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Characterization of Mixing Efficiency in Polymerization Reactors Using Competitive-Parallel Reactions

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Summary: In this article particular attention is paid to processes of mixing fluids with different viscosities relevant for polymerization where the reaction is fast and mixing is the limiting factor. Apart from this, mixing fluids with different viscosities is still one of the challenging tasks in industrial chemistry. Therefore, the characterization of mixing elements is another important topic.Two different multiple chemical reactions, based on the principle of competitive-parallel reactions, were used and compared to investigate (micro)mixing efficiency in polymerization reactors. The well-known *Villermaux-Dushman* reaction and the third *Bourne* reaction were applied. The observed product distribution represents the quantity of segregation of the fluid which gives in turn information about the dependency on certain parameters like type and speed of stirrer, dosing period, feed position, and the viscosity of the fluid. The results from semibatch and continuous stirred tank reactors and two different stirrers, *Rushton* and *INTERMIG*® impeller, are discussed.

Keywords: micromixing; scale-up; segregation; third *Bourne* reaction; *Villeraux-Dushman* reaction; viscosity

Introduction

Mixing in semibatch and continuous (co)polymerization is an important issue, particularly, when distinct differences in viscosities of reaction mass and reactor feed occur and reaction rate is fast. The latter becomes especially relevant for intensified polymerization processes with enhanced space time yield. The former is not only of interest in case of mixing low viscous monomer and initiator feed with high viscous reaction media within the reactor, but also in case of mixing inflows of different viscosities, e.g. in semibatch and continuous graft copolymerization and copolymerization of co-monomers with co-macromers, respectively. Even adjusting the pH by feeding acid or base may significantly affect polymer properties when mixing time and quality change.

Nowadays, useful tools like CFD simulation are very helpful to avoid insufficient mixing. Nevertheless, experimental verification of correlating specific power input, dimensionless Newton number, and mixing or blending number with copolymer properties, e.g. chemical composition and sequence length distribution, is still a challenging task.

Several kinds of methods can be used in order to investigate micromixing efficiency in stirred tank reactors. While conductometric and optical methods are more complex in experimental set-ups, "low molecular" chemical reactions are comparatively easy to use. We propose two different systems of competing parallel reactions.

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Methods for Investigations on Micromixing

Several kinds of methods can be used in order to investigate micromixing efficiency and so to characterize impellers and the entire geometry of stirred tank reactors, including baffles and other built-ins. Besides classical methods like conductometry or thermal *hot-wire anemometry* there are several other optical and tomographical measuring methods. *Laser Doppler anemometry* (LDA) and *Phase Doppler anemometry* (PDA) are used to make optical velocity measurements of fluids at one point of the reactor. *Particle image velocimetry* (PIV) and *Laser induced fluorescence* (LIF) analyze velocities simultaneously all over the reactor.[1]

In comparison to all these methods with considerable complex experimental setups, *chemical micromixing sensitive reactions* are quite simple and inexpensive in experimental setup.

Literature reports many mixing sensitive multiple reactions that are of three basic stoichiometric types. Single reactions $A + B \rightarrow S$, competitive-consecutive reactions $A + B \rightarrow R$, $R + B \rightarrow S$ and competitive-parallel reactions $A + B \rightarrow R$, $C + B \rightarrow S$. Reactants A (and C) can be provided in the reactor or fed separately with the limiting reactant B within the reactor. A good test multiple reaction should fulfill several conditions. The reaction time have to be faster than the time needed for mixing the reactants on molecular scale.

The competition between reaction and mixing can be represented by a mixing *Damkoehler* number, Da_M, which is the ratio of the characteristic mixing time, τ_M, and the reaction time, τ_R.

$$Da_M = \frac{\tau_M}{\tau_R} \tag{0}$$

Small Da_M values indicates less effect of mixing, whereas great values indicates that mixing will be a concern.[2]

Competing reactions are particularly helpful, because their product distribution depends on the grade of segregation.[3 The following reaction systems were chosen because of their known kinetics, easy handling, quite low toxicity and the simple way to analyze the products.

The first mixing sensitive multiple reaction used in this work is the well established *Villermaux-Dushman* method.[4–7] In this case the *Dushman* reaction, the acid catalyzed comproportionation of iodide and iodate to iodine, competes with a neutralization reaction between deprotonated boric acid and acid. The boric acid anion is part of a buffer solution from sodium hydroxide and boric acid in a ratio of 1:2

$$\begin{aligned} NaOH + 2H_3BO_3 \rightleftharpoons\ & Na^+ \\ & + H_2BO_3^- + H_3BO_3 + H_2O \end{aligned} \tag{1}$$

The competitive-parallel reaction is given below.

$$H_2BO_3^- + H^+ \rightleftharpoons H_3BO_3 \tag{2}$$

$$5\,I^- + IO_3^- + 6\,H^+ \rightleftharpoons 3\,I_2 + 3\,H_2O \tag{3}$$

In the case of dosing H^+ to a solution containing $H_2BO_3^-$ and I^-/IO_3^-. The neutralization (2) is quasi-instantaneous, the comproportionation (3) is still a fast reaction but slow in comparison to the neutralization. The comproportionation is then followed by a third reaction (4) with an equilibrium constant of 0.736 $m^3\ mol^{-1}$ (25 °C). In our case, reaction (4) is considered as nearly irreversible.

$$I_2 + I^- \rightleftharpoons I_3^- \tag{4}$$

The intermediately formed iodine can be detected as concentration of the accumulated triiodide by online UV spectroscopy. The nascent iodine can be detected as concentration of the accumulated triiodide by online UV spectroscopy. The segregation index X_S is then calculated by Equation (5).[4]

$$X_S = \frac{n_{I_2} + n_{I_3^-}}{n_{H^+,0}} \left(2 + \frac{n_{H_2BO_3^-,0}}{3 n_{IO_3^-,0}} \right) \tag{5}$$

The second multiple reaction is the so-called third *Bourne* reaction, a parallel reaction where the slower alkaline hydrolysis of ethyl chloroacetate (ECA) proceeds in parallel with the fast neutralization of HCl and NaOH.[8–9] The conversion of ECA leads to formation of ethanol, which can be analyzed by gas chromatography.

$$\mathrm{NaOH} + \mathrm{HCl} \xrightarrow{k_1} \mathrm{NaCl} + \mathrm{H_2O} \tag{6}$$

$$\mathrm{NaOH} + \mathrm{ClCH_2COOC_2H_5} \xrightarrow{k_2} \mathrm{ClCH_2COONa} + \mathrm{C_2H_5OH} \tag{7}$$

The second-order rate constants for these reactions are

$$k_1 = 1.3 \cdot 10^8 \mathrm{m^3 mol^{-1} s^{-1}} \text{ at } 25\,^\circ\mathrm{C}^{[10]} \tag{8}$$

$$k_2 = 30.4 \cdot 10^{-3} \mathrm{m^3 mol^{-1} s^{-1}} \text{ at } 25\,^\circ\mathrm{C}^{[10]} \tag{9}$$

The amount of ethanol produced increases when the mixing rate decreases. The resulting segregation index X_E is given in Equation (10). The mixtures were analyzed immediately to avoid the acid hydrolysis of ECA.

$$X_E = \frac{n_{\mathrm{ECA},0} - n_{\mathrm{ECA}}}{n_{\mathrm{NaOH},0}} \tag{10}$$

The segregation index indicates the homogeneity of a fluid. $X_E = 0$ means that the fluid is completely mixed on the molecular scale only the fast reaction takes place. If all reactants are used in stochiometric quantities, $X_E = 0.5$ means that the fluid is completely segregated with larger regions of non-mixed reactants.

By means of the *Villeraux-Dushman* reaction the mixing efficiency can be tracked during the entire experiment, while the third *Bourne* reaction only determines the resulting efficiency at the end of the mixing process. All reactions in the *Villeraux-Dushman* system are equilibria, whereas the *Bourne* reactions are irreversible and insensitive for changing in reaction conditions like the pH. Using both multiple reactions for investigation on micromixing insufficiencies gives satisfying results.

Experimental Part

Reactors

In the experiments three different reaction vessels were used. First, a simple flat bottom vessel (*Schott*) of 100 mm in diameter, secondly, a standard 1500 mL glass reactor (*Rettberg*) with bumped boiler end and 100 mm in diameter, and finally, a 500 mL steel reactor (*Juchheim*) also with bumped boiler end and with 88 mm in diameter.

Figure 1 shows and Table 1 and 2 summarize the geometry of the 1500 mL tank for the *INTERMIG*® and the *Rushton* impeller. For the 500 mL tank a standard blade impeller was used keeping almost the same geometry.

Preparation and Analysis for the *Villeraux-Dushman* Reaction

The acid solution is prepared with sulfuric acid *Titrisol*® $C_{H_2SO_4} = 0.5$ mol/L (1 N). The buffered iodide/iodate-solution is prepared by first dissolving the needed amount of KI (p.a.) and KIO_3 (volumetric standard, *CertiPUR*®) in H_2O. Then the calculated amount of NaOH (p.a.) and finally the H_3BO_3 is added to the solution. This sequence guarantees that iodide and iodate do not coexist in acid media.

The detection of the reaction product I_3^- is done spectrometrically. The UV spectrometer (*Varian*) is coupled to a fibre optic probe (*Hellma*) to measure the I_3^- concentration in semibatch processes directly in the reaction vessel. Or the spectrometer is used with a flow cuvette (Hellma) for measuring the concentration in the outlet stream of a continuous reactor. Because the I_3^- absorbs at two wavelengths with different extinction coefficient, the whole range covering these two bands from 400 to 250 nm is recorded. Considering the scan rate of 80 nm s^{-1} at a resolution of 1 nm, the instrument can record a spectrum every 1.9 s. For determining the concentration of the I_3^-, both wavelengths at 287 and 352 nm were used.

Preparation and Analysis for the Third *Bourne* Reaction

All chemicals were bought from *Merck* and used without further purification. In

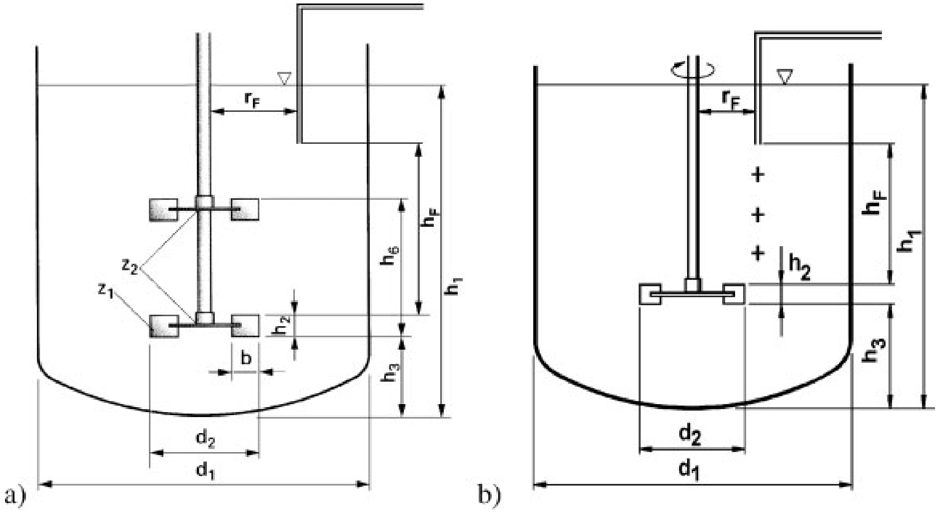

Figure 1.
1500 mL semibatch tank with a) *INTERMIG*® impeller and b) *Rushton* impeller with variable feed positions (marked with crosses). The sketch is not true to scale (modified scheme, original in [11]).

Table 1.
Reactor geometry (1500 mL tank).

Parameter	Symbol	INTERMIG®	Rushton
		mm	mm
tank diameter	d_1	100	
impeller diameter	d_2	67	40
filling level	h_1	142	
(projected) blade height	h_2	19.7	7
distance from bottom	h_3	37	42
stages distance	h_6	50	-
blade width	b	13.1	7
capillary diameter	d_k	1	1
feed position	h_F	var.	var.
distance to stirrer shaft	r_F	28	18
number of blades	z_1	2[a)]	6[a)]
number of stages	z_2	2[a)]	1[a)]

[a)] dimensionless.

general, ethyl chloroacetate ($n_{ECA,0} = 100$ mmol, $C_{ECA,0} = 0.1$ mol/kg) and hydrochloric acid ($n_{H^+,0} = 100$ mmol, $C_{H^+,0} = 0.1$ mol/kg) were provided in the reactor and NaOH solution ($n_{NaOH,0} = 100$ mmol, $C_{NaOH,0} = 5$ mol/kg) was fed with a certain rate according to the mixing experiment.

Table 2.
Length ratios (1500 mL tank).

Length ratio	InterMIG®	Rushton
d_2/d_1	0.68	0.4
h_3/d_2	0.55	1.08
h_6/d_1	0.5	–

The product ethanol and the residual ethyl chloroacetate were analyzed by gas chromatography. The gas chromatograph is a *Chrompack CP 9003* (*Varian*) with FI-detector using a *PoraBond U* column (*Varian*, fused silica, length: 25 m, inner diameter: 320 μm). 2-butanone was used as internal standard.

Results and Discussion

The dependence of the segregation index on type and speed of the stirrer, the position of inlets and outlets, the dosing period, the reactant concentrations and viscosities was investigated in stirred tank reactors of different geometry and size. Application of the results for "low molecular" test reactions to polymerization in solution at a comparable level of viscosity are discussed first for the semibatch experiments, followed by the results from the continuous reactor.

100 mm Flat Bottom Tank (Semibatch Operation)

This experiment was to proof the general applicability of the *Villermaux-Dushman* reaction for our purposes. Therefore, the flat bottom vessel with 100 mm in diameter was used to compare the mixing efficiency of three impellers only different in diameter.

The reaction vessel was filled with the buffered iodide/iodate solution. The acid solution was injected directly at the surface of the iodide/iodate solution. An UV spectrometer was recording continuously the spectra by an online probe connected via fibre optics. The spectra then were evaluated at the two maxima at 287 and 352 nm.

The d_2/d_1 ratio changed from 0.2 over 0.3 to 0.5. As Figure 2 shows, the mixing efficiency increases with increasing ratio of impeller diameter to reactor diameter.This multiple reaction is therefore suitable for investigations on micromixing efficiencies.

1500 mL Tank (Semibatch Operation)

Influence of the Dosing Period t_D and Stirrer Type

Third Bourne Reaction and INTERMIG® Impeller. In order to find conditions where micromixing is almost free from influences of macromixing, it is necessary to find the critical dosing period t_c for the limiting reactant. Usually it is essential to redeter-

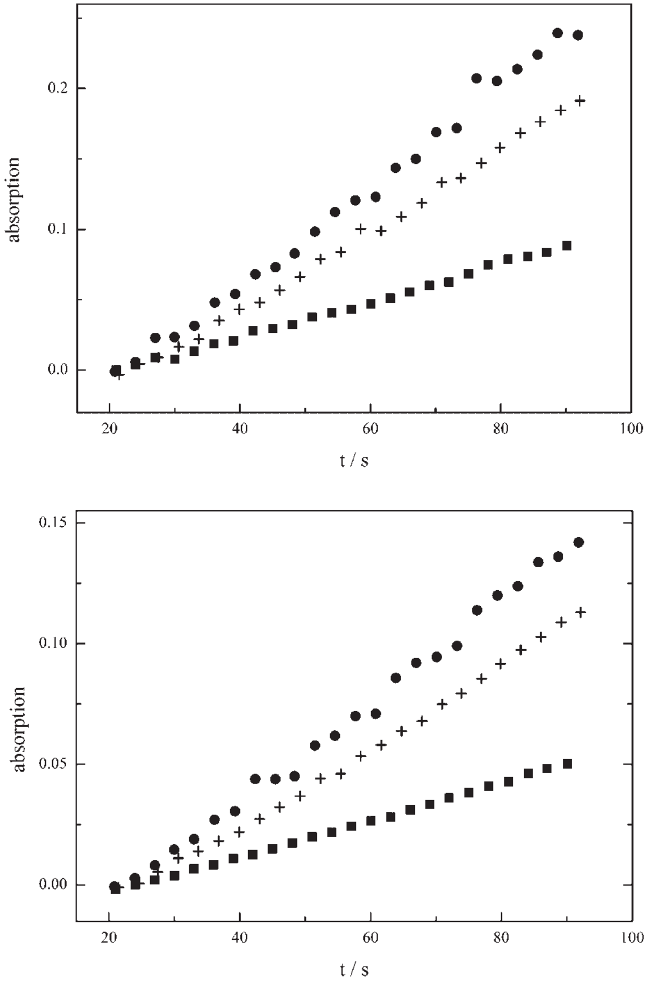

Figure 2.
Absorption as a function of reaction time t for different impeller diameters; experimental condition: $d_1 = 100$ mm, $N = 500\ \mathrm{min}^{-1}$; ● = $d_2/d_1 = 0.2$, + = $d_2/d_1 = 0.3$, ■ = $d_2/d_1 = 0.5$.

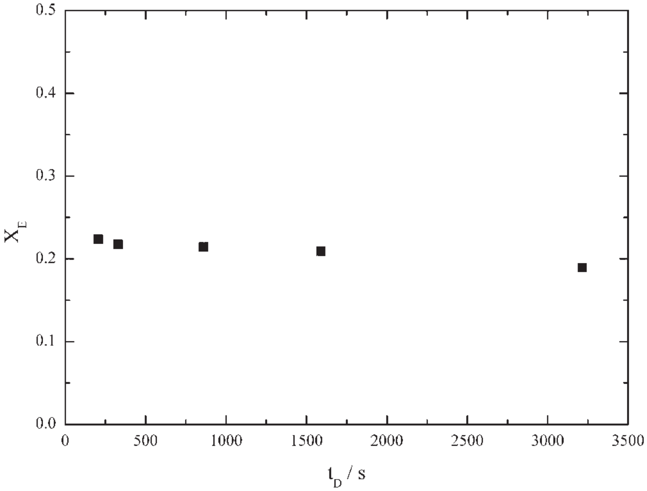

Figure 3.
Segregation index X_E as a function of dosing period t_D; experimental condition: *INTERMIG*® impeller, $N = 100\ \text{min}^{-1}$, $h_F = 13$ cm.

mine this critical dosing period for every new experiment with changed parameters, which is quite time-consuming. Hence, a worst condition scenario became useful, where the lowest stirrer speed and a feed position near the surface were used. In this experiment the stirrer speed was $100\ \text{min}^{-1}$ at feed position $h_F = 13$ cm in Figure 1 with an *INTERMIG*® impeller. The dosing period t_D of the NaOH solution was varied from 200 to 3200 s. The results are shown in Figure 3.

As one can see, the segregation index is almost constant for a dosing time longer than 200 s. In this region the segregation index is only determined by micromixing effects and so far it was not possible to identify t_c. Thus, all micromixing experiments were performed with dosing period values greater than 300 s.

Villermaux-Dushman Reaction and Rushton Impeller

The dosing period of acid was varied from 60 to 540 s in steps of 60 seconds. As shown in Figure 4, the critical dosing time can be obtained at about 350 s. This indicates at dosing periods longer than 350 s, an operation in the domain of micromixing is given. At dosing periods shorter than 350 s macromixing effects occur.

Influence of the Stirrer Speed N

Figure 5 shows the decreasing segregation index with increasing stirrer speed. Even at $400\ \text{min}^{-1}$, a turbulent mixing with high specific power input, the solution is still segregated. Higher stirrer speeds were not realized in view of vortex formation, which can only be suppressed by installation of baffles.

Influence of the Reactant Concentrations

The experiment shows how the acid concentration influences the absorption. As shown in Figure 6, higher acid concentrations result in increased formation of iodine, which in turn leads to higher absorption. The (micro)mixing becomes insufficient with higher acid concentrations at same dosing periods.

Influence of the Feed Position

This experiment was performed in the standard 1500 mL glass reactor, where varying the feed position indicated the local energy dissipation Four different feed positions that lay on a vertical line were considered in view of the energy dissipation of the *Rushton* impeller. Position 1 was beneath the surface (7 cm), position 2 and 3 were in decreasing distance to the impeller (5 and 3 cm), so position 4 was close above

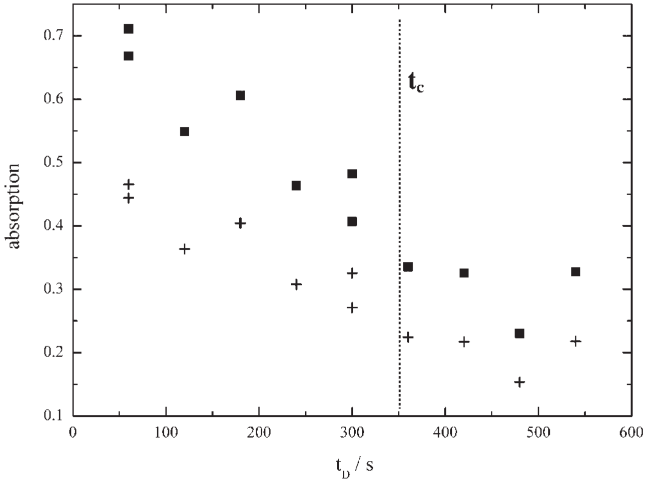

Figure 4.
Absorption as a function of dosing period; experimental condition: *Rushton* impeller; $N = 540\ \mathrm{min}^{-1}$, pH-value (NaOH): ~ 9, $h_F = 0$ cm, $C_{I^-} = 0.0117$ mol/L, $C_{IO_3^-} = 0.00233$ mol/L, $C_{H_2BO_3^-} = 0.091$ mol/L, $n_{H^+} = 0.002$ mol (2 mL, 1 mol/L); ■ = 287 nm, + = 352 nm.

the impeller (1 cm). Figure 1 shows the feed positions marked with crosses in the 1500 mL tank.

Figure 7 shows that close to the *Rushton* impeller, the local energy dissipation is at its highest level. The more the feed position was displaced from the impeller, the less the local energy dissipation was and the local mixing efficiency just as well.

500 mL Reactor (Continuous Operation)

Effect of Viscosity

To show the ability of the reaction to describe the mixing efficiency in continuous reactors with different viscosities, the continuous 500 mL steel reactor setup was used. Hydroxyethyl cellulose (HEC) was

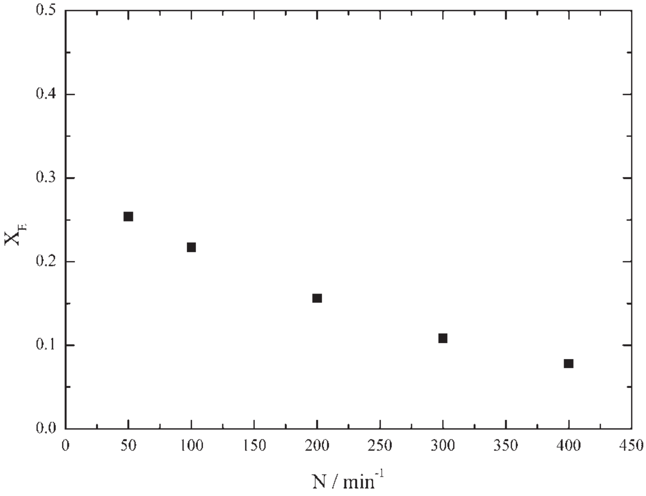

Figure 5.
Segregation index X_E as a function of stirrer speed N; experimental condition: *INTERMIG*® impeller, $t_D = 300$ s, $h_F = 7$ cm.

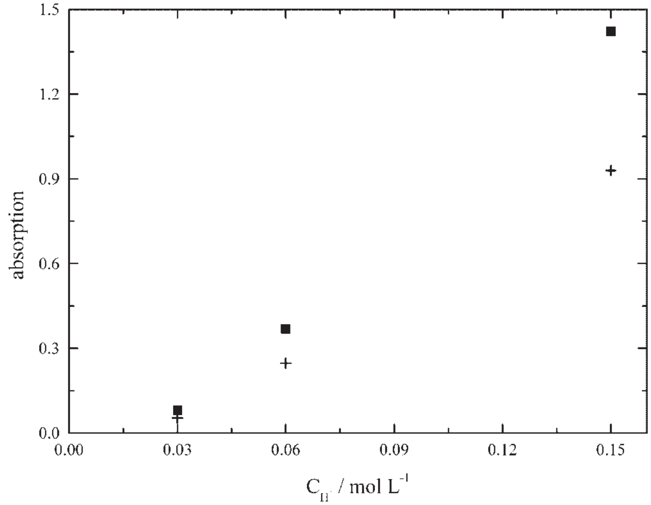

Figure 6.
Absorption as a function of acid concentration; experimental condition: *Rushton* impeller, $N = 120$ min^{-1}, pH-value (NaOH): ~10, $h_F = 7$ cm, $C_{I^-} = 0.015$ mol/L, $C_{IO_3^-} = 0.003$ mol/L, $C_{H_2BO_3^-} = 0.045$ mol/L, $t_D = 30$ s (0.14 mL/s = ~4 mL); ■ = 287 nm, + = 352 nm.

used to increase the viscosity of the aqueous reaction solution. Figure 8 presents three experiments at same reaction conditions besides the amount of HEC, which ranges from zero to 0.375%. The absorption increases with more viscous media. So at the same stirrer speed a higher viscosity leads to a lack of mixing efficiency.

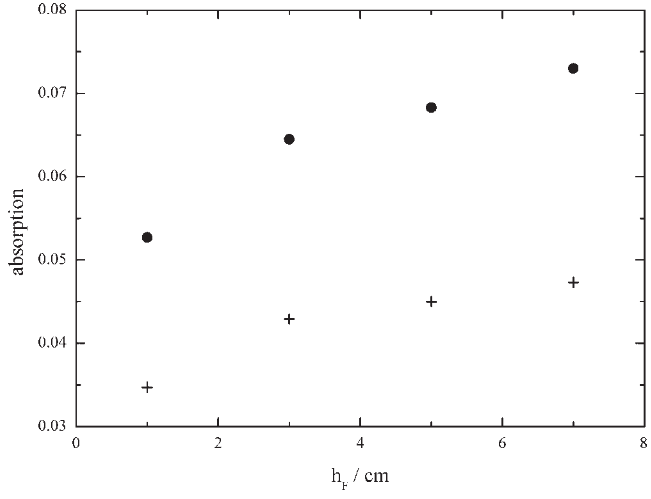

Figure 7.
Absorption as a function of the distance to the impeller; experimental conditions: *Rushton* impeller, $N = 120$ min^{-1}, pH-value (NaOH): ~10, $C_{I^-} = 0.015$ mol/L, $C_{IO_3^-} = 0.003$ mol/L, $C_{H_2BO_3^-} = 0.045$ mol/L, $C_{H^+} = 0.03$ mol/L, $t_D = 30$ s, (0.14 mL/s = ~ 4 mL); ● = 287 nm, + = 352 nm.

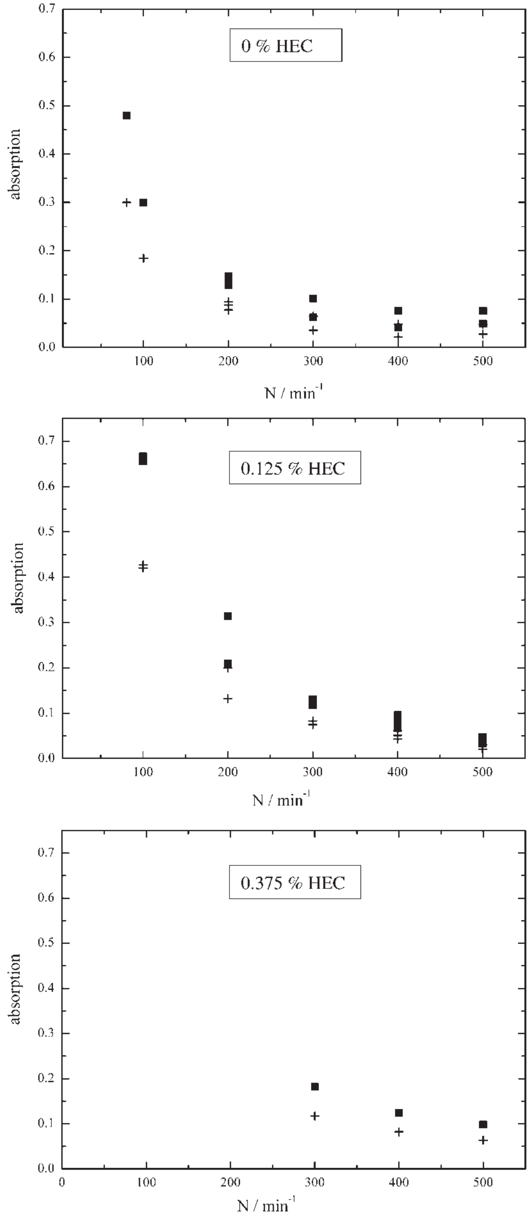

Figure 8.
Absorption as a function of stirrer speed by different viscosities; reaction condition: blade impeller, H^+-feed to the cap (3 g/min, 0.03 mol/L), I^-/IO_3^--feed to the bottom (100 g/min, $C_{I^-} = 0.0175$ mol/L, $C_{IO_3^-} = 0.0025$ mol/L), $C_{H_2BO_3^-} = 0.035$ mol/L, pH (NaOH) ~10, product flow from the cap to UV flow cuvette, ■ = 287 nm, + = 352 nm.

Conclusion

Two competitive multiple reactions were selected to study micromixing effects. The *Villermaux-Dushman* and third *Bourne* reaction were applied to investigate the influence of several parameters on micromixing efficiency. In the 1500 mL glass tank, the critical dosing periods of 300 s for an *INTERMIG®* impeller and 350 s for a *Rushton* impeller were received. With an *INTERMIG®* impeller a higher stirrer speed results in higher mixing efficiency, but even at turbulent stirring mixing can be insufficient. The reactant concentration of the feed stream effects micromixing substantially. The higher the concentration, the shorter the required time for dosing to obtain similar absorption. For the *Rushton* impeller the effect of the feed position on micromixing according to the local energy dissipation could be proved. Decreasing distance to the impeller improves mixing. Mixing efficiency falls off significantly with increasing viscosity of the reaction media.

Notation

b	mm	blade width
C	mol/L, mol/kg	concentration
Da_M	–	*Damkoehler* number
d_1	mm	tank diameter
d_2	mm	impeller diameter
d_k	mm	capillary diameter
h_1	mm	filling level
h_2	mm	(projected) blade height
h_3	mm	distance from bottom
h_6	mm	stages distance
h_F	cm	feed position
k	$m^3\ mol^{-1}$, $m^3 mol^{-1} s^{-1}$	reaction constant
n	mol	amount of substance
N	min^{-1}	stirrer speed
r_F	mm	distance to stirrer shaft
t	s	reaction time
t_c	s	critical dosing period
t_D	s	dosing period
X	–	segregation index
z_1	–	number of blades
z_2	–	number of stages

Greek Letters

τ_M	s	characteristic mixing time
τ_R	s	characteristic reaction time

Indices

0	start condition, start value

Abbreviation

ECA	ethyl chloroacetate
HEC	hydroxyethyl cellulose

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