

[30] measured the striation thickness in the batch mixer agitated by either screw or helical ribbon impeller. These measurements were performed at relatively small area when compared to the whole system and at one direction of the cutting plane. This is a very common situation when optical measurements are interpreted.

The only reliable estimations of mixing efficiency as defined by equations (2.67), (2.71) or (2.74) can be made by means of a proper mathematical description of micromixing allowing to relate conversion or selectivity of homogeneous chemical reactions to the history of stretch parameter. Such investigation was undertaken by Ottino [46] who used the lamellar model to recalculate mixing efficiencies from the conversion of a single instantaneous reaction. However, the computations were conducted for mixing in the turbulent regime, where the lamellar structure mixing model is completely inadequate (the laminar structures are not persistent) - see Baldyga and Bourne [33].

2.5. Stability of Laminar Flows.

The rheological properties and the compatibility of mixed liquids can affect the mixing process and the structure of resulting mixture. The problem was investigated mainly in the context of droplet dispersion in the two-phase systems. Only a few papers discussed mixing of completely miscible liquids of widely different dynamical properties. An interesting paper addressing this problem was published by Ranz [28], who anticipated the possibility of formation of periodic, segregated structures during mixing of liquids widely differing in viscosity and density. These structures are formed from striations of the "minor" component undergoing tensile deformation superimposed by the "major" component.

Looking more generally, the first publications on the hydrodynamic instability were presented in the Fluid Mechanics literature by Taylor [50] and Tomotika [51].

Taylor [50] showed experimentally that a drop of lubricating oil immersed in syrup subjected to the hyperbolic shear field was deformed into a cylindrical thread while the apparatus was running. When the apparatus which was used to produce flow was suddenly stopped, the final thread gradually broke up into a number of small drops of equal size. Taylor [50] suggested that the observed dispersion was related to the equilibrium between the interfacial surface tension and the viscous forces acting in both liquids. Tomotika [51] inspired by Taylor analyzed theoretically stability of a filament of a viscous liquid surrounded by another viscous liquid. For this purpose he used a method of small perturbations and linear stability analysis. The method of small perturbations assumes that the velocity components and pressure can be

expressed as:

$$v_i = V_i + v_i', \quad p = P + p' \quad (2.80)$$

in which (\mathbf{v}', p') denote perturbations of the primary undisturbed flow (\mathbf{V}_i, P) . The velocity and pressure perturbations are assumed to be small enough to neglect the products of these terms with themselves and their derivatives in Navier-Stokes equations. The linear stability analysis applied by Tomotika [51] was based on the assumption that a general solution of Navier-Stokes equations expressed in terms of Stokes stream function has the following form:

$$\psi(r, z) = \phi(r) \cdot \exp[i \cdot \alpha \cdot (z - c \cdot t)] \quad (2.81)$$

where α and c are the wave number and the wave speed respectively. As a result Tomotika [51] showed that infinitely small symmetrical disturbances of the cylindrical interface between liquids can grow in time. This phenomenon leads eventually to dispersion of the long cylindrical thread of a viscous liquid into a number of small drops. The limiting solution of Tomotika was confirmed by Meister and Scheele [52]. These authors provided a full numerical solution of Tomotika's analysis taking into account interfacial, inertial and viscous forces.

Interesting experimental and theoretical work on droplet dispersion in laminar flow was performed by Mason et al. [53] and Grace [54]. They confirmed the influence of viscosity ratio and the shear rate on the dispersion process. Similar effects were observed in the experiments by Van Oene [34], who investigated blending of very viscous polymer components in an extruder. He found that the resulting morphology of mixtures was also dependent on viscosity ratio and the magnitude of shear rate.

There is, however, a lack of experimental data indicating instabilities during laminar mixing of completely miscible liquids. The only experimental results showing existence of segregated structures in this kind of system are reported by Murakami et al. [24] without any theoretical analysis. Let us consider thus the problem of hydrodynamical stability in such a system.

The first theoretical study analyzing the stability of a flow composed of two liquids differing in viscosity and density was given by Hickox [55]. He investigated a steady, axisymmetrical laminar, primary core-annular flow (i.e. composed of two liquids flowing concentrically in a straight circular tube) using the method of small perturbations. Hickox [55] assumed that a general form of velocity and pressure perturbations terms reads:

$$\{v_r', v_\theta', v_z', p'\} = \{f_r(r), f_\theta(r), f_z(r), g(r)\} \cdot \exp[i \cdot n \cdot \theta + i \cdot \alpha \cdot (z - c \cdot t)] \quad (2.82)$$

in which n denotes azimuthal mode number ($n=0,1,2,\dots$). This allowed him to show that the

flow can be disturbed by both axisymmetric and asymmetric disturbances. Hickox [55] analyzed the influence of viscous, inertial and gravity forces; an influence of interfacial tension was considered optionally. The formulation of the problem was general but the author's solution was restricted to very long waves ($\alpha \cdot Re \ll 1$). Nevertheless, Hickox [55] proved that the most important single cause of hydrodynamic instability is the discontinuity of axial velocity gradients at the liquid-liquid interface, directly dependent on the difference in the viscosity between liquids. The main results of Hickox's study, important for this work are summarized below:

- 1) Asymmetric disturbances can grow in any situation, when the less viscous liquid is in the core, including the case of completely miscible liquids (with no interfacial surface tension).
- 2) Axisymmetric disturbances can grow, when the less viscous liquid is in the core and the core radius is larger than the critical value related to the pipe radius; decreasing the core-liquid viscosity decreases the value of limiting radius. This effect is predicted for any value of interfacial tension including $\sigma=0$.
- 3) In the early stage of destabilization the amplitude of disturbances grows or decreases exponentially with time, this conclusion is valid as long as the linear theory can be applied and the nonlinear effects are negligible.
- 4) The rate of growth of axisymmetric disturbances increases as the viscosity ratio (annular liquid viscosity over core liquid viscosity) increases.

Joseph et al. [56] extended Hickox's long-wave analysis to the whole spectrum of waves and concluded that the configuration with less viscous liquid in the core does not have any completely stable solutions; in the region of axisymmetric stability the asymmetric disturbances can still grow. However, when the more viscous liquid flows in the core, the flow can be unstable provided that the core radius is small enough; $R_{core}/R_{pipe} < 0.7$.

Ranz [28] pointed out that flow instabilities which can occur during mixing accomplished by tensile deformation can retard generation of intermaterial area. Ranz [28] considered a case of initially planar layer of the minor component stretched by the flow of the surrounding major component as shown in figure 2.14. Following Ranz [28] the balance of stress components perpendicular to liquid-liquid interface at $y=b$ can be written as follows:

$$-2 \cdot (\mu_d - \mu_c) \cdot \frac{\partial v_y}{\partial y} \Big|_{y=b} - (\rho_d - \rho_c) \cdot v_y^2 \Big|_{y=b} - (\rho_d - \rho_c) \cdot \frac{v_x^2 + v_y^2}{2} \Big|_{x,y=b} = 0 \quad (2.83)$$

The first term in the above equation stands for viscous stress, the second one refers to the inertial stress, whereas the third one expresses the pressure gradient. Ranz [28] assumed that

when the initial thickness of the stretched lamina is smaller than the scale λ_x given by equation (2.36) then the flow within the lamina is imposed by far two-dimensional stagnation flow:

$$v_x = \alpha_c \cdot x, \quad v_y = -\alpha_c \cdot y, \quad (2.84)$$

Elimination of velocity components from equations (2.83) and (2.84) gives an estimation of the half wave length of instabilities:

$$x_{\lambda/2}^2 \cong \frac{4}{\alpha_c} \cdot \frac{\mu_d - \mu_c}{\rho_d - \rho_c} - 3 \cdot b^2. \quad (2.85)$$

Ranz [28] concluded that the growth of instabilities can result in break-up of the layer into drops ($\sigma > 0$) or can deform the layer into lens-like structure as shown in figure 2.15. In both cases mixing performed by laminar stretch ($\alpha_c > 0$) will be restrained if either $\mu_d > \mu_c$ and $\rho_d > \rho_c$ or $\mu_d < \mu_c$ and $\rho_d < \rho_c$. On the other hand, when ratio $(\mu_d - \mu_c)/(\rho_d - \rho_c)$ is negative, the stretching should prevent formation of flow instabilities.

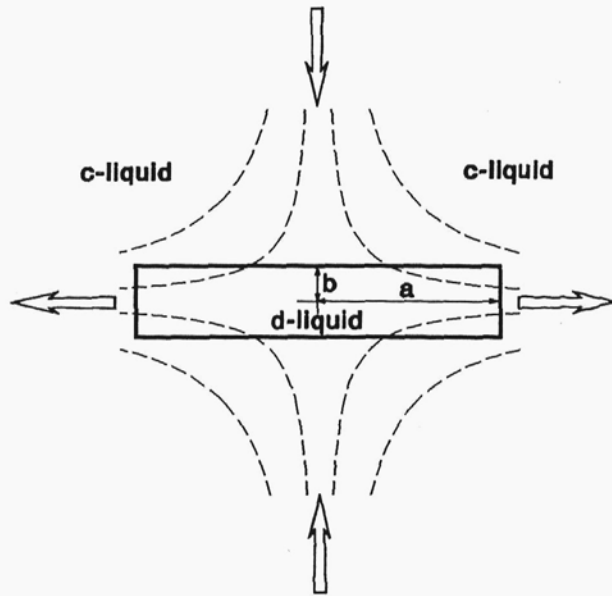


Figure 2.14. Striation in a symmetrical stagnation flow; $a \cdot b = \text{const.}$

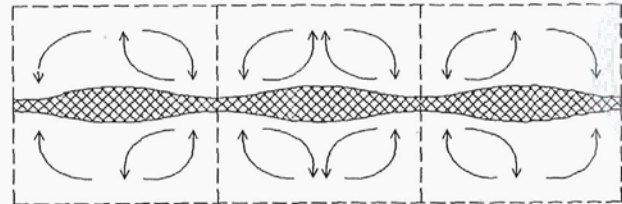


Figure 2.15. Formation of secondary flows and destabilization of a striation being stretched.

2.6. Application of Chemical Test Reactions to Investigate Mixing.

The application of chemical reactions to assess theories and models of mixing in viscous liquids is the main subject of the present chapter. Once the mixing model is verified, the test reaction can be used as a very practical indicator of efficiency of mixing and intensity of segregation.

The process of mixing with chemical reaction should be considered separately for single reaction and for multiple reactions. There are two kinds of single reactions of the type $A \rightarrow \text{products}$ and two-species reactions of the type $\nu_A \cdot A + \nu_B \cdot B \rightarrow \text{products}$. The multiple reactions are combinations of simple reactions; one can distinguish 2 kinds of multiple reactions considering the complexity of reaction system: simple multiple reactions (e.g.