

## Mass Transfer During Dry Spinning of Fibers

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### Synopsis

The present investigation considered the transfer of mass during fiber formation with the dry spinning process, both experimentally and theoretically. Experimental data taken for the dry spinning of poly(methyl methacrylate)-benzene solutions were treated with the equation of continuity of species. Two solutions of this equation were applied to the data. The first, an analytical solution with a number of restraints and assumptions, yielded good, semiquantitative results. The other solution determined by numerical analysis with fewer restraints yielded calculated data which predicted exactly the behavior of average fiber solvent concentration.

Dry spinning is an extensively used industrial process. Despite its wide utility, little is known about the fundamental aspects of this operation. Basically, dry spinning involves extruding a fiber of some polymer solution and then transferring the solvent to the surrounding atmosphere. Thus, we have a case in which momentum, mass, and energy are all involved.

Little attention has been directed to the fundamental treatment of dry spinning. Existing related work included: a series of papers by Ziabicki and co-workers<sup>1-5</sup> which considered only the momentum transport aspects of fiber spinning, a paper by Slattery<sup>6</sup> which considered the momentum transport situation in spinning a Noll fluid; studies of energy transport to melt-spun fibers<sup>7-9</sup> in which little or no mass transfer occurs; a number of dye studies<sup>10-16</sup> of mass transfer<sup>17-19</sup> to wet spun fibers (fibers spun into baths of liquids). The only additional work in dry spinning were the papers of Fok and Griskey<sup>20</sup> and Sano and Nishikawa.<sup>21</sup> The former investigation was an experimental and theoretical consideration of heat transfer to dry-spun fibers. Sano and Nishikawa determined residual solvent content for a variety of conditions and correlated these empirically.

The present investigation involved first an experimental study of mass transfer during dry spinning. These data were then used to check theoretical equations derived to describe this mass transfer process.

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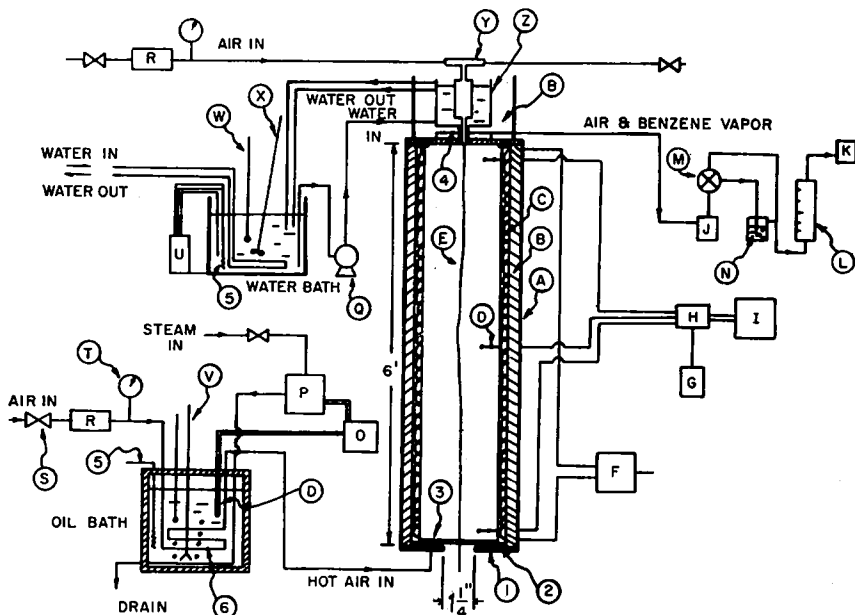


Fig. 1. Schematic diagram of extrusion device: (A) extrusion column; (B) insulation; (C) heating tape; (D) thermocouple; (E) fiber; (F) Powerstat; (F) ice bath; (G) nine-way switch; (I) potentiometer; (J) suction flask; (K) water suction; (L) rotameter; (M) three-way stopper; (N) chemical solution; (O) temperature controller; (P) Magnatrol valve; (Q) pump; (R) regulator; (S) valve; (T) pressure gage; (U) temperature controller; (V) air agitator; (W) thermometer; (X) stirrer; (Y) extrusion head; (Z) extrusion jacket; (1) asbestos plate; (2) jacket; (3) air distributor; (4)  $\frac{1}{4}$  in. elbow; (5) heater; (6) 30-ft.,  $\frac{3}{8}$ -in. copper tubing.

Figure 1 is a schematic of the experimental apparatus. Poly(methyl methacrylate) solutions in benzene were extruded from a single orifice ( $\frac{1}{60}$  in. in diameter) into a glass column wrapped with Nichrome heating wire and insulation. Heated air was passed up through the column countercurrent and parallel to the extruded fiber.

Experiments were made with various column lengths. The procedure was to start the extrusion and take samples of the extruded fiber. The fiber was immediately weighed and then reweighed after thoroughly drying the sample. The difference in weight was the amount of benzene present. Such samples were taken until the apparatus reached a steady state. Steady-state results were then recorded.

The exiting heated air that had passed through the column was also analyzed intermittently by using a wet chemical method.<sup>22</sup>

Figure 2 gives plots of average fiber concentration versus column length. These concentrations were determined by weighing. Data obtained by the intermittent wet chemical technique were somewhat lower. However, the same general behavior with regard to curve shape was observed. The data of Figure 2 resemble somewhat a drying curve with one principal ex-

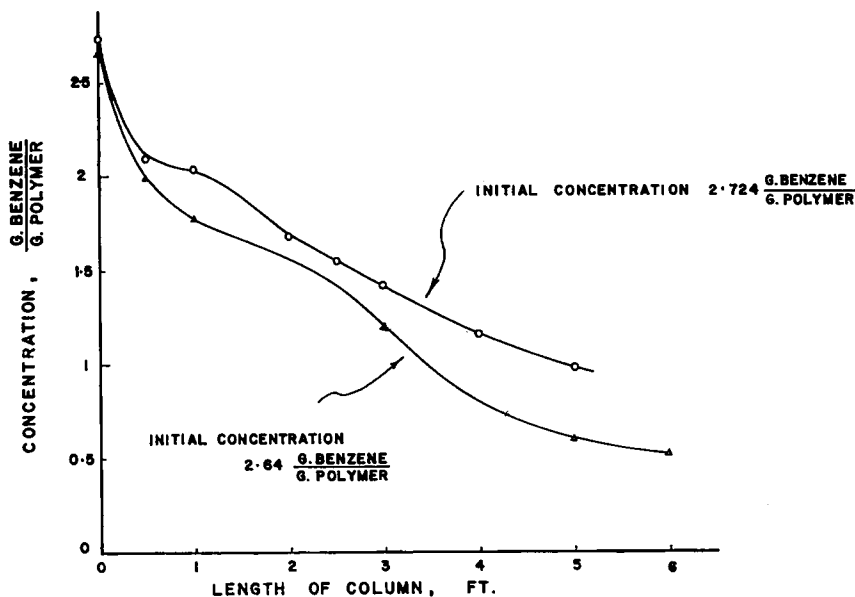


Fig. 2. Average fiber concentration curves.

ception—the appearance of a plateau after the rapid, initial change in concentration. This plateau has been observed in industrial operations.<sup>23</sup>

It was decided to treat the dry spinning process as being primarily a problem in mass transport. This was done for two reasons. First, the work of Fok and Griskey<sup>20</sup> had demonstrated that the small fiber diameter offered only negligible resistance to energy transfer. This then meant that the solvent could be easily and quickly evaporated but still must diffuse through the fiber at some given rate. Furthermore, the velocity profile in the extruded solution would initially be flatter than parabolic because of the non-Newtonian nature of the solution and would be rapidly converted to a flat profile because of the solidification of the fiber. As a result of the rapid heat transfer and the flat velocity profile, the equation of continuity of species<sup>24</sup> itself would properly describe the situation:

$$\frac{\partial C}{\partial t} + V_r \frac{\partial C}{\partial r} + \frac{V_\theta}{r} \frac{\partial C}{\partial \theta} + V_z \frac{\partial C}{\partial Z} = D$$

$$\times \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial Z^2} \right] + R_A \quad (1)$$

where  $C$  is the concentration of A (in moles/cubic centimeter),  $t$  is time (in seconds),  $r$  is the radial dimension (in centimeters),  $V_r$  is the velocity component in the radial direction (in centimeters/second),  $\theta$  is the angular dimension,  $V_\theta$  is the  $\theta$ -direction velocity component (in centimeters/second),  $Z$  is the axial dimension,  $V_z$  is the velocity component in the axial

direction (in centimeters/second),  $D$  is the diffusivity (in square centimeters/second), and  $R_A$  is the molar rate of production of A by chemical reaction.

Equation (1), which assumed constant density and diffusivity, was further simplified by assuming (1) steady state,  $\partial C/\partial t = 0$ ; (2) no diffusion of air into the fiber; (3) no chemical reaction,  $R_A = 0$ ; (4) solvent diffusing was a vapor; (5)  $V_r = V_\theta = 0$ ; velocity component only in  $Z$  direction; (6)  $V_z = \text{constant}$ ; that is, average fiber velocity was constant and flow was plug flow; (7)  $D(\partial^2 C/\partial Z^2)$  was small compared to  $V_z(\partial C/\partial z)$ ; that is, mass transport by convection in the  $Z$  direction exceeded mass transport by diffusion; (8) no mass transport in the  $\theta$  direction,  $D/r^2(\partial^2 c/\partial \theta^2) = 0$ . This yielded

$$\frac{\partial c}{\partial z} = \frac{D}{V_z} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) \right] \quad (2)$$

Most of the above assumptions are similar to those usually taken in problems of this type.

Equation (2) was solved analytically by using the following boundary conditions: (1)  $C = C_0$  at  $Z = 0$ , all  $r$ ; (2)  $C$  is finite at  $r = 0$ , all  $Z$ ; (3)  $C = 0$  at  $r = R$ , all  $Z$ . Here  $C_0$  is the initial concentration of A and  $R$  is the outside radius (in centimeters).

The first two conditions are straightforward. The third, however, needs some comment. There certainly would be some concentration of solvent at the outermost radius of the fiber. It was believed, however, that diffusion from this point to the surrounding air would be much more rapid than diffusion through fiber. Hence, the concentration at the outside diameter should be much lower than those across the fiber diameter helping to justify the use of this condition. It should also be noted that the third boundary makes the equation solvable analytically—otherwise some form of numerical analysis would have to be used.

The solution of eq. (2) was

$$C = C_0 \sum [2/\mu_n J_1(\mu_n)] [J_0(\mu_n r/R)] \exp \{ -(\mu_n/R)^2 (DZ/V_z) \} \quad (3)$$

where  $J_0$ ,  $J_1$  are Bessel functions of the first kind for zero and first order, respectively;  $\mu_n$  is the solution of the equation  $J_0(X) = 0$ .

The above series converges rapidly, and generally the first four terms are sufficient. Concentration profiles were calculated by using eq. (3) and various diffusivity values. A number of different diffusivities were considered, since previous work<sup>25</sup> on diffusion of organic vapors in acrylic polymers had indicated values ranged from 1 to  $5 \times 10^{-5}$  cm.<sup>2</sup>/sec. The velocity values used in eq. (3) were not corrected for changes in fiber diameter and volumetric flow rate.

Figure 3 shows computed curves of average fiber concentrations plotted together with experimental data. As can be seen, no one calculated curve would match the experimental. Actually a combination of the  $2 \times 10^{-6}$

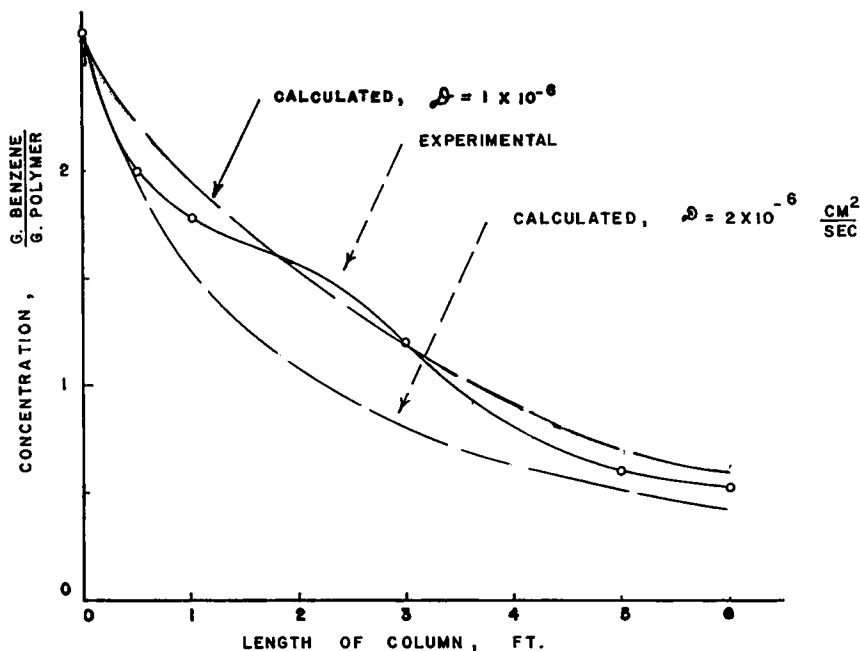


Fig. 3. Average concentration of fiber.

cm.<sup>2</sup>/sec. curve and a  $1 \times 10^{-6}$  cm.<sup>2</sup>/sec. curve would fit the experimental data. The lower diffusivity would hold at the longer column lengths. There is physical precedence for this, since the fiber is more like a solid at the longer lengths and should hence have a lower diffusivity.

It also can be noted that the shape of the experimental curve would not be exactly matched even if different diffusivities were used for various column lengths. Thus, the foregoing approach appears to give acceptable result of only a semiquantitative nature.

In spite of not being completely satisfactory the foregoing did at least give credibility to some of the assumptions made earlier. It was believed that a reconsideration of the solution of eq. (2) might lead to a more satisfying result. It was decided to use eq. (2) with the first two boundary conditions specified earlier but to substitute a new condition for the former assumption of zero concentration at  $r = R$ .

$$C = f(Z) \text{ at } Z = Z, r = R \quad (4)$$

In addition, changes in fiber diameter and volumetric flow rate were to be considered. These adoptions now meant definitely that eq. (2) had to be solved by numerical methods. In order to do this, eq. (2) was first transformed

$$\frac{\partial^2 c}{\partial \phi^2} + \frac{1}{\phi} \frac{\partial c}{\partial \phi} - \frac{Q}{\pi D \rho} \frac{\partial C}{\partial Z} = 0 \quad (5)$$

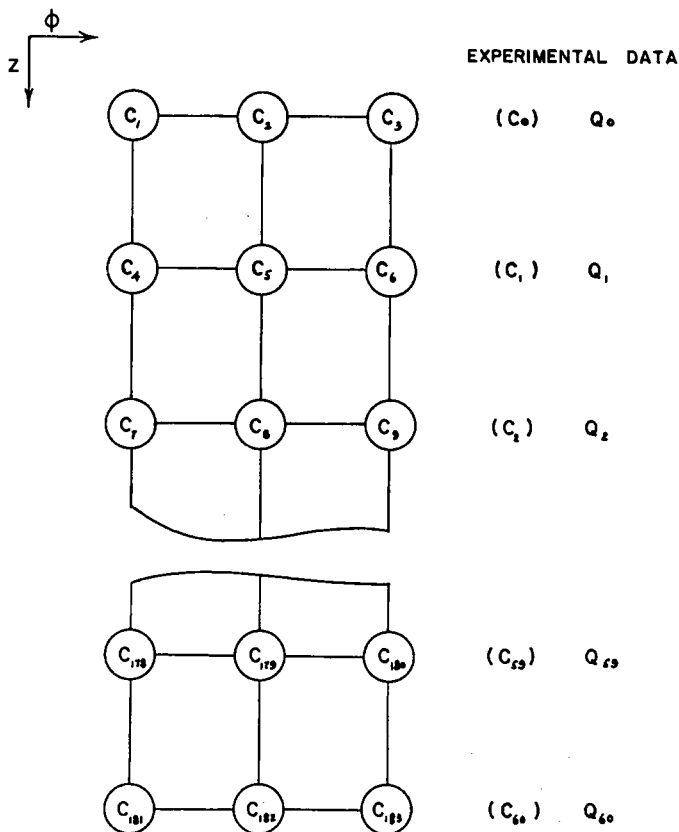


Fig. 4. Scheme for determination of fiber point concentration.

where

$$\phi = r/R$$

and  $Q$  is the volumetric flow rate,

$$Q = R^2 V_z \pi \rho$$

Then, defining  $C_m^n$ , the concentration of A at  $n$  ( $Z$  position) and  $m$  ( $r$  position)

$$C_m^n = C(\phi_0 + m\phi, Z_0 + nZ)$$

and using the Gregory-Newton formula<sup>26</sup> yields

$$C_{m+1}^n \left[ \frac{1}{(\Delta\phi)^2} + \frac{1}{m(\Delta\phi)^2} \right] + C_m^n \left[ -\frac{2}{\Delta\phi} - \frac{1}{m(\Delta\phi)^2} + \frac{Q}{\pi\rho D\Delta Z} \right] \\ + C_{m-1}^n \left[ \frac{1}{(\Delta\phi)^2} \right] - C_m^{n+1} \left[ \frac{1}{\Delta Z} \frac{Q}{\pi\rho D} \right] = 0 \quad (6)$$

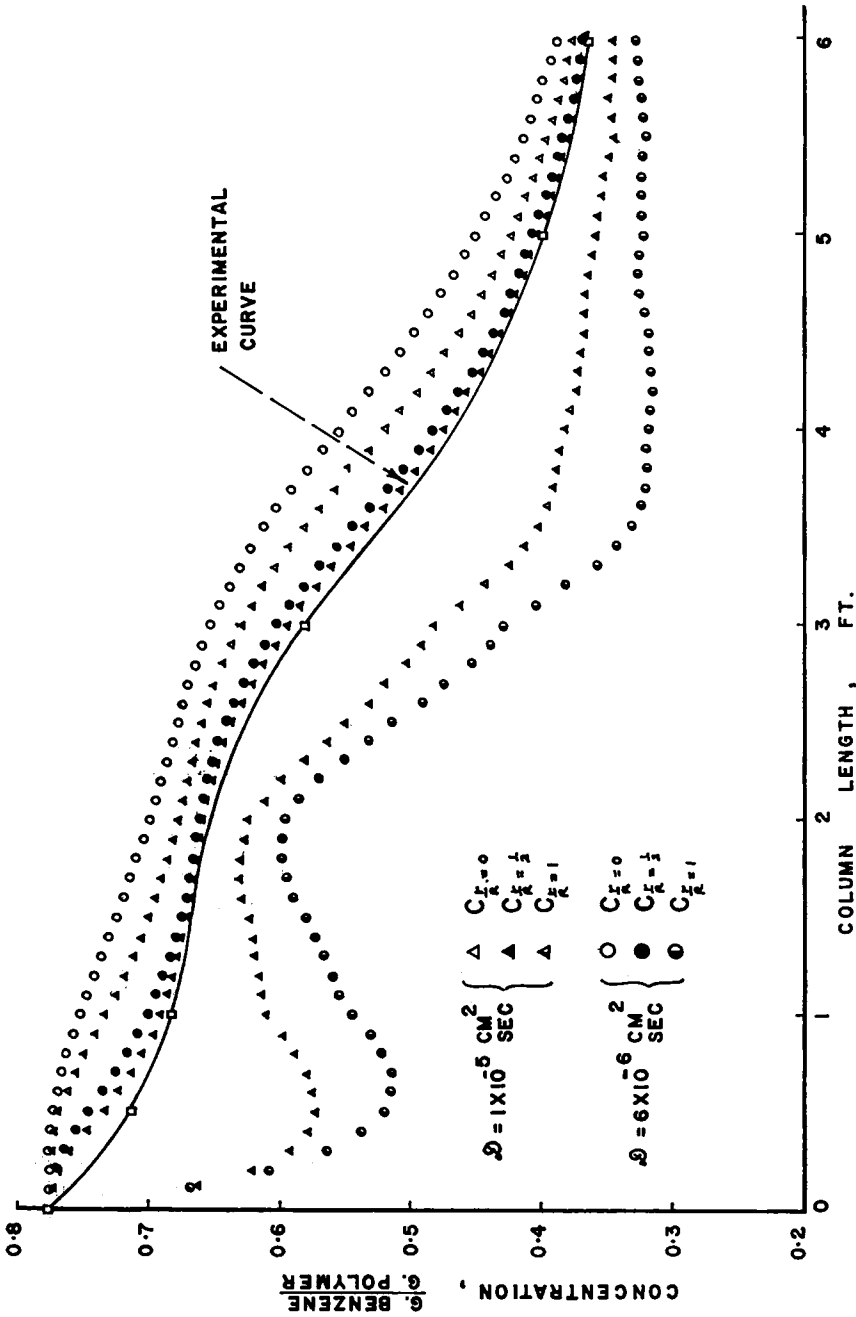


Fig. 5. Analytical concentration distribution curves.

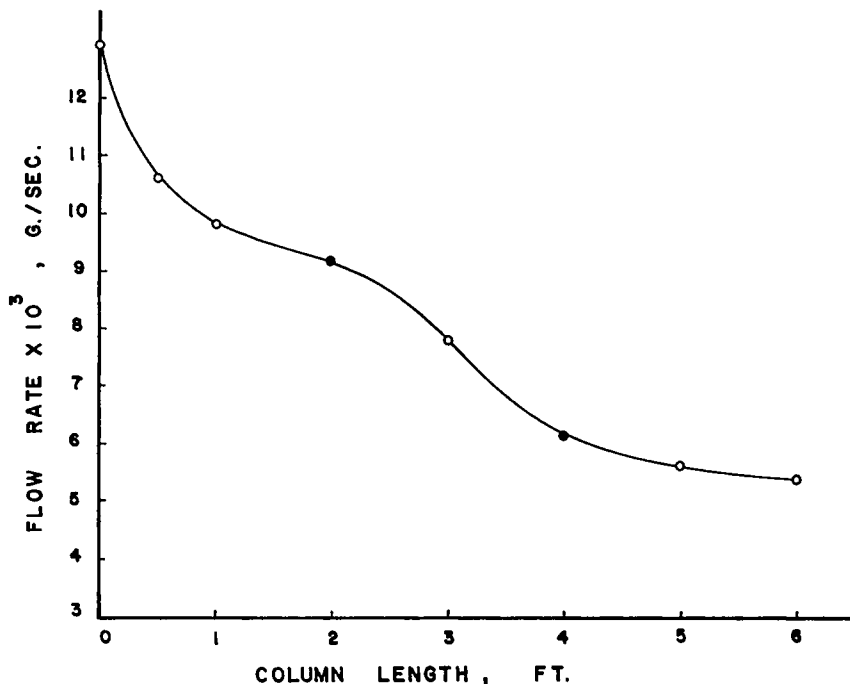


Fig. 6. Flow rate of polymer solution.

$Q$  as a function of  $Z$  was obtained experimentally. The diffusivity as pointed out earlier probably lay in the same range as that for organic vapors in acrylics, i.e.,  $1-5 \times 10^{-5}$  cm.<sup>2</sup>/sec. Also, average concentration values were available from experimental data.

The scheme used to compute point concentration in the fiber was to divide the filament into two segments from the center to the outside radius and into ten segments for each foot of length. A representation of the scheme is given in Figure 4.

Initially  $C_1$ ,  $C_2$ , and  $C_3$  (at  $Z = 0$ ) of Figure 4 are known.  $C_4$  and  $C_5$  can be computed by using the previously derived equation together with eq. (7):

$$C_0^n \left[ \frac{Q}{\pi \rho \Delta Z} - \frac{4}{(\Delta \phi)^2} \right] + \frac{4}{(\Delta \phi)^2} C_1^n - \frac{Q}{\pi \rho D \Delta Z} C_0^{n+1} = 0 \quad (7)$$

which held at  $\phi = 0$  ( $m = 0$ ,  $\partial c / \partial r = 0$ ). This still, however, left  $C_6$  as an unknown. It was then assumed that the average fiber concentration could be represented by Simpson's rule. This assumption made it possible to calculate  $C_6$ .

The same procedure was followed until all  $C$ 's at each  $Z$  were computed.

Figure 5 shows an experimentally determined curve of average concentrations versus column length. Also shown are calculated point concentrations at  $r/R$  values of 0, 1/2, and 1 for two different diffusivities. The



calculated average concentrations were identical for all diffusivities within this range ( $6 \times 10^{-6} \text{ cm.}^2/\text{sec.} \leq D \leq 1 \times 10^{-5} \text{ cm.}^2/\text{sec.}$ ).

The revised approach to solution of eq. (2) produced a more satisfactory solution. First, one diffusivity could be used for the entire column length. Next, the calculated average concentrations were matched identically to the experimental curve. The reason for the excellent match can be seen in Figure 6 which is a plot of experimentally determined volumetric flow rates versus column length. As can be seen there is a definite plateau occurring which matches the plateau of the concentration curve. Hence, the numerical analysis solution which considered such changes correctly predicted the shape of the average concentration curve while the analytical solution of eq. (2) which did not consider volumetric flow rate changes in turn did not match the experimentally determined shape.

Another feature of Figure 5 merits discussion—the  $r/R = 1$  curves. Concentration data calculated for both diffusivities fall well below the data at  $r/R = 0$  and  $r/R = 1/2$ . This appears to be in keeping with physical reality, since diffusivities in air are of the order of  $10^{-1} \text{ cm.}^2/\text{sec.}$  as compared to  $10^{-5} \text{ cm.}^2/\text{sec.}$  in the fiber. The net effect of reduced diffusivity in the fiber is to drive the  $r/R = 1$  concentration down.

As pointed out earlier, the paper of Sano and Nishikawa<sup>21</sup> considered residual solvent concentrations in dry spun fibers for a variety of spinning conditions. However, they treated their data only in a rough empirical manner, correlating the logarithm of solvent concentration with column length divided by the product of fiber density and cross-sectional area. It should be noted that this type of relation is a simplification of eq. (3) in which the logarithm of solvent concentration would be related to column length  $Z$ .

The present work is difficult to evaluate. The possibility, for example, of experimentally determining point concentrations within a spinning fiber is a remote one. In spite of this and other difficulties in confirming the preceding, certain points, however, can be made. First of all, a solution of the equation of the continuity of species appears to yield acceptable calculated average concentration behavior for dry spinning. Furthermore, the assumption of rapid heat transfer, vaporization of a solvent, and subsequent mass transfer seems to be an appropriate mechanism for the dry spinning process. Next, the diffusivities used to compute the results were of the same order of magnitude as those determined experimentally. Finally, and perhaps most important, this work enables an important industrial process to be treated in an engineering sense rather than as an art.

### References

1. A. Ziabicki, *Chemia Stoswana*, **5**, 676 (1961).
2. A. Ziabicki and K. Kedzierska, *Kolloid-Z.*, **171**, 51 (1960).
3. A. Ziabicki and K. Kedzierska, *Kolloid-Z.*, **171**, 111 (1960).
4. A. Ziabicki, *Kolloid-Z.*, **175**, 14 (1961).
5. A. Ziabicki, *Kolloid-Z.*, **179**, 116 (1961).
6. J. C. Slattery, *A.I.Ch.E. J.*, **12**, 456 (1966).

7. E. W. Andrews, *Brit. J. Appl. Phys.*, **10**, 39 (1959).
8. O. L. Anderson, *J. Appl. Phys.*, **29**, 9 (1958).
9. S. Kase and T. Matsuo, *J. Polymer Sci. A*, **3**, 2541 (1965).
10. J. Crank, *Phil. Mag.*, **38**, 794 (1948).
11. J. Crank, *Phil. Mag.*, **39**, 140 (1948).
12. J. Crank, *Phil. Mag.*, **39**, 362 (1948).
13. A. H. Wilson, *Phil. Mag.*, **39**, 48 (1948).
14. C. W. Reese and H. Eyring, *Textile Res. J.*, **20**, 743 (1950).
15. S. M. Katz, E. T. Kubo, and J. H. Wakelin, *Textile Res. J.*, **20**, 754 (1950).
16. H. Fujita, *Textile Res. J.*, **22**, 281 (1952).
17. A. V. Hill, *Proc. Roy. Soc. (London)*, **B104**, 41 (1929).
18. A. Takizawa, *Sen-i Gakkaishi*, **16**, 842 (1960).
19. A. Takizawa, *Sen-i Gakkaishi*, **16**, 950 (1960).
20. R. G. Griskey and S. Y. Fok, *Appl. Sci. Res.*, **16**, 141 (1966).
21. Y. Sano and S. Nishikawa, *Kagaku Kogaku*, **30**, 245 (1966).
22. S. Y. Fok, Ph.D. Dissertation, Virginia Polytechnic Institute, Blacksburg, Virginia, 1965.
23. R. G. Griskey, Celanese Fibers Corporation, unpublished data.
24. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960, p. 559.
25. G. Y. Ryskin, *Zh. Tekh. Fiz.*, **25**, 458 (1955).
26. K. S. Kunz, *Numerical Analysis*, McGraw-Hill, New York, 1957, p. 275.

### Résumé

La présente recherche considérait le transfert de masse au cours de la formation des fibres avec le processus de filature sèche du point de vue expérimental et théorique. Les résultats expérimentaux pris pour le filage sec de solutions benzéniques de polyméthacrylate de méthyle ont été interprétés avec l'équation de la continuité des espèces. Deux solutions d'équation ont été appliquées aux résultats. La première, une solution analytique avec un nombre d'hypothèses et de restrictions, fournissait de bons résultats semiquantitatifs. L'autre solution, déterminée par analyse numérique avec quelques limitations, fournissait des résultats calculés qui prédisaient exactement le comportement de la fibre moyenne.

### Zusammenfassung

In der vorliegenden Untersuchung wurde die Massenübertragung während der Faserbildung beim Trockenspinprozess experimentell und theoretisch behandelt. Auf Versuchsdaten über das Trockenspinnen von Polymethylmethacrylat-Benzollösungen wurde die Kontinuitätsgleichung für die Spezies angewendet und zwar in Form zweier Lösungen dieser Gleichung. Die erste, eine analytische Lösung, mit einer Anzahl von Einschränkungen und Annahmen, lieferte gute, halb-quantitative Ergebnisse. Die zweite, durch numerische Analyse mit weniger Einschränkungen erhaltene Lösung ergab berechnete Werte, welche eine exakte Voraussage des Verhaltens einer mittleren Faser-Lösungsmittelkonzentration bildeten.

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