The Kinetics of Sorption by Ion Exchange Resin Beds

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The kinetics of sorption of dilute aqueous solutions of acetone, *n*-propanol, ethylene glycol, and glycerine by packed beds of Dowex 50W-X8 (H^+) resin have been investigated experimentally. Data indicate that intraparticle diffusion of the solute is rate controlling and that density mixing and nonlinear equilibrium effects must be considered in analyzing this type of operation.

In recent years the feasibility of separating aqueous solutions of ionic and non-ionic solutes by means of ion exchange resins has been well demonstrated. This technique, known as ion exclusion, is based on the selective sorption exhibited by ion exchangers for various solutes. Successful application of this separation process requires a prediction of the shape of the effluent concentration-time profile for a packed column of ion exchange resin fed by a specified feed solution. Such predictions can be made if the equilibrium distribution of solute between resin and solution phases and the mass transfer rate processes involved are known. Although early workers (*10, 14*) showed that in some cases equilibrium data alone are sufficient for such analysis, it is generally necessary to consider also the kinetics of the sorption process in order to permit an accurate calculation of the breakthrough curves (*11, 13, 5*).

It is well known that information on the basic processes involved can be inferred from sorption data for single-solute systems. Thus, the object of this paper is to present some new single-solute sorption data and to demonstrate how these data may be characterized by a suitable mathematical model.

On the basis of previous work in this and related areas, it is clear that an appropriate model must consider the resistance to mass transfer of solute molecules offered by intraparticle diffusion as well as by diffusion across the slow moving liquid film in contact with the resin particle surfaces. Models based on film and/or particle diffusion mechanisms have been previously formulated and utilized by several workers (*8, 3, 1, 6, 7, 12*) to calculate theoretical breakthrough curves for systems exhibiting linear and specific types of nonlinear equilibrium behavior. In addition, such models have been used to analyze experimental data with varying degrees of success. Tayyabkhan (*11*) first considered intraparticle diffusion to be the rate controlling mechanism in his analysis of existing data for the ethylene glycol–water–Dowex 50(H^+) system and the glycerine–sodium chloride–water–Dowex 50(Na^+) system. He was able to obtain fair agreement of experimental data and calculated curves only for the first system, while demonstrating the more complex interactions which are to be found in the second, two-solute system.

Vassiliou and Dranoff (*13*) and Griffin and Dranoff (*5*) used a model incorporating a linear rate equation characteristic of film diffusion in analyzing data for the glycerine-water system with Amberlite IR-120(H^+) and Dowex 50W(H^+) resins. They obtained reasonable agreement between experimental and predicted breakthrough curves. They were able to correlate their results in terms of a rate coefficient which varied with flow rate through the column at low flow rates but was constant in higher regions. The latter behavior suggested that an intraparticle rate mechanism might be involved. Similar data were obtained for both saturation and elution experiments although the elution coefficients were consistently higher.

The present study was initiated in order to extend this single-solute work to other systems and to investigate more thoroughly the rate model involved. The solutes studied were acetone, *n*-proponal, and ethylene glycol, while the resin used was Dowex 50W-X8(H^+).

THEORY

Since the analysis of the transient operation of packed column devices has been well presented previously, only the basic assumptions and differential equations will be noted here. The physical system under consideration consists of a vertical tube packed with spherical ion exchange particles of uniform size. Feed solutions are introduced at the top of the column and flow down through the bed with a constant velocity, uniform over the cross section. Compositions throughout the two phases in the column are considered to be initially uniform and in equilibrium, and the feed composition is considered to undergo a step change, thus initiating the transient behavior of the column. In the analysis to be mentioned below, it is further assumed that the particles do not change size during the saturation or elution steps, there is negligible longitudinal diffusion, operation is isothermal, and the equilibrium is linear, that is, $K_d = (q/c)_{eq}$.

The basic differential material balance equation relating the bulk concentrations in both phases is

$$\frac{u}{A}\frac{\partial c}{\partial z} + \epsilon\frac{\partial c}{\partial t} + f\frac{\partial Q}{\partial t} = 0 \qquad (1)$$

The rate of transfer of solute to the resin phase may be described by an equation for the film diffusion process

$$\frac{\partial Q}{\partial t} = k\,(c - q_s/K_d) \qquad (2)$$

While the instantaneous local resin phase composition is governed by the usual transient diffusion equation

$$\frac{\partial q}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right). \qquad (3)$$

$$\text{Note: } Q = \frac{3}{R^3}\int_0^R q\,r^2 dr \qquad (4)$$

The necessary boundary and initial conditions for this operation are

$$c\left(z, 0 \leq t \leq \frac{\epsilon Az}{u}\right) = c_i \tag{5}$$

$$c(o, t) = c_o \tag{6}$$

$$q\left(r, z, o \leq t \leq \frac{\epsilon Az}{u}\right) = q_i \tag{7}$$

$$q(o, z, t) = \text{finite} \tag{8}$$

$$q(R, z, t) = q_s \tag{9}$$

Equations (1) through (9) may be solved to predict the breakthrough curve for a column of finite length in terms of the indicated system parameters. Such a solution was first obtained by Rosen (6, 7), although solution of the equations for the simpler film diffusion case ($D = \infty$, $Q = q$) was reported many years earlier by Schumann (8).

If the solution concentration is replaced by a dimensionless variable defined as $(c - c_i)/(c_o - c_i)$, the same equations may be used for analysis of both saturation and elution operations.

The values of the parameters K_d, D, and k may be found for a given system by analysis of experimental breakthrough curves. The equilibrium distribution coefficient is first calculated from an overall material balance as indicated in Equation (10).

$$K_d = \frac{uT - V\epsilon - u\int_o^T \frac{c - c_i}{c_o - c_i}\,dt}{Vf} \tag{10}$$

The integral term may be easily evaluated by graphical or numerical means. Thereafter, the rate parameters are determined by a graphical curve matching technique. Details of this procedure are given elsewhere (2).

EXPERIMENTAL

Experimental sorption data were obtained for each of the three solutes mentioned earlier, as well as for glycerine. The latter, taken to check this work with that of Griffin (4), were obtained at 30°C., while the other systems were studied at 25°C. Feed solutions were prepared from reagent grade solutes dissolved in deionized water. Only dilute solutions were used, with concentrations below 0.08 g. of solute/ml. of solution.

The packed column used in this work was a Pyrex tube 90.8 cm. long and 2.54 cm. in diameter. Feed liquid was pumped to the top of the column from a storage bottle immersed in a constant temperature bath. Water from the bath was also circulated through a jacket surrounding the column for temperature control. Feed flow rates ranged from 5.29 to 93.8 cc./min. The column effluent was sampled at timed intervals by a fraction collector and the samples were later analyzed by refractive index measurements. Concentrations were determined from previously measured calibration curves.

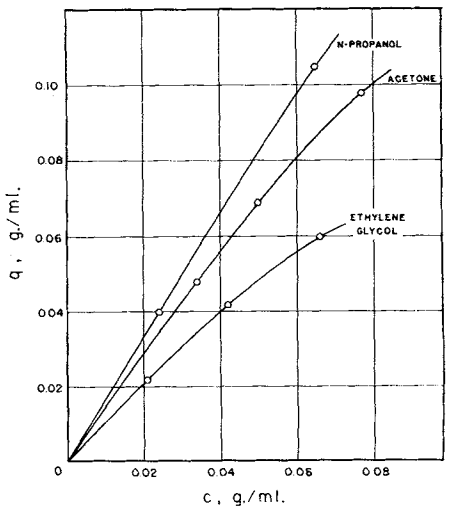

Fig. 1. Equilibrium distribution.

Table 1. Equilibrium Distribution Coefficients

Acetone		*n*-Propanol		Ethylene glycol		Glycerine	
Conc., g./ml.	K_d	Conc., g./ml.	K_d	Conc., g./ml.	K_d	Conc., g./ml.	K_d
0.077	1.27	0.065	1.62	0.063	0.95	0.063	0.64
0.050	1.38	0.024	1.66	0.042	1.00		
0.034	1.42			0.021	1.05		

The resin used was wet-screened in the H^+ form through U. S. Standard screens to obtain a narrow size distribution (20 to 30 mesh). The corresponding average particle diameter was 0.0696 cm. The bed was packed by allowing the resin to settle at random through the water-filled column. External and internal void fractions were determined later by previously described methods (13, 2) and found to be 0.389 and 0.395, respectively.

This equipment was used to make sixty-three saturation and elution runs, the experimental data for which are presented elsewhere (2). The breakthrough curves were then analyzed to determine the effective equilibrium distribution constants and the pertinent rate parameters.

RESULTS AND DISCUSSION

Distribution Coefficients

The appropriate values of K_d for each solute system were first found by analyzing the breakthrough curves according to Equation (10). Experiments were made at several feed compositions, and the corresponding equilibrium data are shown in Figure 1. It is apparent that the equilibrium relations are all slightly nonlinear exhibiting convex upward curvature. However, it would appear that the nonlinearity might be mild enough to permit the safe use of a linear approximation to these curves. With this point in mind, values of K_d were calculated at the various intermediate concentrations where data were obtained, and the results are tabulated in Table 1. Also shown in this table are data obtained for glycerine. The latter agree very well with the value of 0.63 reported by Griffin. It should be noted that the glycerine equilibrium data measured by Shurts and White (9) also display some curvature, being convex downward. The apparent effect of this curvature will be discussed below.

Mass Transfer Rate Parameters

Based on the results of Tayyabkhan, it was felt that intraparticle diffusion would be the rate-controlling process in this work. This was further substantiated by estimates of external film mass transfer coefficients based on existing correlations. Such calculations predicted coefficients thirty to fifty times larger than overall coefficients corresponding to the actual experimental data. However, in view of the earlier success of Vassiliou (13) and Griffin (5) in treating their data with the film diffusion model, considerable care was taken in checking the fit of experimental breakthrough curves to the solutions for both of these two limiting cases. After investigation it was found that the curves corresponding to the intraparticle diffusion model with no film resistance were considerably better in fitting the data. This is clearly indicated for a typical breakthrough curve presented in Figures 2 and 3. As shown it was possible to fit an entire curve with little or no deviation using this model, whereas the film diffusion model curves could be made to fit portions but not entire breakthrough curves. This was true over the entire flow rate

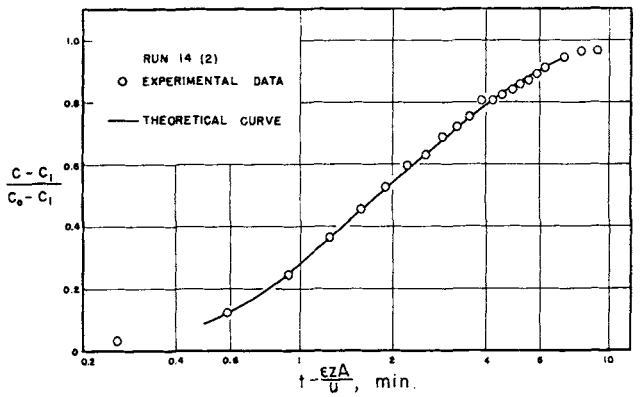

Fig. 2. Internal diffusion model fit to a typical breakthrough curve.

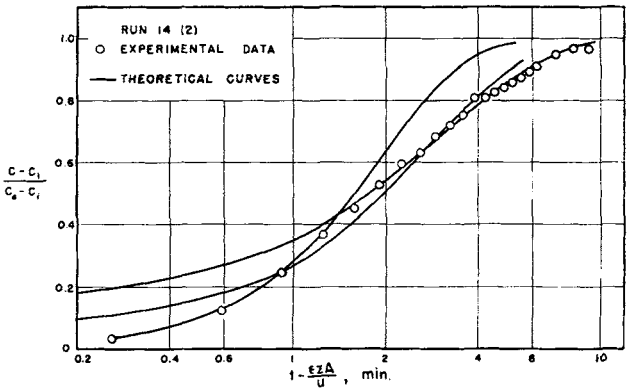

Fig. 3. Film resistance model fit to a typical breakthrough curve.

range investigated, although the fit of the film model was somewhat improved at low flow rates. In view of this behavior, the intraparticle diffusion model was chosen to represent the data and corresponding values of the intraparticle diffusivity were calculated for each run. The data obtained for acetone, *n*-proponal, and ethylene glycol are shown in Figures 4, 5, and 6, respectively. Both saturation and elution results are shown as functions of the Reynolds number for the conditions studied.

Additional saturation data were taken with the glycerine system to check the work of Griffin. His original data were reinterpreted using the diffusion model to permit a direct comparison, which is shown in Figure 7. The consistency of these results is clearly demonstrated in this figure.

The data of Figures 4 through 7 reveal some initially confusing results which require further explanation. It is the thesis of this paper that these results may all be rationalized in terms of the intraparticle diffusion model if one takes note of the specific nature of each system. First of all, both the acetone and *n*-proponal data show saturation behavior in which the effective diffusivity is independent of flow rate over the entire range studied. This is to be expected if the rate-controlling process is truly intraparticle diffusion. Furthermore, the corresponding diffusivities appear to be in a most reasonable range. The elution data for these two solutes exhibit a region of constant diffusivity at high flow rates, but show diffusivity decreasing as flow rate decreases in the low region. Although this type of behavior might indicate the increasing importance of a film diffusion mechanism, the lack of such response for the saturation data casts serious doubt on that interpretation. The ethylene glycol data of Figure 6 show converse trends, with the elution diffusivity independent of flow rate, while the saturation data vary. The same trend is shown by the glycerine system in Figure 7. (Note that the glycerine elution data of Griffin did not, on close examination, appear to be sufficiently self consistent to permit the construction of an elution curve on Figure 7.)

These results suggest that, although intraparticle diffusion is rate controlling in all the systems studied, some additional effects not associated with the sorption process must be at work in those runs which exhibit variable diffusivities. A distinct possibility is the occurrence of axial dispersion in the column such as might be caused by eddy mixing and channeling, molecular diffusion, and viscosity and/or density gradients in the fluids. Of these effects, the ones which might be expected to affect either saturation or elution experiments, but not both, are the existence of mixing due to density and viscosity gradients. It should be noted first that the densities of acetone and *n*-propanol are less than water, while those of ethylene glycol and glycerine are greater. For each of these solutes, the variation of D with flow rate occurred only in those types of runs (saturation or elution) in which a heavier fluid was fed at the top of the column. To illustrate the density effect further, runs were made with more dilute acetone solutions, thus decreasing the density differences between feed and eluting solutions. As shown in Figure 2 the diffusivity of the saturation runs agreed with previous values, while the elution data showed higher D values at low flow rates. Finally, additional experiments were performed in which only longitudinal dispersion was possible. These were carried out using beds of inert glass beads in the same apparatus. Runs of both saturation and elution types were made using feed solutions both heavier and lighter than eluting solutions. In all cases whenever the more dense liquid was fed to the column, the dispersion of the effluent curve was significantly greater than in the other case.

It thus seems evident that density mixing must be either accounted for or eliminated (by appropriate use of upflow or downflow operation) in order to permit a better agreement of the theoretical model and experimental data. The existence of viscosity gradients in the fluid may also lead to mixing. However, the present data do not appear to support the significance of this effect. Further investigation of the importance of both density and viscosity gradients is presently underway.

One additional feature of these data requires explanation. This is the difference observed in the diffusivities for saturation and elution runs in the high flow rate range

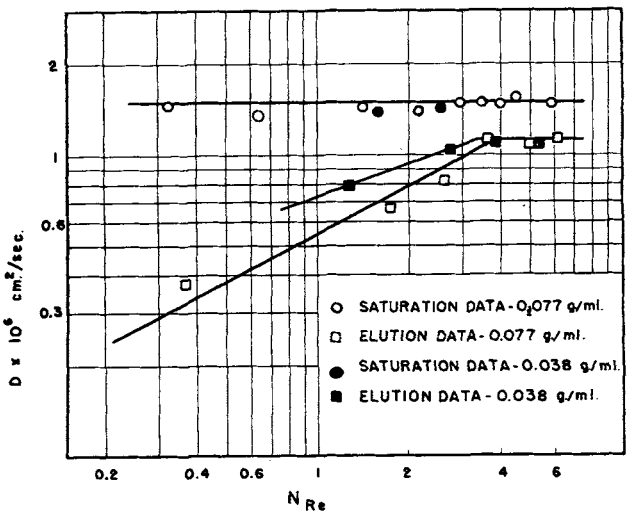

Fig. 4. Diffusivity of acetone in Dowex 50W-X8(H^+) at 25°C.

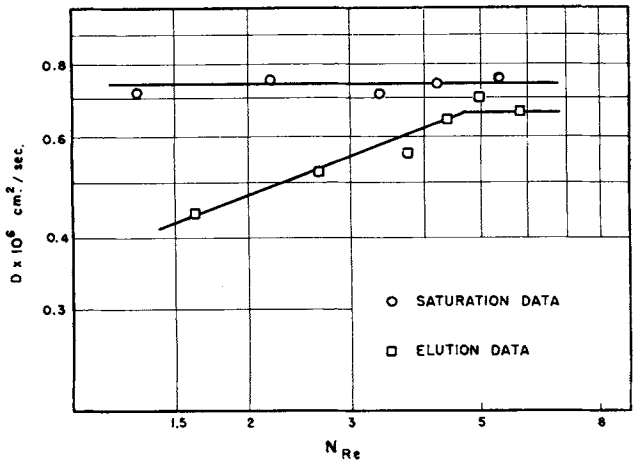

Fig. 5. Diffusivity of *n*-propanol in Dowex 50W-X8(H^+) at 25°C.

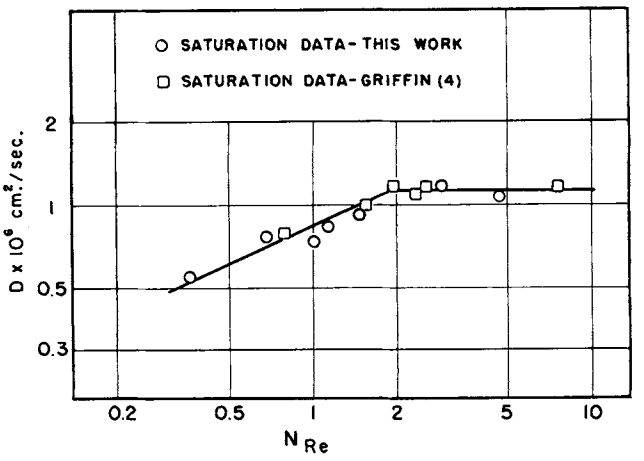

Fig. 7. Diffusivity of glycerine in Dowex 50W-X8(H^+) at 25°C.

where density dispersion should be negligible. Similar behavior has been noted previously by Vassiliou and Griffin in the glycerine system. Tayyabkhan also noted differences in the fit of leading and trailing curves to square wave ethylene glycol data, which might be explained by a difference in the effective diffusivities. Evidence from these studies suggests that this may be a result of the curvature of the equilibrium relation which has been here assumed to be linear. The acetone, *n*-proponal, and ethylene glycol systems all exhibit higher saturation diffusivities as well as equilibrium curves which tend to be convex upwards. Glycerine, on the other hand, has apparently higher elution diffusivities as well as a convex downward equilibrium curve. Qualitatively, this curvature can be seen to be responsible for the observed data. If one considers that there will be a small difference between the actual concentration at the surface of a resin particle and that calculated from the linear equilibrium assumed to represent the data, then it follows that the rate of diffusion into or out of the particle will be somewhat larger or smaller than that calculated from the theory. This will cause a change in the shape of the breakthrough curve and will result in an effective diffusivity correspondingly larger or smaller than the actual value. No quantitative estimate of this effect is presently possible without a recalculation of the breakthrough curves for a nonlinear equilibrium relation. In any case, it appears that the true intraparticle diffusivity should lie somewhere between the values found for saturation and elution experiments. For this reason, the values found in this work are so reported in Table 2. The data for *n*-proponal tend to uphold this explanation further, since this system has the most linear equilibrium curve and shows the least difference between saturation and elution diffusivities.

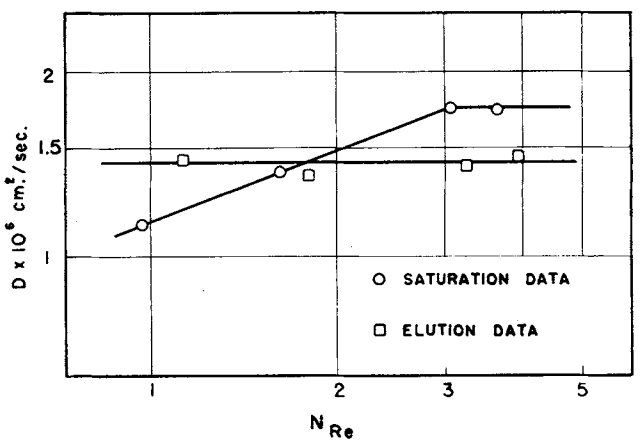

Fig. 6. Diffusivity of ethylene glycol in Dowes 50W-X8(H^+) at 25°C.

TABLE 2. INTRAPARTICLE DIFFUSIVITY

Solute	$D \times 10^6$, sq. cm./sec.
Acetone, 0.077 g./ml.	$1.13 < D < 1.50$
n-Propanol, 0.065 g./ml.	$0.66 < D < 0.74$
Ethylene glycol, 0.063 g./ml.	$1.42 < D < 1.75$
Glycerine, 0.063 g./ml.	$1.14 < D < 1.70$

CONCLUSIONS

Based on the data presented above, it is concluded that:

1. The rate of sorption of organic solutes by packed beds of ion exchange resins is controlled by intraparticle diffusion of the solute. Furthermore, the corresponding mathematical model produces breakthrough curves which can be fitted to experimental data with little or no deviation.
2. When fluids of different densities are used for saturation and elution, longitudinal dispersion due to density gradients is likely to have a significant effect on the spreading of the breakthrough curves. This tends to lower the observed diffusivity determined from the intraparticle diffusion model.
3. Slight nonlinearities in the equilibrium relation will cause deviations between diffusivities calculated from saturation and elution data. This does not however diminish the utility of the linear equilibrium model in representing and correlating actual breakthrough data.

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NOTATION

A = cross-sectional area of column, sq.cm.
c = bulk solution concentration, g./ml.
c_i = initial concentration of column solution, g./ml.
c_o = feed solution concentration, g./ml.
D = intraparticle diffusivity, sq.cm./sec.
D_p = particle diameter, cm.
f = internal void fraction, dimensionless

k = film coefficient, min.$^{-1}$
K_d = equilibrium distribution coefficient, $K_d = (q/c)_{equil.}$, dimensionless
q = solute concentration within resin, g./ml. of internal solution
q_i = initial internal concentration, g./ml.
q_s = internal concentration at surface of resin particle, g./ml.
Q = bulk resin phase concentration, g./ml. of internal solution
r = radial coordinate in resin particle, cm.
R = resin particle radius, cm.
$N_{Re} = \frac{D_p u \rho_{av}}{A \epsilon \mu_{av}}$ Reynolds number, dimensionless
t = time, min.
T = time required to saturate the column, min.
u = volumetric flow rate, cc./min.
V = total volume of packed bed, cc.
z = axial coordinate of column, cm.

Greek Letters

ϵ = external void fraction, dimensionless
μ_{av} = average solution viscosity, g./(cm.)(sec.)
ρ_{av} = average solution density, g./cc.

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Heat Transfer to Molten Flowing Polymers

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A precise, reproducible method has been developed for measuring temperature profiles in flowing molten polymers with heat transfer. Experimental data determined by this method showed that viscous dissipation occurred, but not at the level predicted theoretically. The difference between the actual and theoretical viscous dissipation was possibly due to flattening of fluid velocity profile, changing physical properties, and fluid viscoelasticity. Nusselt numbers calculated from the data checked theoretical Nusselt-Graetz solutions.

The transfer of heat to molten flowing polymers is an important factor in such polymer processing operations as extrusion and injection molding. The situation is a complex one because molten polymers are compressible and exhibit non-Newtonian and viscoelastic rheological behavior. In addition there is considerable viscous heat generation in such flow systems.

Previous studies of heat transfer to non-Newtonian fluids have generally considered polymer solutions where the effects of viscoelasticity, viscous heat generation, and compressibility are considerably reduced. These studies included the investigations of Winding, Kranich, and Dittman (*1*), Bonilla, Cervi, Colven, and Wang (*2*), Chu, Brown, and Burridge (*3, 4*), Pigford (*5*), Metzner, Vaughan, and Houghton (*6*), Christiansen and Craig (*7*), Petersen and Christiansen (*8*), Metzner and Gluck (*9*), and Oliver and Jensen (*10*).

A number of analytical solutions of the equations of energy and motion applicable to heat transfer to molten polymers have been published. These include the work of Topper (*11*), who considered systems with a heat generation term constant across a tube both for a parabolic velocity profile and potential flow; that of Lyche and Bird (*12*), who studied the Graetz-Nusselt problem for an incompressible power law fluid without heat generation; and various papers by Toor which dealt with the effect of expansion on temperatures with little heat generation (*13*), heat generation and conduction in a viscous compressible fluid (*14*), and heat transfer in forced convection with internal heat generation (*15*). None of the foregoing studies presented any experimental data other than calculated quantities.

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