

7.2.4. Effect of the Viscosity Ratio on the Product Distribution.

The last two series of the tests were conducted to find out if the differences in viscosities of the mixed solution can influence the final selectivity of the competitive-parallel reactions. In these experiments the viscosity of the initial reactor content (acid and ester solution) was kept constant, whereas the viscosity of the feeding solution was changed from experiment to experiment. Densities of the mixed solutions were equal to each other. The experiments were conducted for two revolutions speeds of the pitched-blade turbine 100 and 400 rev/min. During these tests the initial volume ratio was constant and equal to 11. The feeding rate of the base solution was equal to 1 cm³/min in all cases. Tables 7.Vabc show agitation speeds, amounts, compositions, physical properties of the solutions and final selectivities measured in the sixth and seventh series. The results are compared in figure 7.5 with the results obtained when liquids of equal viscosity were mixed (exp.no 2 and 5 in tables 7.IV).

Table 7.Va. Sixth and seventh series of tests - initial reactor content; $w_p=40\%$.

Exp.no.	HCl [mol/dm ³]	Ester [mol/dm ³]	V [cm ³]	ρ [g/cm ³]	μ [Pa·s]	KCl [g/kg]
1 and 4	0.01100	0.01074	667.71	1.0822	0.291	33.13
2 and 5	0.01098	0.01071	667.71	1.0747	0.291	21.75
3 and 6	0.01070	0.01065	667.78	1.0606	0.316	0.0

Table 7.Vb. Sixth and seventh series of tests - feeding solutions.

Exp.no.	w_p [%]	NaOH [mol/dm ³]	V [cm ³]	ρ [g/cm ³]	μ [Pa·s]	KCl [g/kg]
1 and 4	52	0.1179	60.68	1.0821	1.141	0.0
2 and 5	46.5	0.1172	60.68	1.0750	0.645	0.0
3 and 6	33	0.1174	60.68	1.0615	0.146	10.88

Table 7.Vc. Sixth and seventh series of tests - final solutions after experiment;
 $Q_f=1\text{cm}^3/\text{min}$, $a=11$.

Exp. no.	n [rev/min]	Ester [mol/dm ³]	X [%]	V [cm ³]	ρ [g/cm ³]	μ [Pa·s]
1	100	0.006337	35.76	728.39	1.0822	0.326
2	100	0.004997	35.20	728.41	1.0747	0.313
3	100	0.006264	35.80	728.58	1.0605	0.298
4	400	0.008663	12.07	728.39	1.0822	0.326
5	400	0.006844	10.95	728.41	1.0747	0.313
6	400	0.008420	13.76	728.58	1.0605	0.298

Analysis of the experimental results shows that either decreasing the viscosity ratio below one or increasing it above one decreases degree of mixedness in the reactor. It should be pointed out that mechanisms leading to such a situation may be different in both cases.

In the case when a more viscous base solution is fed into a less viscous acid and ester solution,

the deformation of liquid elements constituting the feeding stream by the stress generated by the surrounding liquid is slower than in the case when both solutions have equal viscosities. This may restrain reduction of segregation scales and slow down mixing on the molecular scale. Higher viscosity of the base solution means also smaller diffusivity of sodium hydroxide (see chapter 6.4) and, consequently slower mixing in the reaction zone. When the viscosities of mixed solutions are different, there is a possibility of flow instabilities in the system. These instabilities retard the process of thinning of liquid elements. An influence of this effect on the course of mixing and reaction should be stronger when a less viscous base solution is fed into a more viscous acid and ester solution, because of shorter time scale of the instabilities growth. Then faster deformation of liquid elements constituting the feeding stream by the

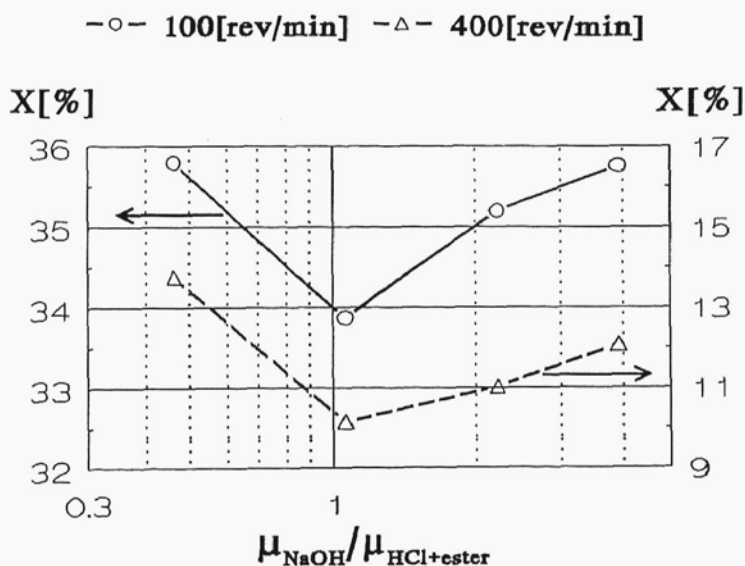
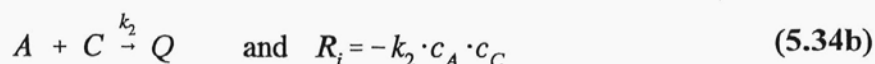
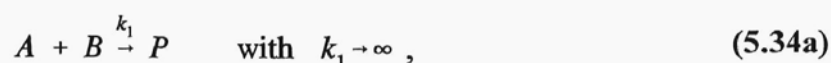


Figure 7.5. Effect of the viscosity ratio on the final selectivity in the semi-batch mixer - experimental data.

surrounding liquid instead of accelerating molecular diffusion may result in arising segregated structures in the system [24,28,35]. This is probably the main reason why decreasing viscosity of the base solution elevates the final selectivity in the semi-batch reactor. In the case of no flow instabilities in the system one would rather expect an opposite effect.

7.3. Modelling of Micromixing in the Semi-Batch Reactor.

The model of concentration moments proposed in chapter 5.1 was applied to interpret the experimental results and determine energetic efficiency of mixing in the semi-batch reactor. According to this model, the selectivity of competitive-parallel reactions:



depends on five dimensionless parameters:

$$\text{– volume ratio} \quad a = V_{(B,C)0} / V_{A0}, \quad (5.42b)$$

$$\text{– stoichiometric ratios} \quad F_B = N_{B0} / N_{A0}, \quad F_C = N_{C0} / N_{A0}, \quad (5.42c)$$

$$\text{– characteristic times ratio} \quad \theta = t_D / t_F, \quad (5.42d)$$

$$\text{– Damköhler number} \quad \overline{Da} = k_2 \cdot \overline{c_{A0}} \cdot t_D = k_2 \cdot \frac{c_{A0}}{a+1} \cdot t_D. \quad (5.49)$$

For the case of the test reactions (6.1), symbols **A**, **B** and **C** represent NaOH, HCl and CH₂ClCOOC₂H₅, respectively. Values of **a**, **F_i** and **c_{A0}** depend on volumes of mixed solutions and initial concentrations of the reactants in these solutions. The rate constant of alkaline hydrolysis was taken as for water solution at 25°C ($k_2=33.2 \text{ dm}^3/(\text{mol} \cdot \text{s})$ [77]) - see results presented in chapter 6.4.

The characteristic diffusion time, appearing in expressions (5.42d) and (5.49) is given by

$$t_D = \delta_0^2 / D_A. \quad (5.43)$$

The diffusivity coefficient of sodium hydroxide can be calculated from empirical correlation (6.14); for the solutions used in the experiments one receives $D_A=6.28 \cdot 10^{-10} \text{ m}^2/\text{s}$.

The visual observations of the feeding stream coloured with phenolphthalein showed that for