

CRITICAL EFFECTS RESULTING FROM REACTION-INDUCED CHANGES IN VISCOSITY

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UDC 532.542:660.095.26

Chemical reactions induce changes in viscosity, this effect being quite pronounced in the case of polymerization processes. The fact that the coefficient of viscosity changes as the degree of chemical advancement increases gives rise to specific hydrodynamic effects in a flowing liquid. Some of these effects are discussed in the present paper.

1. Let us consider the passage of the reacting liquid through a tube. Let us designate by z_0 the tube length, by P_0 the pressure drop through the tube, by v the bulk flow rate per unit tube cross section, by t_0 the characteristic reaction time, by μ , μ_0 , and μ_* the instantaneous, initial, and final coefficients of viscosity, the latter measured at the end of the reaction, by r the tube radius, by z a distance measured from the tube entrance, and by η the degree of advancement of the reaction. Let the liquid density be considered as constant, so that v becomes identical with the mean flow rate.

Let us introduce the quantities

$$\kappa = P_0 / \left(8 \frac{\mu_0}{r^2} \frac{z_0}{t_0} z_0 \right); \quad \theta = \left(\frac{z_0}{v} \right) / t_0; \quad \omega = v / \left(\frac{z_0}{t_0} \right) = \theta^{-1}, \quad (1.1)$$

κ being the dimensionless pressure drop along the tube, ω the dimensionless stationary flow rate, and θ the dimensionless time of steady-state passage of the liquid through the tube.

In general, the pressure drop and the flow rate are related by the equation

$$\kappa = \lambda \omega, \quad (1.2)$$

λ being the dimensionless coefficient of resistance to liquid flow, a factor determined by the instantaneous viscosity distribution in the tube. If the viscosity is constant and the flow laminar, the Poiseuille law [1] requires that $\lambda = 1$.

A stationary flow will be established under constant pressure drop or flow rate. Here the value of λ will be a function of θ , the time of passage of the liquid through the tube, i.e.,

$$\lambda = F(\theta), \quad (1.3)$$

and can be determined experimentally.

The lack of thermal homogeneity in liquids undergoing exothermic reaction can render $F(\theta)$ indeterminate. Since, however, the characteristic aspects of the effects in question here can be brought out by study of simple systems, attention will be limited to the case in which $F(\theta)$ is well defined.

2. Let us now consider the liquid flow under a constant pressure drop. Here the stationary flow rate can be obtained by combining (1.2) and (1.3) to get

$$\kappa \theta = F(\theta). \quad (2.1)$$

Working in a θ , λ coordinate system, the solution of this equation is represented by the point of intersection of the graphing function curve $\lambda = F(\theta)$ and a straight line of slope κ passing through the origin.

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Technicheskoi Fiziki, No. 2, pp. 168-172, March-April, 1975. Original article submitted August 7, 1974.

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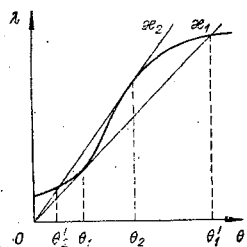


Fig. 1

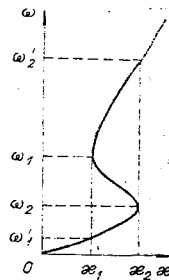


Fig. 2

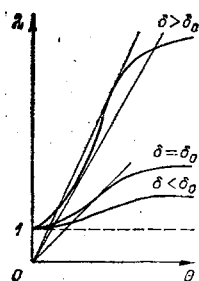


Fig. 3

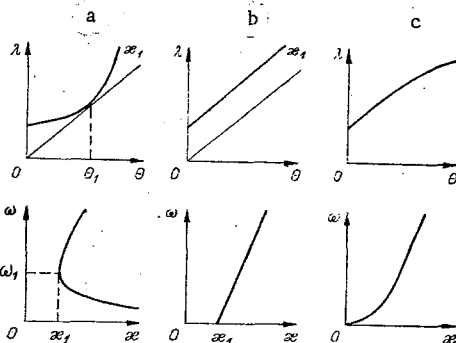


Fig. 4

Stationary flow can be established under any pressure drop, which is to say that there will be a solution of Eq. (2.1) for each value of κ . In certain cases, however, the solution of Eq. (2.1) will not be single valued. Let us now consider a situation of this type.

If Eq. (2.1) does have a single valued solution for each value of κ , the stationary flow rate will be a continuous function of the pressure drop; with a correct choice of drop value one can assure any desired value of the time of transit of the liquid through the tube, or, what is the same thing, any desired value of the degree of reaction advancement in the tube discharge.

Let it now be supposed that Eq. (2.1) has three different solutions with $\kappa_1 < \kappa < \kappa_2$. Graphically this is equivalent to saying that lines with these κ values each cut through the plotting function graph $\lambda = F(\theta)$ at three points (Fig. 1). Lines passing through the origin with slopes κ_1 and κ_2 will each cut through the $\lambda = F(\theta)$ curve at one point and be tangent to it at another. Parameter values for the points of tangency will be indicated by the use of subscripts 1 and 2, while parameter values for an intersection point will be indicated by a super prime.

Here the values of κ , θ satisfying Eq. (2.1) will plot up to a characteristic S-curve in the coordinates κ , $\omega = \theta^{-1}$ (Fig. 2). It is clear that the stationary value of ω will approach ω_1 by moving along the upper branch of this curve as κ falls and approaches κ_1 . Even an infinitesimal reduction of κ beyond this point must lead to a discontinuous alteration in the stationary value of ω , passage being from $\omega = \omega_1$ to $\omega = \omega'_1 < \omega_1$. The stationary value of ω is found on the lower branch of the S-curve for low κ 's such that $\kappa < \kappa_1$, remaining on this branch as κ rises to $\kappa = \kappa_2 > \kappa_1$. From this it can be concluded that there is an alteration in stationary states on passing through the interval $\kappa_1 < \kappa < \kappa_2$, the controlling factor being the direction of passage through this region. The passage from lower to upper branch of the S-curve occurs at $\kappa = \kappa_2$ and is accompanied by a discontinuous alteration in ω , change being from ω to $\omega = \omega'_2 > \omega_2$, with a corresponding alteration in the degree of advancement of the chemical reaction in the tube discharge.

Thus the existence of three solutions for Eq. (2.1) leads to hysteresis effects in the functional dependence of the liquid flow rate, the time required for passage through the tube, and the degree of advancement of reaction in the tube discharge on the pressure drop.

The pressure drop corresponding to a discontinuous decrease, or a discontinuous increase, in the flow rate will be designated as a lower, or upper, critical value, as the case may be. For fixed flow rate, these critical values correspond, respectively, to minima and maxima on the curve showing stationary pressured drop plotted as a function of rate.

Stationary states corresponding to points lying between the two branches of the S-curve of Fig. 2 cannot be reached by altering the pressure drop. These states are also inaccessible to flow at fixed pressure drop.

3. A simple one-dimensional model can be used to illustrate these points.

Let us assume the temperature, concentration, and viscosity to each be constant, over the tube cross section, as is generally done in setting up a one-dimensional model of the tubular reactor. Supposing the flow to be stationary and laminar, the pressure gradient dP/dz is given by [1]

$$dP/dz = -8\mu v \quad (3.1)$$

Integrating (3.1) along the tube, and introducing the dimensionless parameters of (1.1), leads to

$$\lambda = \int_0^{z^*} \mu dz / \mu_0 z_0, \quad (3.2)$$

i.e., λ becomes identical with the dimensionless viscosity.

Let us now assume an isothermal flow in which effects from transverse diffusion can be neglected. In the steady state, the degree of advancement of the reaction and the liquid viscosity at any point will be determined by z/v , the time required for the liquid to reach the section in question. Here the z/v dependence of the viscosity is of exactly the same form as the time dependence of the degree of advancement in a stationary liquid, this latter written as

$$\mu = \mu_0 f(\tau), \quad (3.3)$$

with $\tau = t/t_0$; $f(0) = 1$; $f(\infty) = \mu_*/\mu_0$. By combining (3.2) and (3.3), one obtains the following expression for the $F(\theta)$ function of (1.3):

$$F(\theta) = \theta^{-1} \int_0^{\theta} f(\tau) d\tau, \quad F(0) = 1, \quad F(\infty) = \mu_*/\mu_0.$$

Let us rewrite the expression for the time dependence of the viscosity, i.e., (3.3), in the form

$$\mu/\mu_0 = f(\tau) = 1 + \delta f_0(\tau), \quad (3.4)$$

$\delta = (\mu_* - \mu_0)/\mu_0$ being the relative alteration in the viscosity, and $f_0(\tau)$ a function describing the time variation of this latter quantity, with $f_0(0) = 0$, $f_0(\infty) = 1$. For low values of η , the relation between the viscosity and the degree of advancement of the reaction can be approximated by a power function. Let us now enter (3.4), setting

$$f_0 = \eta^\nu, \quad \nu < 1 \quad (3.5)$$

and considering a first-order reaction with

$$d\eta/d\tau = 1 - \eta. \quad (3.6)$$

The resulting equation will have the form

$$d^2f/d\tau^2 = \delta \nu \eta^{\nu-2} (1-\eta)(\nu-1-\eta\nu).$$

Assume $\nu > 1$ and $\delta > 0$. Since $\eta < (\nu-1)/\nu$, $d^2f/d\tau^2 > 0$, and

$$\frac{d^2F}{d\theta^2} = \theta^{-3} \int_0^{\theta} \tau^2 \frac{d^2f}{d\tau^2} d\tau,$$

the function $F(\theta)$ is convex downward for small values of θ , and $d^2F/d\theta^2 > 0$. When δ is sufficiently large ($\delta > \delta_0$), Fig. 3 shows that various lines fanning out from the origin will cut the graphing function curve $\lambda = F(\theta)$ in several points, i.e., Eq. (2.1) will have multiple roots. The value of δ_0 is determined by the relative alteration in viscosity as measured by the dimensionless time τ , being entirely independent of t_0 , the absolute characteristic time for the chemical reaction.

For the case of the zero-order reaction with the liquid viscosity-degree of advancement relation satisfying the power-function relation of (3.5), i.e., with

$$\mu/\mu_0 = f(\tau) = \begin{cases} 1 + \delta \tau^\nu & \text{when } \tau \leq 1, \\ 1 + \delta = \mu_*/\mu_0 & \text{when } \tau > 1, \end{cases} \quad (3.7)$$

Eq. (2.1) can be simplified considerably, the expressions for the critical parameters taking the form

$$\delta_0 = \frac{\nu+1}{\nu-1}; \quad \kappa_1 = \frac{\nu}{\nu-1} \left(\frac{\delta}{\delta_0} \right)^{1/\nu}; \quad \kappa_2 = \frac{\nu+1}{\nu} \frac{(1+\delta)^2}{4\delta}, \quad (\nu > 1). \quad (3.8)$$

Increasing the rate of increase of the viscosity with respect to time diminishes the value of δ_0 at which critical effects put in their appearance. The value of δ_0 is, however, limited on the lower side, passage to ∞ in (3.7) and (3.8) showing that $\nu \rightarrow \infty$ for even the most abrupt increase in viscosity. Critical effects do not arise when it is a matter of a viscosity which diminishes with increasing degree of advancement.

4. There are cases in which the "liquid" is no longer fluid at the end of reaction, a situation formally covered by the condition $\mu_* = \infty$. Here an increase in the time of retention of the liquid in the tube would lead to continued increase in the resistance, the lower branch of the S-curve of Fig. 2 coming into coincidence with the axis of abscissas. In terms of the one-dimensional model described above, the order of the increase of resistance at $\theta \rightarrow \infty$ becomes equal to the order of the increase of viscosity with the passage of time.

Figure 4 can be used in discussing effects related to the rate of increase of resistance. If, for example, λ increases more rapidly than required by a linear law (Fig. 4a), the lower critical pressure drop κ_1 and the corresponding liquid flow velocity $\omega_1 = 1/\theta_1$ will take on finite, nonzero, values. When the increase in λ follows a linear law (Fig. 4b) $\omega_1 = 0$, but $\kappa_1 > 0$. If, finally, the increase in λ proceeds more slowly than required by a linear law (Fig. 4c), $\kappa_1 = \omega_1 = 0$.

From this it can be concluded that if the increase of resistance with liquid retention time is more gradual than required by a linear law, there will then be a critical pressure drop below which stationary liquid flow becomes impossible. On the other hand, if the resistance tends to infinity more slowly than required by a linear law, it will be possible to establish stationary finite-rate flow at any nonzero value of the pressure drop.

The processes involved in the clogging of tubular reactors can be considered as special instances of the critical effects under discussion here. Let us suppose that the pressure drop in a reaction falls below its lower critical value. The system will then tend to pass over into a stable stationary state corresponding to a point on the lower branch of the S-curve. If the liquid viscosity at completed reaction should prove to be high, it may be that the upper critical pressure drop will be greater than that which can be realized in the reactor, while the stationary states corresponding to points on the lower branch of the curve can be established only at extremely low flow rates. At points on the lower branch, liquid movement ceases when $\mu_* = \infty$; since $\kappa_2 = \infty$ it is impossible to move off of this branch by increasing the pressure drop. Here passage to stationary states on this lower branch becomes equivalent to reactor clogging.

Other, more complex, forms of the $\lambda = F(\theta)$ relation are also possible but they can be analyzed in the same manner. Despite differences in origin and effects, the analysis presented here has much in common with that used in discussing critical phenomena of thermal origin [2]; moreover, Fig. 1 is reminiscent of the Semenov diagram employed in the theory of thermal explosions [3]. In view of this analogy, critical effects arising from accelerated increase in viscosity might be designated as viscous "explosions."

The author wishes to thank V. G. Abramov and A. M. Stolin for valuable advice and suggestions.

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