

when the initial thickness of the stretched lamina is smaller than the scale  $\lambda_x$  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.

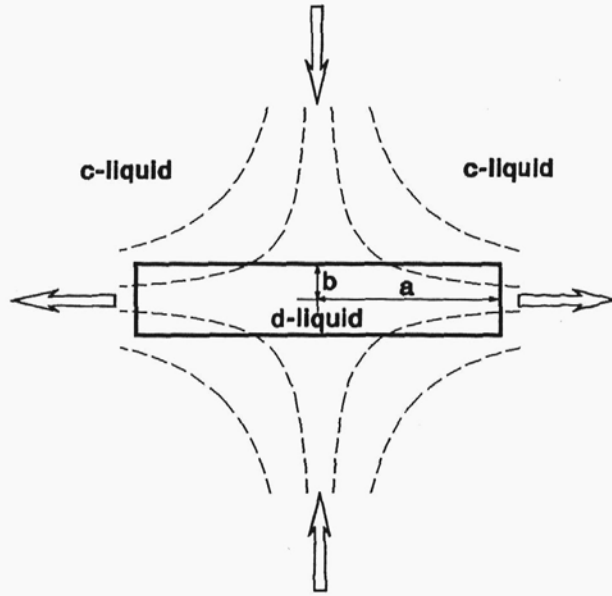


Figure 2.14. Striation in a symmetrical stagnation flow;  $a \cdot b = \text{const.}$

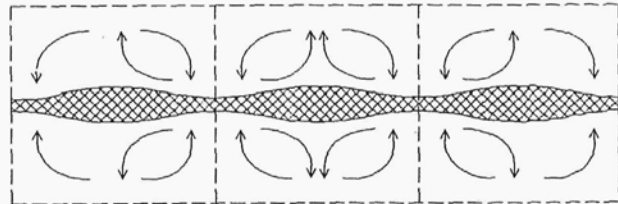


Figure 2.15. Formation of secondary flows and destabilization of a striation being stretched.

## 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.

competitive-consecutive  $A+B \rightarrow R$ ,  $R+B \rightarrow S$  or parallel  $A+B \rightarrow R$ ,  $A+C \rightarrow S$ ) and complex multiple reactions (e.g. polymerization, polycondensation etc.).

The reactions can occur in two kinds of systems: premixed feed systems and unpremixed feed systems. In premixed feed systems a single stream of reactants (uniform solution of A, uniform mixture of A and B or uniform mixture of A, B and C for single-species, two-species or three-species respectively) is fed into the reactor; the process of mixing occurs only between material elements of different age and thus differing in progress of the reaction. In the unpremixed feed case two (or more) streams of different reactants are introduced into the reactor and there occurs the process of mixing of different species as well as mixing of material elements of different age. Mixing of different species is particularly important from the point of view of sensitivity to the mixing conditions because it must proceed chemical reaction. In the case of premixed feed systems micromixing has no effect on reactions of first-order kinetics (they are however sensitive to macromixing so to RTD); however, micromixing influences reactions with non-linear kinetics.

In premixed feed systems the effects of micromixing are rather small in the case of simple kinetics; the difference between complete segregation and maximum mixedness is smaller than 7% in the case of second order reactions - see [10,p.141]. A serious increase can be observed when the reaction is autocatalytic or autothermal (higher nonlinearity) but really high sensitivity can be expected only in the case of fast complex reactions (polymerization, series-parallel or parallel reactions) - however, in such a case reactions start in a premixer, which is usually an unpremixed feed system.

In unpremixed feed systems the effects of mixing on the course of chemical reactions is much higher than in premixed feed systems [57, 58]. In the case of second-order reaction between two species the conversion for complete segregation equals zero, whereas in the case of maximum mixedness can approach one. In many situations the distribution of products of multiple reaction is very sensitive to details of mixing, provided that the reactions are sufficiently fast.

Comparing the simple and multiple reaction one can say that in both cases the reaction should be fast enough to compete with micromixing. However, in the case of single reaction, micromixing and reaction should be slow enough as not to be completed in the reactor. This problem does not occur in the case of multiple reactions when the product distribution "remembers" the history of mixing and reaction even when the reactions are completed in the reactor.

When the goal of investigation is to characterize the level of segregation, the efficiency of

mixing or to verify the mixing model, the reaction system should not be too complex to enable direct and univocal interpretation of experimental data. The test reaction to be sensitive to mixing must be from definition fast or instantaneous. The definition of characteristic mixing times cited in chapter 2.3 are not very precise so another definition is proposed here.

The micromixing time for turbulent mixing was defined by Baldyga and Bourne [57]; this definition can be well adopted to the process of mixing of viscous liquids, giving:

$$t_{DF} = \operatorname{arcsinh}(0.76 \cdot \alpha \cdot s_0^2/D) / (2 \cdot \alpha) . \quad (2.86)$$

The advantage of definition (2.86) over the definitions (2.38) and (2.41) results from the fact that it includes influence of both: molecular diffusion and deformation on mixing time. Thus, the conditions for test reactions are:  $t_{DF} \gg t_R$  or  $t_{DF} \approx t_R$ .

One can conclude that the best choice for the system of test reactions is the fast or instantaneous system of multiple (but not too complex) chemical reactions proceeding in the unpremixed feed system. There are of course some further requirements [57]:

- one needs to know the kinetics of each step of the reaction and influence of such processing parameters as temperature, concentrations of all species, solvent used, pH and ionic strength on reaction kinetics,
- the reliable and exact method of quantitative analysis should be available,
- one should consider such aspects as toxicity and cost of reactants, regeneration or disposibility of all the species, fire hazard, etc.

In the following part of this chapter the experimental work on test reactions and on using the test reactions in viscous media is reviewed.

Literature provides several examples of application of simple reactions in a study of mixing in highly viscous liquids and in unpremixed systems.

Mitsusihi et al. [26] used the second-order, irreversible reaction of ethylene halohydrins and hydroxyl ions proceeding in highly viscous aqueous methyl cellulose solution to reveal the effect of molecular diffusion on mixing in batch reactor.

Geurden and Thoenes [59] utilized the second-order irreversible reaction between sodium hydroxide and ethyl acetate carried out in aqueous solution of polyox coagulant to test their micromixing model. The experiments were conducted in a continuously stirred tank reactor. Saito et al. [32] tested Ottino's lamellar micromixing model using a second-order, irreversible reaction between iodine and sodium thiosulfate or disodium phosphate. In this case reaction progress was monitored visually due to colour changes during reaction.

The test reactions proposed by Mitsuishi et al [26], Geurden and Thoenes [59], and Saito et

al. [32] were fast enough to be affected by mixing. The proposed test reactions were carried between diluted substrates so the thermal effect of reaction was negligible.

Using a single chemical reaction in experimental tests, as presented above has some disadvantages. Firstly, it requires tracking of the concentration changes in time and space to obtain mass balance for the investigated reactor. These measurements should be performed in a way minimizing the interference with the process. In the case of highly non-uniform mixtures, as it is often encountered during mixing of very viscous liquids, concentrations should be measured in many points to avoid errors in determining mass balance. Secondly, tests with a single irreversible reaction do not provide consistent information on mixing history, especially when mixing occurs between molecules of different age.

Polymerization reactions are the most commonly used in experimental works mainly concerned with a reaction injection moulding technique (RIM). In a typical RIM operation the fast polymerization reactions are triggered by putting in contact initially unpremixed molten monomers and catalyst in an impingement mixing head (see Macosko [27]).

Kolodziej et al. [61] evaluated the influence of Reynolds number on an adiabatic temperature rise and molecular weight distributions obtained in fast polyurethane polymerization performed by RIM technic.

Lee et al. [62] also used polyurethane polymerization reactions to test several mixing head geometries in terms of adiabatic temperature rise.

The cited above treatments refer to the particular polymerization reaction occurring in strongly non-isothermal conditions affecting reaction kinetics, viscosities and diffusion coefficients. This makes any generalizations of the observed phenomena hardly possible.

The literature provides only one example of a simple multiple reaction system developed for investigation of micromixing in very viscous liquids.

Frey [63] proposed a competitive-consecutive imidization reactions:



in which **A** = p-phenylene diamine, **B** = phthalic anhydride, **R** = N-(p-amino phenyl) phthalimide and **S** = 2-[[[(1,3-dihydro-1,3-dioxo-2H-isoinold-2-yl)phenyl]amino]carbonyl] benzoic acid. The test reactions proceed in molten polyethylene at temperatures ranging from 100°C to 150°C according to second-order scheme. The first reaction is approximately ten

times faster than the second one. Frey [63] showed that when the reactions are carried out in the kinetic regime and initial amounts of **A** and **B** are equal to each other, then the final selectivity

$$X = \frac{2 \cdot [S]}{2 \cdot [S] + [R]} \quad (2.88)$$

is equal to 23%. In a diffusion controlled regime this selectivity can approach 100%. As indicated later by Frey and Denson [64] the two-step imidization reaction should be sensitive on micromixing at scales ranging from 0.08 mm to 10 mm but did not provide any experimental evidence of this thesis. Besides, it should be pointed out that the analytical method proposed by Frey [63] to find the products distribution can lead to serious errors. This method consists of two steps: first the solution of products is cooled and solidified, then concentrations of species are determined by infrared spectroscopy. As indicated by Frey [63] depending on the rate of cooling, solidified polyethylene can have different densities what affects the accuracy of spectroscopic measurement. Moreover, although reactants are soluble in polyethylene melt, they are not compatible with solid polymer and can precipitate again lowering down accuracy of infrared spectroscopy.

The single and competitive-consecutive reactions reported in the literature are not fully suitable for investigations of micromixing in very viscous liquids. One can conclude that there is still a need to develop a better reaction tracer method.

