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A New Approach to Coagulation Phenomena in Wet-Spinning

A. RENDE, *S.T.I.R., Studio Tecnico Industriale, 80055 Portici, Italy*

Synopsis

A new physicochemical model was built to describe the phenomena occurring during wet-spinning of polyacrylonitrile, in order to relate the integral time of coagulation to the major variables of the spinning bath. According to this model, counterdiffusion of solvent and coagulant leads the system to overcome the thermodynamic equilibrium conditions, so that precipitation of polymer occurs, at a distance from the fiber axis variable with time. This causes a moving-interface dope-coagulated polymer to build up. The integral time required by this interface to reach the fiber axis, i.e., the coagulation time, is related, by simple equations to initial radius, to temperature via diffusional coefficients, to "bath hardness" (i.e., coagulant content), and to thermodynamic phase equilibrium conditions.

INTRODUCTION

The phenomena occurring in wet-spinning of such polymers as polyacrylonitrile are well known. When the very viscous dope leaves the spinneret to enter the coagulation bath, precipitation of the polymer in fibrillar form takes place.

The protofibers so formed show an outer skin more or less ruptured, while the inner core is more regular. In addition, in the protofiber there may be a number of voids, the shape and size of which depend upon such factors as temperature, bath "hardness," draw ratio, etc.

Because of the dependence of subsequent textile properties of the fiber on its structure, particularly on the regularity of the cross-sectional shape, the integrity of the external skin, and the number and size of voids, accurate knowledge of the phenomena regulating these features is of great importance for spinners.

Early studies,[1–3] particularly those of Knudsen,[1] were just empirical attempts to correlate the actual spinning variables with the final properties of the fibers, without any investigation on the dynamics of the phenomenon.

In 1963, Bozza[4] showed first the role played by the diffusion in the coagulation process. But so far, the only mathematical model available[5] is quite difficult to handle for practical calculations of design parameters, and no account has been taken of the thermodynamic aspect of the whole phenomenon, which we think is the most important.

We therefore have tried to build a new physicochemical model in which the thermodynamic concept of phase equilibrium plays a role as important as that played by counterdiffusion of solvent and coagulant.

NEW PHYSICOCHEMICAL MODEL

According to this model, we have two diffusional motions, which carry the solvent out of the protofiber to the bath and the coagulant from the bath into the protofiber, respectively. When, because of these diffusional motions, the concentrations of polymer, solvent, and coagulant overcome the phase equilibrium conditions, precipitation of polymer (and hence coagulation) takes place. This happens clearly step by step, from the outer layer of the protofiber toward the core itself, so that we have a moving interface, coaxial to the protofiber, which separates the coagulated (outer) polymer from the noncoagulated (inner) dope. When this interface reaches the axis of the protofiber, the coagulation is complete. If we want to calculate the time from the beginning of the diffusion when this happens, we must first determine the distance ρ^* of the interface from the axis of the fiber at a given time t, and hence the integral time needed for ρ^* to vary from 0 to ρ_0 total protofiber radius.

At the very outlet from the spinneret, a sudden desolvatation of the outer layer of protofiber occurs, so that a skin of coagulated polymer builds up. This skin has properties different from those of the inner core of the fiber, and remains so even when the fiber is dried, stretched, and dyed.

Across this skin, whose thickness ξ is generally very low, a counterdiffusion of the solvent and the coagulant takes place. Because the skin acts as a semipermeable membrane, we can state that no high molecular weight molecule diffuses, so that the polymer weight in the fiber is constant. If we do not consider the actual (small) volume contraction of the protofiber, the volume ratio v_p of the polymer is also roughly constant during the complete coagulation process.

This "working hypothesis" will allow us to calculate the critical volume ratios v_1^* and v_2^* (for the solvent and the coagulant, respectively), starting from the external v_1 and v_2 (in the spinning bath) and the original v_p (in the dope).

Another "working hypothesis" must be established: that the protofibers are isotropic with respect to z and θ (see Fig. 1). If this is the case, the diffusional motions of the solvent and the coagulant are regulated by the well-known Fick's law:

$$\frac{dw_1}{dt} = -D_1\Omega_1\frac{dc_1}{d\rho} \qquad \frac{dw_2}{dt} = -D_2\Omega_2\frac{dc_2}{d\rho} \tag{1}$$

where w_j = weight of the jth species that entered or left the protofiber in time t, D_j = diffusional coefficients, Ω_j = diffusion surface area, and c_j = concentration of the jth species in the protofiber at radius ρ.

For integrating eq. (1), we must consider the physical aspect of the phenomenon. After a given time t_1, the penetration of the coagulant (see

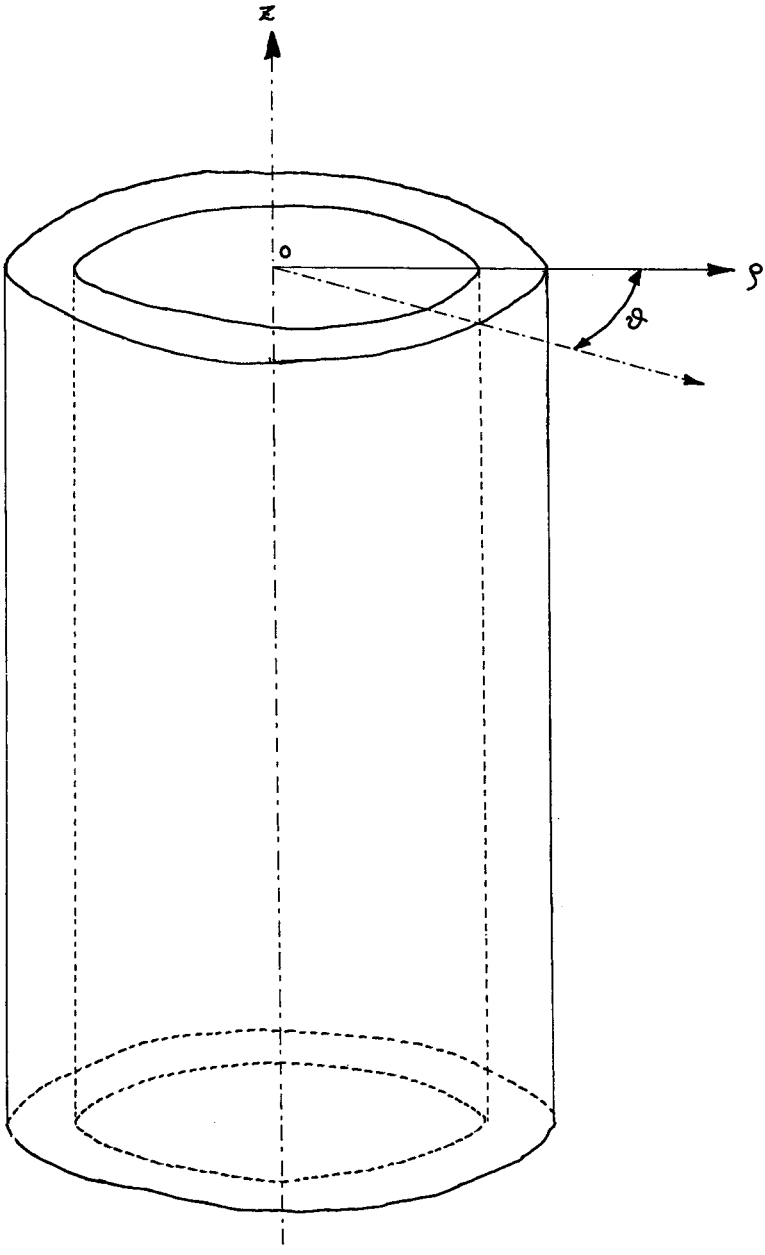

Fig. 1.

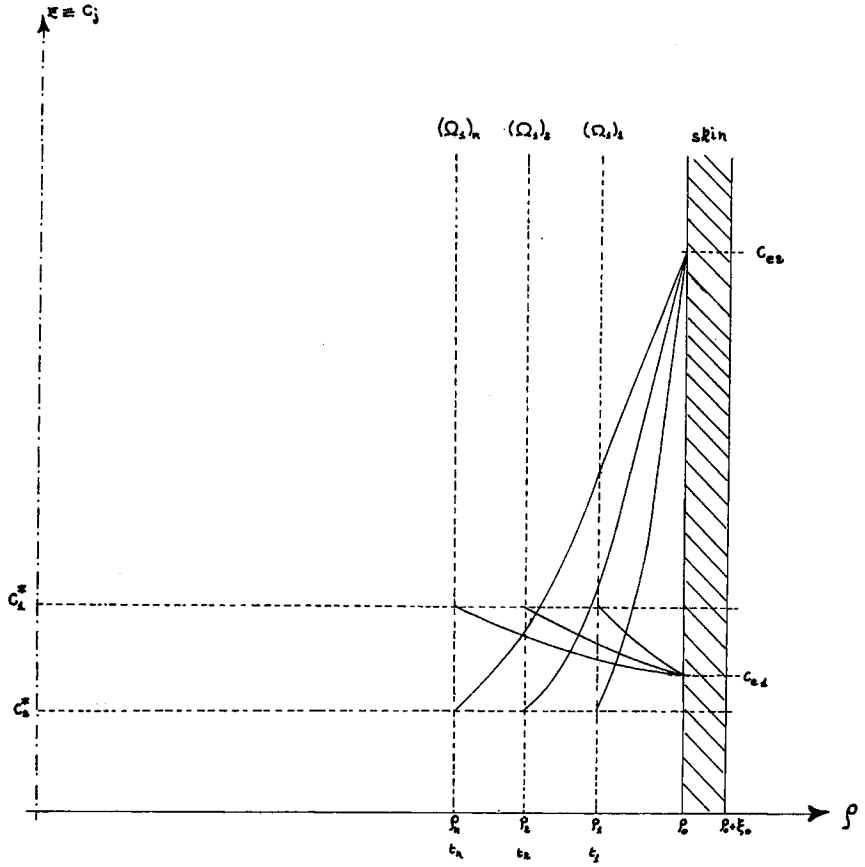

Fig. 2.

Fig. 2) will have reached a certain distance ρ_t; between this radius and the skin, c_2 and c_1 will have reached their equilibrium values c_2^* and c_1^* at a distance ρ_1, so that ρ_1 is the position of the interface dope-coagulated polymer. Across ρ_1, a gradient will have built up, from the external c_{e2} and c_{e1} and the inner c_2^* and c_1^*. After a time $t_2 > t_1$, the same situation will appear, but at a radius $\rho_2 > \rho_1$, and so on.

In this case, we can note that Ω_1, the diffusion surface area for the solvent, will decrease as the time increases,

$$\Omega_1 = 2\pi\rho z$$

where $\rho = \rho(t)$ by means of Fick's law. The weight of solvent passing through this surface will be given by the difference of concentrations between the inner face of Ω_1 and the external one, times the volume in which this change has happened, i.e.,

$$w_1 = \Delta c_1 \cdot \pi z(\rho_0^2 - \rho^2) \qquad (2)$$

where $\rho = \rho(t)$ and $\Delta c_1 = c_{e1} - c_1^*$, and hence

$$\frac{dw_1}{dt} = -2\pi z \Delta c_1 \rho \frac{d\rho}{dt}. \tag{3}$$

For the coagulant, on the other hand, Ω_2 is always the same and is clearly the inner surface area of the skin, i.e.,

$$\Omega_2 = 2\pi\rho_0 z \tag{4}$$

while w_2, the weight of coagulant passing through the skin toward the protofiber, will be

$$w_2 = \Delta c_2 \pi z(\rho_0^2 - \rho^2) \tag{5}$$

where $\rho = \rho(t)$ and $\Delta c_2 = c_{e2} - c_2^*$. Hence,

$$dw_2/dt = -2\pi z \Delta c_2 \rho d\rho/dt. \tag{6}$$

If we substitute eqs. (2), (3), (4), and (6) in eq. (1), we obtain

$$\begin{aligned} \Delta c_1 \frac{d\rho}{dt} &= -D_1 \operatorname{grad} c_1 \\ \Delta c_2 \rho \frac{d\rho}{dt} &= -D_2 \rho_0 \operatorname{grad} c_2. \end{aligned} \tag{7}$$

Clearly, the term $d\rho/dt$, that is, the "speed of progress" of the interface, is the same for both equations, so that we can write

$$\frac{D_1}{\Delta c_1} \operatorname{grad} c_1 = \frac{D_2}{\Delta c_2} \frac{\rho_0}{\rho} \operatorname{grad} c_2. \tag{8}$$

The analytical form of grad c_2 can be found when $dw_2/dt = 0$. This, physically, means finding grad c_2 across the protofiber at steady state.

Rewriting eq. (5) in the case of $\Delta c_2 = c_{e2} - c_2$, we have

$$\frac{dw_2}{dt} = 0 = \pi z \left[(c_{e2} - c_2) \frac{d}{dt}(\rho_0^2 - \rho^2) + (\rho_0^2 - \rho^2) \frac{d}{dt}(c_{e2} - c_2) \right] \tag{9}$$

which can be integrated as follows:

$$\int_{\rho}^{\bar{\rho}} \frac{d(\rho_0^2 - \rho^2)}{(\rho_0^2 - \rho^2)} = -\int_{c_2}^{c_{i2}} \frac{d(c_{e2} - c_2)}{(c_{e2} - c_2)}. \tag{10}$$

As for the integration limits, we must note that $\bar{\rho}$ is that ρ at which we first found $c_2 = c_{i2}$ (inner concentration of 2). By integrating eq. (10) and then passing at limit for $\bar{\rho} \to 0$ and rearranging, we obtain

$$c_2 = c_{e2} - \Delta' c_2 \frac{\rho_0^2}{\rho_0^2 - \rho^2}. \tag{11}$$

Referring to eq. (8), we can easily calculate grad c_1 and grad c_2:

$$\text{grad } c_1 = -\frac{D_2}{D_1}\frac{\Delta c_1}{\Delta c_2}\frac{\rho_0^2}{\rho^2}\Delta' c_2 \frac{d}{d\rho}\left(\frac{1}{\rho_0^2 - \rho^2}\right) \tag{12}$$

$$\text{grad } c_2 = -\rho_0^2 \Delta' c_2 \frac{d}{d\rho}\left(\frac{1}{\rho_0^2 - \rho^2}\right) \tag{13}$$

where $\Delta c_j = c_{ej} - c_j^*$ and $\Delta' c_j = c_{ej} - c_{ij}$, with c_{ij} the inner concentration of the jth species.

Equation (12) can be integrated with respect to ρ, between limits as for eq. (10), to give c_1 as a function of c_{e1}, as for c_2 in eq. (11).

The coagulation speed, i.e., the "speed of progress" of the interface, is quickly calculated by inserting eq. (13) in eq. (7):

$$u = \frac{d\rho}{dt} = -\rho_0^2 D_2 \frac{\Delta' c_2}{\Delta c_2} \cdot \frac{1}{\rho}\frac{d}{d\rho}\left(\frac{1}{\rho_0^2 - \rho^2}\right) \tag{14}$$

and the integral time required for complete coagulation will be given by $t_c = \int u\, dt$:

$$t_c = \frac{1}{2}\rho_0^2 \frac{1}{D_2}\frac{\Delta c_2}{\Delta' c_2}. \tag{15}$$

At this point, we can note that the form of t_c is as foreseen by the experimental data; in fact, t_c increases as c_{e1} decreases, i.e., the bath gets "softer"; t_c increases as ρ_0 increases; t_c decreases as D_1 increases, i.e., the actual temperature increases. Furthermore, we find the same dependence of ρ_0 on $t_t^{1/2}$ as found by Paul.[5]

However, to determine numerically this coagulation time, we need to know c_1^*. In order to determine the c_j^*, we can schematize the whole process as follows (see Fig. 3).

Let us consider a given volume V_{tot} of dope. Due to the counterdiffusion of solvent [1] and coagulant [2], a volume V_1 of solvent will get out of the protofiber and a volume V_2 of coagulant will enter, while V_{tot} will remain constant (see "working hypothesis" above), so that a continuous change in the concentrations will take place. When the phase equilibrium point is reached, the system will separate into two phases of volumes $d \cdot V_{tot}$ and $c \cdot V_{tot}$ for the diluted and concentrated phases, respectively. Clearly, $d + c = 1$. The v_j^* values, the volume ratios of the jth species in the whole volume V_{tot} (related to the c_j^* by $v_j^* = c_j^*/\rho_j$, where ρ_j is the specific gravity), are given by the equations

$$\begin{aligned} dv_1 + (1 - d)v_1' &= v_1^* \\ dv_2 + (1 - d)v_2' &= v_2^* \\ dv_p + (1 - d)v_p' &= v_p^* \\ v_1^* + v_2^* + v_p^* &= 1 \end{aligned} \tag{16}$$

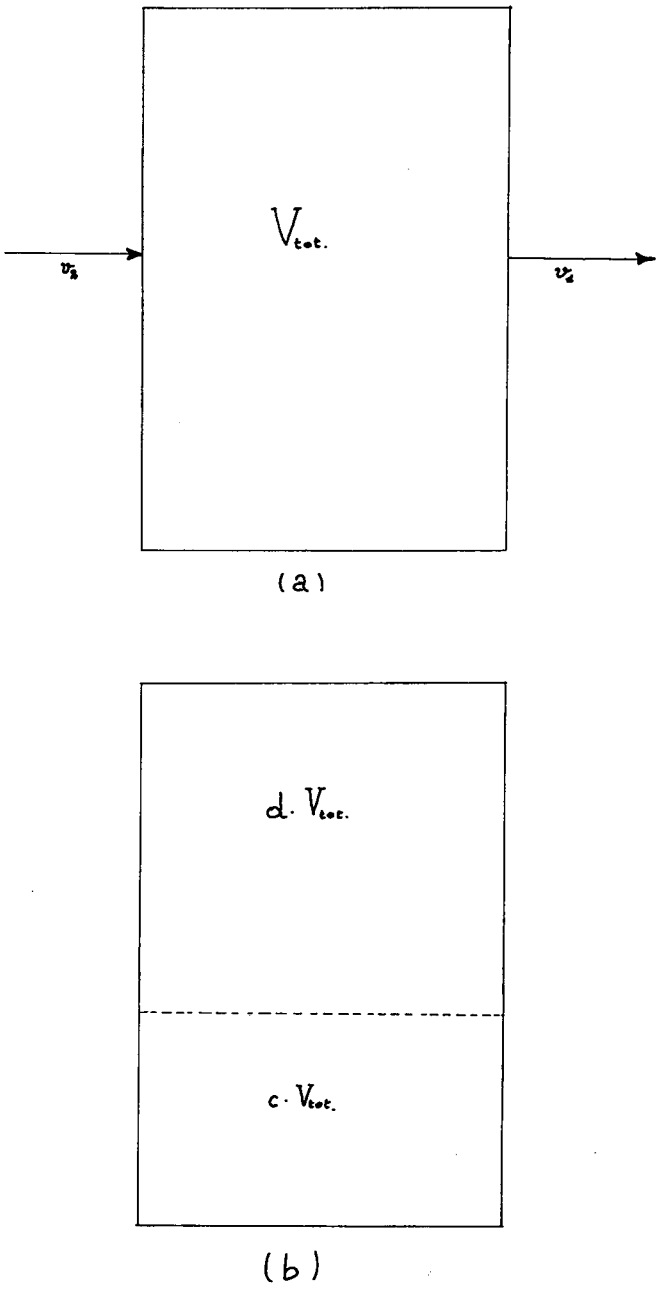

Fig. 3. Protofiber model during diffusion (a) and after coagulation (b): v_1 solvent flow; v_2, coagulant flow; d, dilute and c, concentrated phases.

where v_j and v_j' are the volume ratios of the jth species in the diluted and concentrated phases, respectively, at the thermodynamic equilibrium.

The values of v_j and v_j' are determined starting from the assumption that, at equilibrium, the chemical potentials μ of each species must be equal in both phases, i.e.,

$$\mu_j = \mu_j' \tag{17}$$

where the subscript refers to the most concentrated phase.

According to Flory,[6] these equations can be written as

$$\begin{aligned}
&\ln v_1 + (1 - v_1) - v_2(x_1/x_2) - v_p(x_1/x_p) \\
&\qquad + (\chi_{12}v_2 + \chi_{1p}v_p)(v_2 + v_p) - \chi_{2p}(x_1/x_2)v_2v \\
&\quad = \ln v_1' + (1 - v_1') - v_2'(x_1/x_2) - v_p'(x_1/x_p) \\
&\qquad + (\chi_{12}v_2' + \chi_{1p}v_p')(v_2' + v_p') - \chi_{2p}(x_1/x_2)v_2'v_p' \\
&\ln v_2 + (1 - v_2) - v_1(x_2/x_1) - v_p(x_2/x_p) \\
&\qquad + (\chi_{21}v_1 + \chi_{2p}v_p)(v_1 + v_p) - \chi_{1p}(x_2/x_1)v_1v_p \\
&\quad = \ln v_2' + (1 - v_2') - v_1'(x_2/x_1) - v_p'(x_2/x_p) \\
&\qquad + (\chi_{21}v_1' + \chi_{2p}v_p')(v_1' + v_p') - \chi_{1p}(x_2/x_1)v_1'v_p' \\
&\ln v_p + (1 - v_p) - v_2(x_p/x_2) - v_1(x_p/x_1) \\
&\qquad + (\chi_{p2}v_2 + \chi_{p1}v_1)(v_2 + v_1) - \chi_{12}(x_p/x_2)v_2v_1 \\
&\quad = \ln v_p' + (1 - v_p') - v_2'(x_p/x_2) - v_1'(x_p/x_1) \\
&\qquad + (\chi_{p2}v_2' + \chi_{p1}v_1')(v_2' + v_1') - \chi_{12}(x_p/x_2)v_2'v_1'
\end{aligned} \tag{18}$$

where χ_{ij} is a pair interaction parameter, with $\chi_{ij} = f(kT)^{-1}$; x_j is the number of segments of the jth species molecule; and v_j and v_j' have the same meaning as in eq. (16).

This quite complicated system could be simplified bearing in mind that: $x_1/x_2 = 1$, both solvent and coagulant being monomeric species; $\chi_{ij} = \chi_{ji}(V_i/V_j)$, where V_i and V_j are molar volumes.

In the actual case of polyacrylonitrile, where $V_2 \cong 4V_1$,*

$$\chi_{12} = 0.25\ \chi_{21}. \tag{19}$$

Furthermore, $V_p \cong 10^4 V_2$ (or V_1), so that

$$x_1/x_p \cong x_2/x_p \cong 0 \tag{20}$$

and

$$\chi_{2p} = \chi_{p2} \cdot 10^{-4} \cong 0. \tag{21}$$

Finally, according to Tompa,[7]

$$\chi_{1p} = 0, \text{ and hence } \chi_{p1} = 0. \tag{22}$$

* The coagulant usually is water and the solvent, dimethylformamide or other such solvent.

By introducing eqs. (19)–(22) into eq. (18), we obtain

$$\ln v_1 + v_p + 0.25\chi_{21}v_2(v_2 + v_p) = \ln v_1' + v_p' + 0.25\chi_{21}v_2'(v_2' + v_p')$$

$$\ln v_2 + v_p + \chi_{21}v_1(v_1 + v_p) = \ln v_2' + v_p' + \chi_{21}v_1'(v_1' + v_p') \quad (23)$$

$$\ln v_p + (1 - v_p) - v_2(x_p/x_2) - v_1(x_2/x_1) + \chi_{p2}v_p(v_2 + v_1) + 0.25\chi_{21}(x_p/x_2)v_pv_1 = \ln v_p' + \text{etc.}$$

The equations, although simplified, cannot be solved explicitly, and the numerical methods which one is obliged to resort to are tedious undertakings.

This difficulty can be overcome by hypothesizing that the more diluted phase no longer contains polymer species, while the more concentrated phase consists solely of the precipitated polymer. So, while we have

$$v_p = 0$$
$$v_p' = 1,\ v_1' = v_2' = 0$$

we can rewrite eqs. (16) and (23) as follows:

$$dv_1 = v_1^* \quad (24)$$
$$dv_2 = v_2^*$$
$$(1 - d) = v_p^*$$

$$\ln v_1 + 0.25\,\chi_{21}v_2^2 = \ln v_1' + 1 \quad (25)$$
$$\ln v_2 + \chi_{21}v_1^2 = \ln v_2' + 1$$
$$v_1 + v_2 = 1$$

Note that, owing to the roughly constant V_{tot}, we have $v_p = (1/\rho_p)c_p$, as in the original dope. Equation (25) can be solved by using the approximate series expansion of logarithms:

$$\ln (1 + x) = x - {}^1/_2x^2$$

to obtain

$$\frac{v_2}{1 - v_2} = \frac{1 - \sqrt{1 - (1.5 - \chi_{21})(\chi_{1.2} + 0.5)}}{(\chi_{12} + 0.5)}. \quad (26)$$

The values so calculated are quite reliable. The actual value of χ_{21}, however, must be determined experimentally, together with D_j in the diffusion equations.

Equations (15), (24), (25), and (26) allow us to calculate the integral time of coagulation in a way that is sufficiently simple and that gives results which can be used directly in actual calculations of wet-spinning problems.

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