\beta_c) \quad (18)$$

can be derived by using the fact that the fluxes must be equal at either side of the boundary.

Now, it will be interesting to apply this model to the experimental data, to see how well it fits. First, the experimental density of the liquid in the coagulated solution, ρ_c, will be compared with eq. (11). Since the density of liquid behind the boundary is assumed to be constant, it can be calculated from ρ_∞ and the degree of swelling data. The comparison is shown in Figure 11. The parameter w_3^* is unknown, so several values are used in eq. (11), to see how well the form of the equation fits the data. The magnitude of w_3^* is taken as the value that best reproduces the ρ_c data. At 30°C. a value of $w_3^* = 0.075$ gives an excellent fit. At 50°C. no value gives a perfect fit, but still the form is not bad. The shape of the curve is determined by the experimental values of k'. The next test is to combine known values of w_{30}, M_{3t}/M_0, k, plus the estimates of w_3^*,
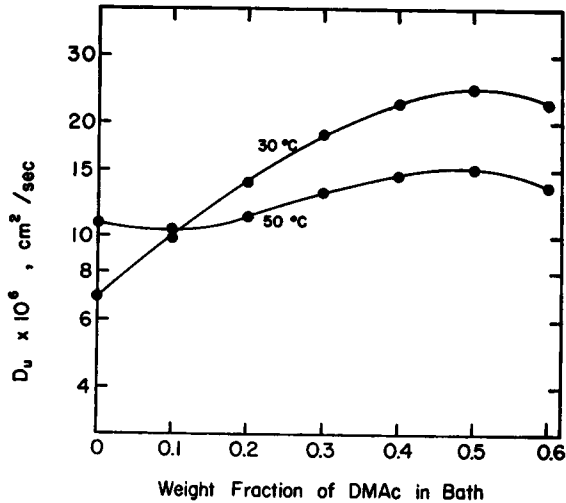
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Fig. 12. Diffusion coefficient in the uncoagulated solution.

in eq. (17) to get the relationship β_c versus D_c. Once this is done, values of D_c can be selected that best duplicate the experimental $\xi/2 \ t^{1/2}$ data. At 30°C. a constant value of D_c gives an excellent fit, as seen in Figure 9. At 50°C., however, no constant value of D_c will reproduce the data, but an adequate reproduction can be had by assigning a slight concentration dependence to D_c. Actually, one should not be surprised that D_c depends on the liquid concentration and, thus, on the bath concentration. The test just applied shows that the mass-transfer rates must be related to the boundary motion data through eq. (17); however, to relate it directly, one must have information about D_c. Since we have no a priori knowledge of this parameter, it is necessary to estimate if from the data. The estimates obtained in this way are of the magnitude expected for liquid systems.

The other diffusion coefficient can be evaluated from eq. (18). The values are shown in Figure 12, plotted against the bath composition as a convenient means of presentation. Actually, D_u depends on the bath concentration only indirectly. The bath composition influences the composition of the water and the polymer in the uncoagulated region, and these do determine the values of D_u. This may explain in part the peculiar fact that D_u is lower at 50 than at 30°C. in some regions. The value of k is higher at 50 than at 30°C., so higher solids levels are attained in the region $x > \xi$; hence, the diffusion coefficients are not properly compared at constant composition, as they should be. Of course, it must be remembered that a diffusion coefficient cannot be calculated unless a model is used; then all values reflect the model. Certainly this is not an exact model, so part of the anomalous temperature behavior of D_u may be no more than a reflection of the inadequateness of the model. The model actually fits the data rather well and supplies a reasonable physical picture of coagulation.

A Variable-Flux Ratio Model

The last model contained a mathematical inconsistency in that one is not free to let both the flux ratio and the density be constant. Several arguments can be given, which show that the density behind the coagulation boundary must remain constant compared with the prediction given by eq. (11), which assumes a constant-flux ratio. Another approach would be to consider the flux ratio to be constant at the surface (denote this ratio by $k^{0'}$) but variable elsewhere in the coagulated region. For convenience, let the flux ratio in the uncoagulated region still be constant but at a new value of $k^{*'}$. The situation in the region $0 < x < \xi$ is now similar to the Arnold problem discussed by Bird et al.,[12] except that there the ratio at the surface was taken to be zero.

The general Arnold problem was solved here, i.e. $k^{0'} \neq 0$, and the major results are as follows.

$$k^0(w_{30} - w_3{}^*)/(1 + k^0 w_{30}) = -\pi^{1/2}\varphi \exp \varphi^2[\text{erf } \varphi + \text{erf } (\beta_c - \varphi)] \quad (19)$$

$$M_{3t}/M_0 = 4(1 - w_{20})[-\varphi/k^0(1 + k^* w_3{}^*)] (D_c t/R_0{}^2)^{1/2} \quad (20)$$

$$k^0/k^* = (1 + k^0 w_{30}) \exp \{2\varphi\beta_c - \beta_c{}^2\} - k^0 w_3{}^* \quad (21)$$

$$\rho_c = \rho_u/(1 + k^* w_3{}^*) \quad (22)$$

where $\varphi = -k^* w_3{}^*(D_u/D_c)^{1/2}/\pi^{1/2}$. The following new symbols are used:

$$k_0 = k^{0'} - 1$$

$$k^* = k^{*'} - 1 \quad (23)$$

The problem to the right of the boundary is the same as before except for the replacement of k with k^*. These equations are very unwieldy, and parameter evaluation must be done by a very laborious trial-and-error approach. It is easy to see, however, that the flux ratio increases markedly from the value $k^{0'}$ at the surface to a value $k^{*'}$ at the boundary with a tenfold increase being typical. Relating the experimental density to these values by eq. (22) gives a composition of water at the boundary, $w_3{}^*$, of 1% or less. Such a composition seems totally unrealistic on the basis of the data in Figure 1 and other work.[7,11] Consequently, it is concluded that, although the variable-flux ratio model is mathematically more consistent with eq. (6) than the earlier constant-flux ratio model, it gives a less realistic picture of coagulation. This can mean only that the ideas built into the models are not totally correct. For example, it seems that the present dilemma could be solved by considering a slight liquid density variation in the coagulated phase. This would greatly reduce the flux ratio predicted by eq. (21). One would have, however, a very difficult mathematical problem.

Summary

The experimental data given here were obtained by using samples many times the size of commercially interesting fibers, because this made accurate

and convenient experiments possible. The results were used here only for interpreting the mechanism of coagulation. The same results could be scaled down for fiber dimensions by well-known equations. The calculations would give such information as the minimum bath length required. Of course, the data do not reflect any of the important effects of transport within the bath liquid itself or the rheological phenomena associated with spinning. Further, the effect of the gelled state of the sample on the absolute diffusion rates is unknown.

None of the mathematical models discussed are precise, for several legitimate objections to any of them can be cited. However, it was pointed out earlier that this is an extremely complex problem for fundamental treatment; therefore, one cannot expect better than approximations. The constant-flux ratio model offers a reasonable physical picture of the situation and a good fit of the experimental data. By a judicious use of such approximate theories one can learn much about a process that is ordinarily inaccessible to investigation. For example, in this case estimates of the solids level and the water content at the moving boundary were obtained by fitting a model to the data. There seems to be no purely experimental method of arriving at this particular piece of information, owing to the nature of the phase change in the system.

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