

6. An Experimental Method for Investigation of Micromixing in Very Viscous Liquids.

Experimental investigations of micromixing require indirect methods involving processes occurring at the molecular level, e.g. single or multiple chemical reactions. In this chapter a system of competitive-parallel reactions and a viscosity increasing agent, suitable for performing such an experimental study in very viscous liquids are proposed.

The properties of test reactants and the viscosity increasing agent which can affect the course of micromixing and experimental methods applied are described and discussed in this chapter, including:

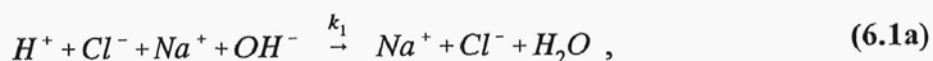
- the kinetic scheme of test reactions,
- the molecular structure and physical (solubility, viscosity and density) and chemical properties (chemical reactivity) of the viscosity increasing agent,
- molecular diffusion coefficients of the reactants in aqueous solutions containing the viscosity increasing agent,
- the rate constant of the test reaction in the aqueous solutions containing the viscosity increasing agent.

Also, an analytical method for determination of the final product distribution is described and tested.

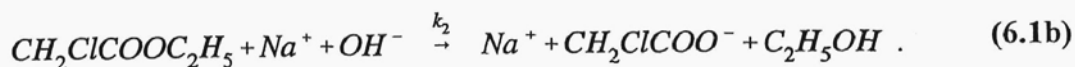
6.1. Description of the Test Reaction System.

A system of two competitive-parallel chemical reactions was chosen for experimental investigations of micromixing in very viscous liquids:

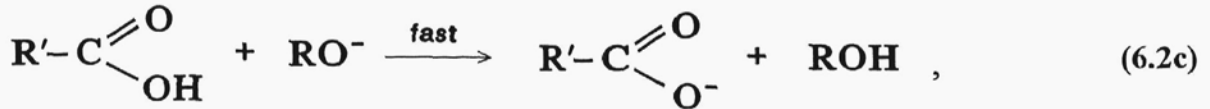
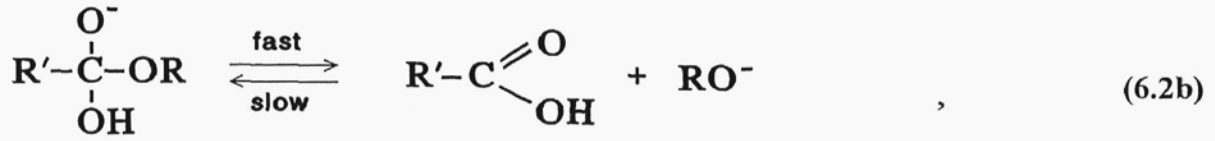
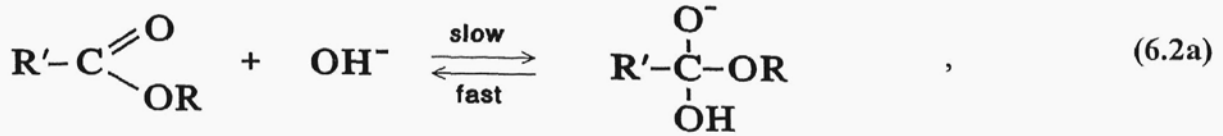
- neutralization reaction between hydrochloric acid and sodium hydroxide



- hydrolysis of ethyl chloroacetate with sodium hydroxide



The first reaction is irreversible and of second order. According to Crooks [76] the rate constant of the neutralization reaction in pure water is of the order of $10^{11} \text{ dm}^3/\text{mol/s}$. The second reaction proceeds according to the following scheme [77,78]:



where $\text{R}=\text{CH}_2\text{Cl}$ and $\text{R}'=\text{C}_2\text{H}_5$. The first reaction in the scheme (6.2) is reversible. The tetrahedral product is unstable and can easily lose carbanion RO^- (equation 6.2b), forming an acid molecule. The third reaction between acid and strong base RO^- (equation 6.2c) is very fast and practically irreversible. Consequently, the rate of alkaline hydrolysis (6.2) is controlled by the first, slowest stage (6.2a) and the whole reaction system can be interpreted as a single second-order, irreversible reaction. The rate constant of this reaction in pure water is given by Arrhenius equation:

$$k_2 = A_0 \cdot \exp \left\{ -\frac{E}{R \cdot T} \right\} , \quad (6.3)$$

In this equation R is the universal gas constant equal to $8.314 \text{ J}/(\text{mol} \cdot \text{K})$, whereas the constants A_0 and E can be found from kinetic data reported by Kirby [77]; when the reaction proceeds in water then $A_0=4.134 \cdot 10^7 \text{ dm}^3/(\text{mol} \cdot \text{s})$ and $E=34.79 \text{ kJ/mol}$ (at $T=298.15 \text{ K}$ $k_2=33.2 \text{ dm}^3/(\text{mol} \cdot \text{s})$).

The half reaction time of the neutralization reaction ($t_{R1}=1/(k_1 \cdot c_0)$) equals 10^{-9} s when $c_0=0.01 \text{ mol/dm}^3$. Similarly, the half reaction time of the hydrolysis reaction ($t_{R2}=1/(k_2 \cdot c_0)$) equals 3.01 s for $c_0=0.01 \text{ mol/dm}^3$. On the other hand, the micromixing time defined by Bałdyga and Bourne [57] (see chapter 2.6) and computed for: $\alpha=1 \text{ s}^{-1}$, $D=10^{-9} \text{ m}^2/\text{s}$ and $s_0=10^3 \text{ m}$ equals

$$t_{DF} = \text{arcsinh}(0.76 \cdot \alpha \cdot s_0^2/D)/(2 \cdot \alpha) = 3.66 \text{ [s]} \quad (6.4)$$

Comparison of t_{R1} , t_{R2} with t_{DF} clearly indicates that the first reaction (6.1a) is completely controlled by mixing, whereas the second reaction (6.1b) is fast enough to compete with mixing. In such a case the product distribution of the test reactions (6.1) should be strongly

related to the history of mixing.

It should be noted that ethyl chloroacetate also undergoes neutral and acid-catalyzed hydrolysis but these reactions are too slow to interfere with alkaline hydrolysis; according to Jencks and Carriuolo [94] the rate constants of neutral and acid-catalyzed hydrolysis are equal to $1.08 \cdot 10^{-7} \text{ s}^{-1}$ and $3.67 \cdot 10^{-5} \text{ dm}^3/(\text{mol} \cdot \text{s})$ at 298.15 K, respectively.

6.2. Properties of Polyethylenepolypropylene Glycol.

6.2.1. Molecular Structure.

Polyethylenepolypropylene glycol was chosen as substance increasing viscosity of aqueous solutions of the test reactants. Polyethylenepolypropylene glycol is a polymer of ethylene oxide and propylene oxide, as shown in figure 6.1. The polymer is a non-volatile, non-toxic, highly viscous and transparent liquid.

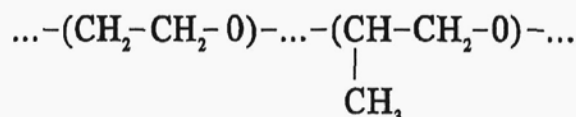


Figure 6.1. Molecular structure of polyethylenepolypropylene glycol.



Polyethylenepolypropylene glycol belongs to the family of polyethers, which results in its low polarity and increased ability to form hydrogen bonds [78]. These features should make the polymer soluble both in organic solvents and in water. Indeed, the experimental tests confirmed that the polymer is miscible in all proportions with: non-polar solvents e.g. tetrachloride and methylene chloride, moderate-polar solvents e.g. ethyl chloroacetate and polar solvents e.g. ethyl alcohol and water. According to literature [79] only paraffin hydrocarbons are immiscible with polyethylenepolypropylene glycol.

The polyalkylene glycol used in the experiments was manufactured by BP Chemicals Ltd. under the trade name Breox 75W 18000.

6.2.2. Viscosity of Aqueous Solutions.

Viscosity of aqueous solutions of the polyethylenepolypropylene glycol was measured with the use of viscometer - Rheotest 2.1 in a system of two coaxial cylinders at shear rates ranging from 13.25 s^{-1} to 1325 s^{-1} . Polymer contents in these solutions were ranging from 30