TEST REACTIONS TO STUDY EFFICIENCY OF MIXING

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Effects of mixing on the course of fast chemical reactions are relatively well understood, especially in homogeneous systems. This enables to design and operate chemical reactors with the goal to achieve a high yield of a desired product and use systems of complex reactions as a chemical probe (chemical test reactions) to identify progress of mixing and quality of mixture. Recently, a number of studies have focused on the application of chemical test reactions to identify energy efficiency of mixing, being a convenient way of comparing mixers and reactors in terms of their mixing efficiency. This review offers a presentation of chemical test reactions available in the literature and methods of applications of test reactions to identify the energy efficiency of mixing. Also methods to assess the extent of micromixing by measuring product distribution or segregation index, and to determine the time constant for mixing are presented for single phase homogeneous systems and two-phase liquid-liquid systems.

Keywords: micromixing, efficiency of mixing, IEM model, engulfment model, chemical test reactions

1. INTRODUCTION

In this paper the author is concerned with the influence of mixing on the course of complex chemical reactions. This problem is considered as important in the chemical reaction engineering literature (Bałdyga and Bourne, 1999; Bourne, 2003; Levenspiel, 1972) for two reasons. The first reason is obvious: one wants to design and operate chemical reactors with the goal to achieve a high yield of a desired product. The second reason is related to the fact that complex chemical reactions are used as test reactions to investigate progress of mixing, quality of mixture and efficiency of mixing. One can thus identify the index of segregation, time constants for mixing and energy efficiency of mixing and use this information to improve the process.

When reagents are not mixed sufficiently rapidly, a single chemical reaction can be retarded, which requires then a larger reactor vessel or longer residence time to achieve a particular conversion. In this context a single, very fast reaction can be used for visualisation of mixing processes. A good and simple example proposed here is the neutralisation reaction in the presence of phenolphthalein. In two-phase liquid-liquid systems, mixing, drop dispersion and mass transfer can greatly retard the rate of very fast reactions when reagents are initially present in different phases (Bourne, 2003; Doraiswamy and Sharma, 1984).

The effective rates of fast complex reactions can also be retarded by mixing. Desirable chemical reactions are often accompanied by side reactions, so retardation of desired reactions can promote the creation of undesired by-products. This affects product purity and requires product recovery, which is expensive. Moreover, at the same time raw materials are wasted. In many cases, by improving mixing

one can obtain more selective syntheses, and with ecological and economic benefits (Bałdyga and Bourne, 1999; Doraiswamy and Sharma, 1984; Levenspiel, 1972). Because the product distribution and selectivity of chemical reactions, transient and final, depend on mixing processes, they can be used as very sensitive indicators of mixing intensity and efficiency in process equipment (Jasińska et al., 2013a; Jasińska et al., 2013b; Malecha et al., 2009). In the present paper a review on the application of test reactions to investigate efficiency of mixing in reactors and mixers is presented.

2. REVIEW OF TEST REACTIONS

There are many schemes of complex chemical reactions with mixing sensitive product distributions that can be used to characterise mixing (Bałdyga and Bourne, 1999; Levenspiel, 1972). All such reaction schemes consist of a combination of two primary reaction types: competing or parallel second order reactions,

$$A + B \xrightarrow{k_1} R \; , \; A + C \xrightarrow{k_2} S \tag{1}$$

and consecutive or series second order reactions.

$$A + B \xrightarrow{k_1} R \; , \; R + B \xrightarrow{k_2} S \tag{2}$$

To use test reactions quantitatively one needs to have complete information about them, including reaction thermodynamics, reaction kinetics, and reaction mechanism. However, for many technological problems such information is not readily available and the reactions give just a semiquantitative or qualitative information; then one can just check in which apparatus mixing is better, and if any action taken to improve mixing is successful.

Properly designed test reactions can be used quantitatively; hence, it should be possible to use them together with adequate models of micromixing describing a coupling between mixing and chemical reactions. Prior to working out test procedures, such micromixing models should be validated using the well defined test reactions.

2.1. Criteria for test reactions

When designing a system of test reactions to study mixing, at least one reaction should be very fast relative to mixing. Its progress is then controlled by mixing. The rate of second reaction should be of comparable magnitude to the mixing rate or smaller, i.e. with the time constant either of comparable magnitude or larger than the time constant for mixing. Hence, to design a set of complex test reactions one needs to start from a rough estimate of the time scales that can characterise any specific equipment and afterwards choose chemical reactions adequately.

Let us start from defining the time constants for chemical reactions. The time constant of the first reaction in both reaction schemes, (1) and (2), can be referred to the local average feed or initial concentrations, and can be expressed by

$$\tau_{R1} = \frac{1}{k_1 \left(\overline{c}_{A0} + \overline{c}_{B0} \right)} \tag{3}$$

For the second reaction in scheme (1) we have similarly,

$$\tau_{R2} = \frac{1}{k_2 \left(\overline{c}_{A0} + \overline{c}_{C0} \right)} \tag{4}$$

A definition of the time constants for the second reaction in scheme (2) requires more attention. It is worth noting that after Reynolds averaging of the chemical kinetics term $k_i c_\alpha c_\beta = k_i \left(\overline{c}_\alpha \overline{c}_\beta + \overline{c'_\alpha c'_\beta} \right)$, the time constant can be defined by a comparison of the decay rate of $\overline{c}_\alpha \overline{c}_\beta$ due to the progress of chemical reaction with the decay rate of $\overline{c'_\alpha c'_\beta}$ due to mixing (Bałdyga and Bourne, 1999). The smallest value of the time constant of the second reaction in scheme (2) reads:

$$\tau_{R2} = \frac{1}{k_2 \overline{c}_{B0}}$$

(5)

This has been obtained assuming that in scheme (2) only R is created from A and B. Then for $\overline{c}_{A0} > 0.5 \overline{c}_{B0}$ the smallest time constant is for $\overline{c}_R = 0.5 \overline{c}_{B0}$ and $\overline{c}_B = 0.5 \overline{c}_{B0}$, whereas for $\overline{c}_{A0} < 0.5 \overline{c}_{B0}$ this happens for $\overline{c}_R = \overline{c}_{A0}$ and $\overline{c}_B = \overline{c}_{B0} - \overline{c}_{A0}$.

The time constant for turbulent mixing can be defined as the time scale of decay of the concentration variance of the passive scalar, α:

$$\tau_M = \frac{\overline{\left(c_\alpha - \overline{c}_\alpha \right)^2}}{\dfrac{d \overline{\left(c_\alpha - \overline{c}_\alpha \right)^2}}{dt}}$$

(6)

For laminar mixing by fluid elongation, one can define the characteristic mixing time by (Bałdyga and Bourne, 1986),

$$\tau_M = \frac{1}{2\dot{\gamma}} \arcsin h \left(0.76 \dot{\gamma} \, \delta_0^2 / D_\alpha \right)$$

(7)

where $\dot{\gamma}$ is the rate of elongation and δ_0 represents original thickness of the striation to be elongated.

In the case of simple shear the mixing time is much longer than that expressed by Eq. (7), because the rate of elongation is then not constant but decreasing with process time (Bałdyga and Bourne, 1986). In fact for the process time $t \gg \dot{\gamma}^{-1}$ one has $\dot{\gamma} \propto t^{-1}$ and the mixing time increasing and efficiency of mixing decreasing in time. It is clear that to have efficient mixing one should design the flow that is creating elongation and avoiding shear.

In the case of turbulent mixing, the rate of elongation can be expressed as $0.5(\varepsilon/\nu)^{1/2}$ and the striation thickness estimated as the Kolmogrov microscale, λ_K, yielding

$$\tau_M \cong \left(\frac{\nu}{\varepsilon} \right)^{1/2} \arcsin h \left(0.1 Sc \right)$$

(8)

where $Sc = \nu/D$ is the Schmidt number, ε is the rate of energy dissipation, and ν represents kinematic viscosity.

If we try to identify more than one time constant for turbulent mixing to describe dynamic aspects of concentration spectrum development, in the case of liquids ($Sc \gg 1$) we can distinguish the time constant for the inertial-convective mixing (Bałdyga and Bourne, 1986)

$$\tau_{M1} = \frac{1}{R} \frac{k}{\varepsilon} = \frac{1}{2} \frac{k}{\varepsilon} = \frac{3}{4} \frac{L^{2/3}}{\varepsilon^{1/3}}$$

(9)

and the viscous-convective mixing (Bałdyga and Bourne, 1999),

$$\tau_{M2} \cong 17 \left(\frac{\nu}{\varepsilon} \right)^{1/2}$$

(10)

whereas the characteristic time constant for viscous-diffusive mixing can be characterised by Eq. (8).

The time constant of mass transfer can be defined by (Jasińska et al., 2013b, Jasińska and Bałdyga, 2014)

$$\tau_{Mi} = \frac{1}{k_{Li}a} \tag{11}$$

where $a = A_d/V_d$ is the characteristic surface per unit volume of the dispersed phase.

For drops of spherical shape, small enough to exclude internal circulation, one can use the model of Batchelor (1980) to calculate the external mass transfer coefficient

$$k_L = \left[2\frac{D_{Ci}}{d_d} + 0.689\left(\frac{D_{Ci}^2}{d_d}\right)^{1/3}\left(\frac{\varepsilon}{\nu}\right)^{1/6} \right] \tag{11a}$$

Where D_{Ci} denotes the molecular diffusivity of i in the continuous phase. The drop size, d_d, can be expressed through the equation derived by Kolmogorov (1949).

$$d_d = 0.23\frac{\sigma^{0.6}}{\varepsilon^{0.4}\rho_C^{0.6}} \tag{11b}$$

Because $a = A_d/V_d = 6/d_d$ for drops of spherical shape, one gets finally

$$k_L a = \left[2\frac{D_{Ci}}{d_d} + 0.689\left(\frac{D_{Ci}^2}{d_d}\right)^{1/3}\left(\frac{\varepsilon}{\nu}\right)^{1/6} \right]\frac{6}{d_d} \tag{11c}$$

For large values of the Sherwood number ($Sh \gg 2$) one gets a simple relation between the rate of energy dissipation, ε, and the time constant for external mass transfer (Jasińska et al., 2013b, Jasińska and Bałdyga, 2014)

$$\tau_{Mi} = \frac{1}{k_{Li}a} \approx 0.034\frac{\sigma^{4/5}\nu^{1/6}}{D_{Ci}^{2/3}\varepsilon^{7/10}\rho_C^{4/5}} \tag{12}$$

A set of chemical reactions can be mixing or mass transfer-sensitive but still not suitable. This is because the test reactions must be fully chemically characterised, so that any measured change in product distribution should be unequivocally attributed to "mixing" and not to a chemical artefact. The most important criteria for test reactions can be summarised as follows (Bałdyga and Bourne, 1999):

1. Multiple reactions can be employed as test reactions provided that the product distribution depends strongly on mixing.
2. Reactions should be irreversible, so that the product distribution stores the mixing history over the reaction zone.
3. Unequivocal knowledge of all reactions and their kinetics and the mechanism is essential. This includes the dependence of the reaction rate on all concentrations, ionic strength, pH, solvent, temperature and homogenous catalysts including acids and bases.
4. Second-order kinetics with few (preferably two) products and no side reactions are desirable.
5. Rate constants should differ, as it is required to detect differences in product distribution relative to the chemical regime. Reaction rate constants differing by approximately 2 orders of magnitude are suitable.
6. All reactants and products should be soluble, to avoid any phase change that can affect the overall rate of the process. Hence, the solubilities of reagents and products should be known.
7. Accurate quantitative analysis is essential to determine product distribution. A routine, inexpensive, and accurate instrumental analytical method should be available.

8. Low concentrations of highly reactive reagents, which should be directly available on the market and sufficiently pure, so that they do not require further purification.

9. Reagents, products, etc. should be rigorously screened for toxicity, disposability, corrosion, fire and explosion hazards, and should be relatively inexpensive.

2.2. Efficiency of mixing and mass transfer

Notice that when the first reaction from both schemes (1) and (2) is very fast, it is controlled not by the reaction rate resulting from kinetics but by the rate of mixing, such that there is competition between the mixing process controlling the first reaction and chemical kinetics controlling or at least significantly affecting the second one. The extend of the second reaction can be thus used to characterise the effectiveness of mixing.

The process of mixing between elongated striations in a homogeneous system can be represented by the rate of creation of the intermaterial area per unit volume, a_v [m^{-1}], and expressed by

$$\left| \frac{1}{a_v} \frac{da_v}{dt} \right| = \text{eff}(t) \cdot \left(\bar{D} : \bar{D} \right)^{1/2} \tag{13}$$

where $\bar{D}$ [s^{-1}] represents the deformation tensor.

$$\bar{D} = \frac{1}{2} \left[\text{grad}(v) + \text{grad}(v)^T \right] \tag{14}$$

That is defined using the velocity gradient, $\text{grad}(v)$ (Ottino, 1981).

Eq. (13) depicts the fact that orientation of the intermaterial area with respect to the principle axis of deformation determines the effectiveness of mixing. It characterises the ratio of mechanical energy really applied to increase the intermaterial area to the energy dissipated during the flow. Using this concept one can define the effectiveness of mixing either by (Ottino, 1981)

$$\text{eff}(t) = \frac{1}{a_v} \frac{da_v}{dt} \left(\frac{\varepsilon_T}{2\nu} \right)^{-1/2} \tag{15}$$

or more precisely by (Rożeń, 2008),

$$\text{eff}(t) = \frac{1}{a_v} \frac{da_v}{dt} \left(\frac{\varepsilon_T}{3\nu} \right)^{-1/2} \tag{16}$$

where ε_T [m^{2}s^{-3}] represents the total rate of energy dissipation per mass unit.

In this paper the average values of efficiency during residence time t in the mixer, $\overline{\text{eff}}$, will be considered.

The proposed procedure to characterise the efficiency of mixing in homogeneous systems includes modelling of effects of mixing on the course of the test chemical reactions to create a calibration curve, using micromixing models in ideal situation and afterwards a comparison of model predictions with experimental data obtained using test reactions (Jasińska et al., 2013a; Malecha et al., 2009).

Comparing now the theoretical rate of energy dissipation, ε, necessary to obtain the same product distribution as observed in the considered experiment, characterised by the total rate of energy dissipation, ε_T, one can express the average efficiency of mixing, $\overline{\text{eff}}$, by

$$\overline{\text{eff}} = \left(\frac{\varepsilon}{\varepsilon_T} \right)^{1/2} \tag{17}$$

where $\overline{\text{eff}}$ means here the fraction of the real rate of deformation that is used directly to increase the intermaterial area.

A similar method of the application of reactive tracers can be used to characterise the efficiency of mass transfer in two-phase liquid-liquid systems (Jasińska et al., 2013b). The results of modelling representing effects of mass transfer on the product distribution of complex reactions can be used as the calibration curve; comparing now the theoretical rate of energy dissipation, ε, necessary to obtain the same product distribution as observed in considered experiment one can find the fraction of energy used directly to enhance mass transfer.

2.3. Examples of test reactions

Many reports on the influence of mixing on chemical reactions have been published but it is quite uncertain whether these reactions satisfy all the criteria for test reactions. As will be shown in the subsequent sections, all of the proposed reactions in the literature have strong and weak points. It is important to emphasise that using the unsuitable reaction or using it in the wrong way can give misleading results regarding mixing intensity in examined devices.
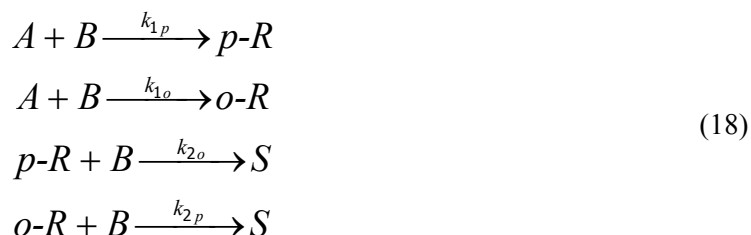
In what follows I present the results of a literature search for test reactions. It is convenient to divide them in two categories: firstly single phase, homogenous test reactions, and secondly biphasic (liquid-liquid) test reaction.

2.3.1. Single phase (homogenous) reactions

2.3.1.1. Diazo coupling between 1-naphthol and diazotized sulphanilic acid (Bałdyga and Bourne, 1999; Bourne et al., 1990)

Reaction mechanism/scheme
The scheme, showing competitive-consecutive reactions may be written as follows:

$$
\begin{aligned}
A + B &\xrightarrow{\;k_{1p}\;} p\text{-}R \\
A + B &\xrightarrow{\;k_{1o}\;} o\text{-}R \\
p\text{-}R + B &\xrightarrow{\;k_{2o}\;} S \\
o\text{-}R + B &\xrightarrow{\;k_{2p}\;} S
\end{aligned}
\tag{18}
$$

with A and B being 1-napthol and diazotized sulphanilic acid respectively; the couplings take place when B, the limiting reagent, is added to A. The reaction scheme includes two primary couplings giving isomeric monoazo dyes, p-R and o-R, and their secondary couplings to give finally one bisazo dye, S.

Kinetics of products formation
The formation of the monoazo dye coupled in the p- and o- position is well defined by the second order kinetic equations with A and B being overall concentrations of 1-naphthol and diazotized salt:

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$$r_{1o} = k_{1o}[A][B]$$
$$r_{1p} = k_{1p}[A][B]$$

(19)

The monoazo dye (p-R), coupled in the p-position, can further couple with the diazonium ion in the o-position to yield the bisazo dye (S).

$$r_{2o} = k_{2o}[p\text{-}R][B]$$

(20)

The second route to S is when o-R couples further in the p-position.

$$r_{2p} = k_{2p}[o\text{-}R][B]$$

(21)

It is important to mention that these kinetic equations are presented for a total concentration of the reagents (in contrast to ions) so as unaffected by pH of the solution. To ensure maximum rates, the highest sensitivity of this diazo-coupling to mixing effects, pH equal to 9.9 should be used. To keep pH constant a sodium carbonate/bicarbonate buffer ($Na_2CO_3/NaHCO_3$) is recommended (in conc. = 111.1 mol/m^3 of each).

Using the stopped flow technique and standardised conditions (298K, pH = 9.9, $I = 444.4$ mol/m^3), rate constants based on overall reagent concentrations were determined (Bourne et al., 1990) giving:
$k_{1p} = 12238 \pm 446$ m^3/(mol·s), $k_{1o} = 921 \pm 31$ m^3/(mol·s), $k_{2p} = 22.25 \pm 0.25$ m^3/(mol·s), $k_{2o} = 1.835 \pm 0.018$ m^3/(mol·s)

Analytical method, yield and selectivity
After the reaction, the concentrations of unreacted 1-naphthol and the three dyes present in solution are measured spectrophotometrically and recalculated based on multiple regression method. It is recommended to check the mass balance based on the amount of the limiting reagent B after completing reaction. Typically the balance closes within $\pm$ 3%.

$$c_{B0} = c_{oR} + c_{pR} + 2c_S$$

(22)

The yield of the bis-azo dye (S), is used as a measure of mixing intensity or segregation index,
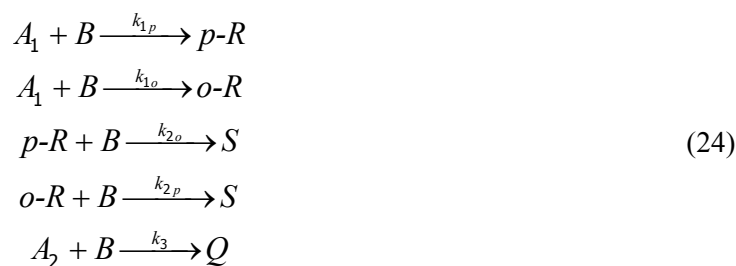
$$X_S = 2c_S/(c_{oR} + c_{pR} + 2c_S)$$

(23)

Range of application and limitations
- At room temperature the solubility of diazonium salt is about 60 mol/m^3, so higher concentrations cannot be employed. This means that the reactions are fast enough to examine mixing in stirred tanks, but not in fast mixers, such as rotor-stator devices.
- A diazonium salt solution should not be allowed to dry out, because in acidic solutions at room temeprature diazonium salt is not stable, so the reaction mixture should be analysed within a few hours and the balance, Eq. (22) always checked after the experiment.
- Application of this scheme has been extended by introducing 2-naphthol to the scheme

2.3.1.2. Simultaneous Diazo coupling between 1- and 2- naphthol and diazotized sulphanilic acid, (Bourne et al., 1992)

Reaction mechanism/scheme
Diazotized sulphanilic acid (B) also couples with 2-napthol forming single monoazo dye, Q. Representing 1- and 2- naphthols by A_1 and A_2 the scheme for their coupling reads:

$$A_1 + B \xrightarrow{\ k_{1p}\ } p\text{-}R$$
$$A_1 + B \xrightarrow{\ k_{1o}\ } o\text{-}R$$
$$p\text{-}R + B \xrightarrow{\ k_{2o}\ } S \qquad (24)$$
$$o\text{-}R + B \xrightarrow{\ k_{2p}\ } S$$
$$A_2 + B \xrightarrow{\ k_3\ } Q$$

The first four reactions are the same as in the previous section. The last one follows the same principles.

Kinetics of products formation
Defining A_2 as the total of dissociated and undissociated 2-naphthol concentrations, the kinetics of the last equation is given by:

$$r_3 = k_3 [A_2][B] \qquad (24a)$$

at 298 K and pH = 9.9, $k_3 = 124.5 \pm 1.0 \ \mathrm{m^3/(mol \cdot s)}$.

Analytical method, yield and selectivity
The product distribution can now be represented by the yields of secondary product S (X_S) and of competitive product Q (X_Q), which are defined as:

$$X_S = 2c_S / \left(c_{oR} + c_{pR} + c_Q + 2c_S \right) \qquad (25)$$

$$X_Q = c_Q / \left(c_{oR} + c_{pR} + c_Q + 2c_S \right) \qquad (26)$$

Mass balance is very similar to the previously presented equation and reads $c_{B0} = c_{oR} + c_{pR} + c_Q + 2c_S$ and closes within ± 3%.
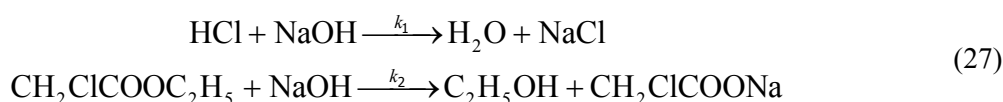
Range of application and limitations
- The coupling of 2-naphthol is much faster than the secondary couplings of 1-naphthol, so it can be used to resolve higher energy disspation rates. The yield of Q, X_Q is sensitive to the energy dissipation rates as high as 10^5 W/kg. X_S at this level, is close to zero.
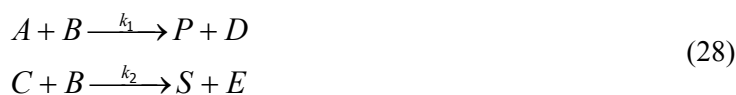- Limitations regarding safety are the same as in the previous case.

2.3.1.3. Competitive neutralisation of hydrochloric acid and alkaline hydrolysis of monochloroacetate esters with sodium hydroxide. (Bałdyga and Bourne, 1999; Yu, 1993; Bourne and Yu, 1994)

Reaction mechanism/scheme
In this case there are two competitive reactions:

$$HCl + NaOH \xrightarrow{\ k_1\ } H_2O + NaCl$$
$$CH_2ClCOOC_2H_5 + NaOH \xrightarrow{\ k_2\ } C_2H_5OH + CH_2ClCOONa \qquad (27)$$

There is competition for NaOH (the limiting reagent), in both reactions, which means that NaOH concentration becomes zero when reactions are complete. For acid, base, ester and alcohol denoted by A, B, C, and S, respectively, this reaction can be represented as:

$$A + B \xrightarrow{\ k_1\ } P + D$$
$$C + B \xrightarrow{\ k_2\ } S + E \qquad (28)$$

In experiments alkali is usually added to an acidic ester solution.

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Kinetics of products formation

At 298K, k_1 is about $1.3 \cdot 10^8$ m³/(mol·s) so the first reaction can be regarded as instantaneous compared to mixing. The second rate constant reads $k_2 = 0.030$ m³/(mol·s) at 25 °C and $k_2 = 0.023$ m³/(mol·s) at 20 °C; an average value estimated in work (Bałdyga and Bourne, 1999; Yu, 1993); more generally it can be expressed by Eq. (29) over the range between 2 and 26°C (Bałdyga and Bourne, 1999; Yu, 1993):

$$k_2 = 2.0 \times 10^5 \, exp\left(-3.891 \times 10^4 / RT\right) \tag{29}$$

Hydrolysis is limited by the solubility of esters (at 288 K the solubility of ethyl monochloroacetate is equal to 183 mol/m³) (Bałdyga and Bourne, 1999).

Analytical method, yield and selectivity

Quantitative analysis of the ester and alcohol has been carried out by GC/FID. The final product mixture is acidic and should be quickly analysed to limit any acid-catalysed hydrolysis. Measurement of both ester and alcohol concentration allows to check mass balance with typical errors being in the range between 2% to 4% of the initial ester quantity.

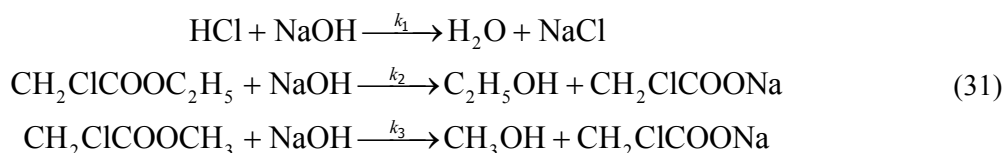The product distribution is represented by the yield of alcohol relative to the limiting reagent and denoted by X_S:

$$X_S = c_S / c_{B0} = c_S / \left(c_P + c_Q\right) \tag{30}$$

Range of application and limitations
- The reaction is simple and robust.
- The solubility of ethyl monochloroaceate limits its concentration in the acidic solution prior to reaction to about 120 mol/m³. Weaker flow fields, e.g. in stirred tanks can thus be resolved if the energy dissipation rate in the reaction zone does not exceed roughly 1 W/kg.
- The reaction is not environmentally friendly. Ethyl monochloroacetates are volatile and flammable.
- Somewhat more intense turbulence can be resolved when methyl ester is employed instead of ethyl ester, because its solubility is higher. Energy dissipation rates up to about 10 W/kg can be then resolved.

2.3.1.4. Competitive neutralisation of hydrochloric acid and alkaline hydrolysis of some other esters with sodium hydroxide. (Bałdyga et al., 2012; Yu, 1993)

In the same work (Yu, 1993) another scheme involving alkaline hydrolysis of esters was proposed in the form:

$$HCl + NaOH \xrightarrow{k_1} H_2O + NaCl$$
$$CH_2ClCOOC_2H_5 + NaOH \xrightarrow{k_2} C_2H_5OH + CH_2ClCOONa \tag{31}$$
$$CH_2ClCOOCH_3 + NaOH \xrightarrow{k_3} CH_3OH + CH_2ClCOONa$$

introducing the third parallel reaction competing for sodium hydroxide

$r_3 = k_3 c_{NaOH} c_{CH_2ClCOOCH_3}$ with the second-order kinetic constant: $k_3 = 56.4 \cdot 10^{-3}$ m³/(mol·s).

The extended scheme allows investigation of mixromixing in devices characterised by somewhat higher values of energy dissipation rates than those in the previous case. However, too small differences in reaction rate constant ($k_3/k_2 \cong 2$) and not much higher solubility of methyl ester (in comparison to ethyl ester) does not increase significantly the range of applications.
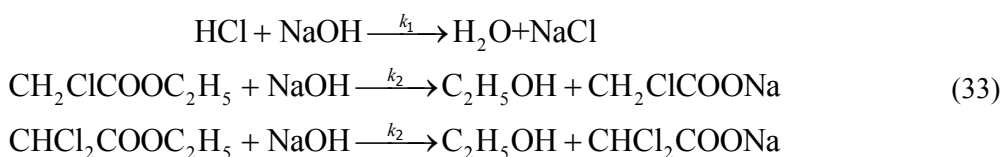
For this reason another reaction scheme was proposed by Bałdyga et al. (2012):

$$HCl + NaOH \xrightarrow{k_1} H_2O + NaCl$$

$$CHCl_2COOC_2H_5 + NaOH \xrightarrow{k_2} C_2H_5OH + CHCl_2COONa \tag{32}$$
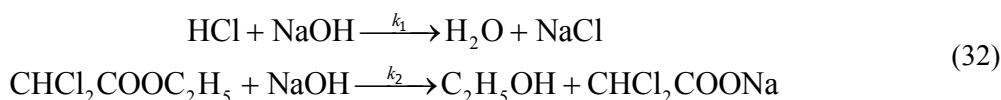
where $k_2 = 68\cdot10^{-2}$ m³/(mol·s) and successfully used to describe micromixing in stirred tank reactors.

The comparison between monochloroacetate and dichloroacetate used as a substrat in the second reaction, presented in a paper (Bałdyga et al., 2012), shows some spectacular differences in measurements of selectivity, even for a stirred tank reactor. Clearly, a reaction with dichloroacetate serves as a much more sensitive indicator of mixing (reported in the paper in terms of stirrer speed), and can be used in a broader range of stirrer speeds with a lower experimental error.

In order to further extend the range of applications another reaction scheme can be used. In this case the selectivity of second reaction is responsible for lower intensities (as discussed earlier in this section) whereas the yield of third reaction was responsible for higher intensities as in the previous case:

$$HCl + NaOH \xrightarrow{k_1} H_2O+NaCl$$

$$CH_2ClCOOC_2H_5 + NaOH \xrightarrow{k_2} C_2H_5OH + CH_2ClCOONa \tag{33}$$

$$CHCl_2COOC_2H_5 + NaOH \xrightarrow{k_2} C_2H_5OH + CHCl_2COONa$$

2.3.1.5. An acid-catalysed hydrolysis of 2,2-Dimethoxypropane (DMP) (Bałdyga et al., 1998; Johnson and Prud'homme, 2003)

Reaction mechnism/scheme
A next pair of competitive (or parallel) reactions reads:

$$A + B \xrightarrow{k_1} R + S$$

$$C + (A) \xrightarrow{k_2} Q + 2P(+A) \tag{34}$$
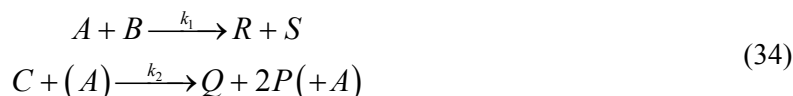
where A is a reactant in the first equation but a homogeneous catalyst in the second one. Eqs. (34) correspond to:

$$HCl + NaOH \xrightarrow{k_1} NaCl+H_2O$$

$$H_3CC(OCH_3)_2 CH_3 + H_2O \xrightarrow{k_2} (CH_3)_2 CO + 2CH_3OH \tag{35}$$
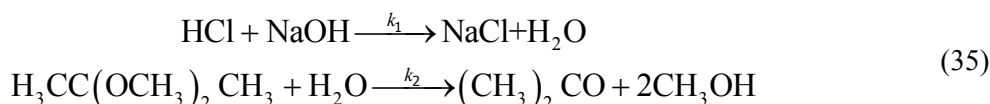
The fast reaction is the neutralisation of acid with base, which is instantaneous relative to mixing. The slower reaction is the hydrolysis of reagent C, dimethoxypropane, (DMP). The limiting reagent is acid; concentrated acid is added to an alkaline solution of acetal, where it is neutralised in the first reaction and catalyses hydrolysis of acetal in the second reaction. The first reaction is irreversible and moderately exothermic (Δh_1 = -55.8 kJ/mol, Bałdyga et al., (1998)), the second one is irreversible in dilute aqueous solutions when catalysed by acids and weakly endothermic with Δh_2 = 18.0 kJ/mol.

Kinetics of products formation
The reactions are of second-order; the fast (instantaneous) reaction of neutralisation has a second-order rate constant $k_1 = 1.4\cdot10^8$ m³/(mol·s), and kinetics of the second one reads

$$r_C = -k_2 c_A c_C \tag{36}$$

with the rate constant measured by Walker (1996) for sodium chloride concentrations c_S of 100 to 1200 mol/m³, and a temperature range from 298 to 313 K.

$$k_2 = Z_2\exp(-E_2 / RT) \tag{37}$$

where $Z_2 = 7.32\cdot10^7$ m³/(mol·s), $E_2 = 7.32\cdot10^7$ kJ/mol

The value of Z_2 given above refers to 25 wt% ethanol. For NaCl concentrations exceeding 100 mol/m^3, k_2 increases to k_2' according to

$$\log(k_2' / k_2) = K_S + ac_S \tag{38}$$

while for salt-free hydrolysis k_2 is given by Eq. (37) and $K_S = 0.05435$, $a = 7.066 \cdot 10^{-5}$ m^3/mol. At 298 K $k_2 = 0.60$ m^3/(mol·s) in a solvent containing 25 mass% ethanol (rest water) when employing initial HCl concentrations up to 1333 mol/m^3.

Analytical method, yield and selectivity
Analysis of product mixtures was carried out by gas chromatography (GC). The yield, X_Q is defined by Eq. (39), and ranges from 0 to 1 as segregation rises.

$$X_Q = n_Q / n_{C0} \tag{39}$$

In this case also temperature segregation was taken into account. The results have shown that temperature segregation is negligible, as in previous cases, but the mode of operation is important - isothermal or adiabatic.

Range of application and limitations (constrains)
- This competitive reaction scheme is fast enough for investigation of impinging jets, has stable reactants and products, and is easily quantified by gas chromatography.
- Because NaCl is formed in the neutralisation reaction, its influence on DMP solubility has to be considered.
- One should be careful with HCl concentration in excess of 1000 mol/m^3 because of possible change in reaction mechanism at high acid concentrations.
- Johnson and Prud'homme (2003) have also investigated the stability of the DMP and found that the decomposition rate was less than 0.6% per day for 30 days at room temperature and 200 mmol/dm^3 DMP.

2.3.1.6. The iodine-iodate reaction (Villermaux-Dushman reaction)

Reaction mechanism/scheme
The iodide/iodate method, introduced in the 1990's (Fournier et al., 1996) and described in more detail by Guichardon and Falk (2000) and Guichardon et al. (2000) is based on measuring the mixing-sensitive yield of iodine in the competition between the neutralisation of an acid, and its role in liberating iodine through the Dushman reaction.

$$H_2BO_3^- + H^+ \rightleftharpoons H_3BO_3 \tag{40}$$

$$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O \tag{41}$$
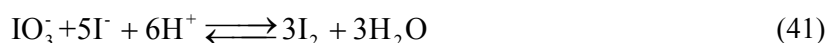
Iodine may further react with iodide to form triiodide

$$I_2 + I^- \rightleftharpoons I_3^- \tag{42}$$
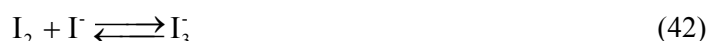
This last reaction is characterised by equilibrium constant at 25°C (Palmer and Lietzke, 1982)

$$K_B = \frac{\left[I_3^-\right]}{\left[I_2\right]\left[I^-\right]} \tag{43}$$

Before mixing, the two aqueous solutions, (a) and (b) contain: (a) sulphuric acid, which is the limiting reagent and (b) iodide, iodate and borate ions, which also act as buffer. Released iodine complexes with iodide to form triiodide.

Kinetics of products formation

The first reaction is neutralisation and may be considered instantaneous. The rate of the second one has been studied since 1888, but there are still discussions about its applicability (Bourne, 2008; Kölbl et al., 2013; Kölbl and Schmidt-Lehr, 2010). Because the ionic strength I_S varies during the micromixing process, the kinetics have to be expressed as a function of I_S. The rate equation (Fournier et al., 1996) can be written as

$$r = k \left[\mathrm{H}^+ \right]^2 \left[\mathrm{I}^- \right]^2 \left[\mathrm{IO}_3^- \right] \tag{44}$$

where k, reaction rate constant [mol^4/(dm^3)^4/s] depends on the ionic strength according to

$\log(k) = 9.28105 - 3.664\sqrt{I_S}$, for $I_S < 0.166$ mol/dm^3

$\log(k) = 8.383 - 1.5115\sqrt{I_S} + 0.23689 I_S$, for $I_S > 0.166$ mol/dm^3

The rate constant, k, is about 10^{11} dm^3 mol^{-1} s^{-1} so that neutralisation is almost instantaneous. The equilibrium of iodide/triiodide is also reached much faster than the Dushman reaction-kinetics.

Analytical method, yield and selectivity

Released iodine reacts with iodide to form triiodide. The concentration of triiodide is determined photometrically, and together with the equilibrium constant and the initial quantities of all reagents allows the iodine yield to be obtained (Guichardon and Falk, 2000; Guichardon et al., 2000). When mixing is much faster than Dushman reaction, the acid is almost totally consumed in neutralisation reaction. When, however, micromixing is slower than in reaction (41), iodine forms and its yield is a measure of an incomplete micromixing. The final observed yield of the second reaction under imperfect mixing conditions is

$$Y = \frac{2\left(n_{I_2} + n_{I_3^-}\right)}{n_{H_0^+}} = \frac{4\left(\left[I_2\right] + \left[I_3^-\right]\right)}{\left[H^+\right]_0} \tag{45}$$

whereas the limit in value in a totally segregated system, the yield of the second reaction becomes

$$Y_{ST} = \frac{6\left[IO_3^-\right]_0}{6\left[IO_3^-\right]_0 + \left[H_2BO_3^-\right]_0} \tag{46}$$

The segregation index is then defined as

$$X_S = \frac{Y}{Y_{ST}} \tag{47}$$

For perfect micromixing, X_S is equal to zero and in a totally segregated medium, X_S is equal to one.

Range of application and limitations

- The iodide/iodate method for characterising the extent of micromixing through the iodine yield gives qualitatively consistent results. It is suitable to rank different mixers or different operating conditions. Its quantitative application requires the kinetics of all equations in the scheme to be fully known. However, according to Bourne (2008), none of the kinetic models of the Dushman reaction scheme satisfies this requirement and the models show little mutual agreement. There is a need for a kinetic study of the Dushman reaction employing modern techniques for fast reactions and concentrations relevant to mixing investigations.

- The temperature-independence of k and the high kinetic order (fifth) indicate a multistep reaction mechanism. Problems with reaction kinetics might be responsible for discrepancies observed when simulating these reactions (Bourne, 2008).

- Kölbl et al., (2013) concluded recently that for estimation from the experimental product distribution of measures such as mixing times, the choice of acid has to be carefully considered. They suggest employing a very strong acid in the experiment or including the dissociation

constant of HSO_4^- in the reactive mixing models as suggested by Bourne (2008) and Kölbl and Schmidt-Lehr (2010).

Villermaux-Dushman reaction is simple and the reaction mixture is easy to analyse with a small error. That is why this reaction has been frequently used to examine mixing in various devices; it seems to be a basic method to investigate micromixers. In many papers very good mixing in some new-developed micromixing devices is reported. However, as presented in subject literature (Bourne, 2008; Kölbl et al., 2013; Kölbl and Schmidt-Lehr, 2010) this reaction should be used with special precautions and its results interpreted very carefully. Its kinetics is limited to a narrow range of concentrations and also the use of sulpuric acid seems to be in doubt (Bourne, 2008; Kölbl et al., 2013; Kölbl and Schmidt-Lehr, 2010).

2.3.2. Reactions in two-phase liquid-liquid systems

When reactions involving reagents initially present in different phases occur, interphase mass transfer can influence their rates and product distributions.

The criteria for test reaction in a 2-phase system are not as clear as those of single phase. The requirement of second-order is more difficult to fulfill. Reactants are present initially in separate phases, usually very soluble in one phase and hardly soluble in another, which in many cases leads to pseudo-first order reactions.

Reactions in liquid-liquid systems have not been extensively reported as test reactions so far in the literature. For gas-liquid systems Danckwerts (1970) proposed a method for determining mass transfer rate using complex reactions. Much has been done by Doraiswamy and Sharma (1984) to describe systematically the effects of mass transfer for different reaction schemes. Nevertheless the main problem lies in the fact that there are not many reactions in liquid-liquid systems that fulfill criteria similar to those listed in Section 2.1. Moreover, some additional conditions need to be satisfied. They can be summarised as follows:

- Two liquid solvents which are almost completely immiscible are required. The presence of two phases introduces complexity. For a reaction to occur between two reagents, say A and B, initially present in different phases, it is necessary to identify the phase (A-rich or B-rich) within which the reaction takes place. Often this is obvious but when solvents are partially miscible it is not so clear.
- Time constant of chemical reaction depending on solubility, and solubility can be a complex function of composition. The reaction can thus be located at the interface, near the interface but within the diffusion layer or in the bulk far removed from the interface. This location depends also on solubility and influences reaction rate and thus selectivity. High selectivity is favored when dissolved and dissolving reagents form products in the film, whilst byproducts form in the bulk. Various scenarios, having widely different selectivities, were illustrated for competitive as well as competitive-consecutive reactions (Bourne, 2003; Doraiswamy and Sharma, 1984).

In the case of biphasic reactions we have several extra degrees of freedom. One can start from considering two main types of competitive-consecutive reactions of a scheme given either as

$$A + B \xrightarrow{k_1} R$$
$$R + B \xrightarrow{k_2} S$$

(48)

or

$$A + B \xrightarrow{\ k_1\ } R$$
$$A + R \xrightarrow{\ k_2\ } S \tag{49}$$
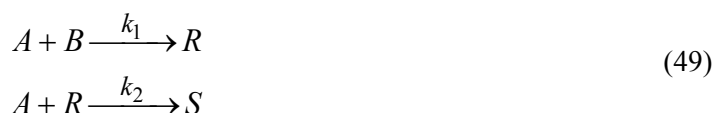
Let the dispersed phase be called phase 1 and the second, continuous one, phase 2. In both cases, (48) and (49), the reactions occur in the phase 2, where A is present (A-rich phase) and into which B is transferred from phase 1.

Let in the system expressed by Eq. (48), B be initially present in phase 1 with a low solubility in phase 2 ($c_{Bi}/c_A \ll 1$). In many practical cases the intermediate R is the required product and $k_1 > k_2$, so that when the reaction conditions are properly chosen a high selectivity for R can be expected. For example, when the first reaction is fast, the second reaction slow or very slow, $Ha_1 > 3$, $Ha_2 < 0.3$, reagent B will react completely in the diffusion film of phase 2 and most of B will react with A, not R. So in this scenario a high selectivity for R will be observed. Ha_i represents here the Hatta number:

$$Ha_i = \frac{\left(k_i c_A D_i\right)^{1/2}}{k_{Li}} \tag{50}$$

The system represented by Eq. (49) looks similar to Eq. (48) but the situation is different. If as in Eq. (48) B is initially present in phase 1 and has a low solubility in phase 2, so $c_{Bi}/c_A \ll 1$ and again we consider $k_1 > k_2$ and expect that the selectivity for the intermediate R should be high. However, as the reaction takes place in A-rich phase 2, R reacts mostly with excess of A to form S.

A parallel-competitive scheme of chemical reactions can be considered as well:

$$A + B \xrightarrow{\ k_1\ } R$$
$$A + C \xrightarrow{\ k_2\ } S \tag{51}$$
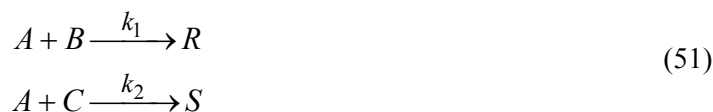
In the case of a scheme represented by Eq. (51) there are two possibilities that can be considered as candidates for the test system:
1. A is present in phase 2 where the reactions take place. B and C, initially present in phase 1, are both transferred into phase 2.
2. B and C are present in phase 2 (the reactive phase) and A initially present only in phase 1, is transferred into phase 2.

Similarly as in the case of competitive-consecutive reactions each reaction can take place in the film or the bulk depending on the value of Hatta number and the results of competition between mass transfer and chemical reaction determines reaction selectivity.

Several examples of industrially relevant reactions of the types presented above are given elsewhere (Bourne, 2003; Doraiswamy and Sharma, 1984). However, (Bourne, 2003; Doraiswamy and Sharma, 1984) these reactions were not discussed and considered in the context of using them as possible test reactions to validate mass transfer models in various types of equipment.

The application of complex test reactions of the type (51), case (a) for liquid-liquid two-phase systems was proposed recently by the author of the present work (Jasińska et al., 2013b). In experiments carried out in a batch reactor the continuous phase was an aqueous solution of sodium hydroxide (A) of the initial concentration equal to 0.005 mol/dm^3 and the dispersed phase was a solution of benzoic acid (B) and ethyl chloroacetate (C) in toluene, both of the initial concentration equal to 0.5 mol/dm^3, so $\overline{C}_{B0} = \overline{C}_{C0}$. The volume fraction of the organic phase was equal to 0.01. During experiments the reactions between sodium hydroxide and either benzoic acid (instantaneous) or ethyl chloroacetate (fast) were localised in the aqueous phase.

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The concentration of ethyl chloroacetate was measured after the experiment using the Gas Chromatography Mass Spectroscopy system. The product distribution, defined as a fraction of moles of ester reacting with NaOH, was calculated using:

$$X_S = \Delta N_C / N_{C0} \tag{52}$$

where ΔN_C represents the number of ester moles reacting with NaOH and N_{C0} is the complete number of ester moles introduced into the system. The measured value of product distribution was sensitive to agitation rate and type of equipment.

3. MODELS OF MICROMIXING APPLIED TO INTERPRET RESULS OF TEST REACTIONS

Two micromixing models are applied in the literature to identify the efficiency of mixing based on experimental data: the Engulfment model (E-model) (Bałdyga and Bourne, 1989; Bałdyga and Bourne, 1999) and the Interaction by Exchange with the Mean (IEM) model (Costa and Trevissoi, 1972a; Costa and Trevissoi 1972b; Harada et al., 1962; Villermaux and Devillon, 1972).

3.1. The Engulfment model (E-model)

The engulfment or E-model was proposed by Bałdyga and Bourne in 1989 (Bałdyga and Bourne, 1989) and discussed in detail by the authors in 1999 (Bałdyga and Bourne, 1999). They interpreted the fluid as a set of phenomenological points or fluid elements; in this model the flow of fluid elements, mixing and chemical reactions are followed for fluid elements marked by the reactant α contained initially and entering the system through a defined feed port. The E-model represents simplification of the (Engulfment-Deformation-Diffusion model, EDD-model) and this simplification is valid for $Sc < 4000$, when the effects of molecular diffusion are negligible when compared with effects of viscous-convective stretching of fluid resulting in fluid incorporation into the reaction zone. For $Sc > 4000$ the complete EDD model should be used as presented by Bałdyga and Bourne (1984); However, when micromixing is controlled by viscous-convective engulfment process only, then the c_α concentration history can be calculated from the engulfment equations, that are much simpler to use.

$$\frac{dc_\alpha}{dt} = E\left(\langle c_\alpha \rangle - c_\alpha\right) + r_\alpha \tag{53}$$

$$\frac{d\left(\delta V_\alpha\right)}{dt} = E \cdot \delta V_\alpha \tag{54}$$

$E = 0.058(\varepsilon/\nu)^{1/2}$ is the engulfment parameter that depends on the flow conditions and fluid viscosity and $\langle c_\alpha \rangle$ represents here the concentration of reactant α in the environment of the considered fluid element. In the form presented by Eq. (53) the model can be applied only to cases with small values of the volume fractions $\delta V_\alpha / V$ of the solution containing reactant α. For larger values of the volume fraction $X_\alpha = \delta V_\alpha / V$, a phenomenon of self-engulfment should be included and the engulfment equations read:

$$\frac{dc_\alpha}{dt} = E\left(1 - X_\alpha\right)\left(\langle c_\alpha \rangle - c_\alpha\right) + r_\alpha \tag{55}$$

$$\frac{d\left(\delta V_\alpha\right)}{dt} = E\left(1 - X_\alpha\right) \cdot \delta V_\alpha \tag{56}$$

The model describes turbulent mixing when a fluid is introduced to a system at a scale of the order of the Kolmogorov microscale $\lambda_K = \nu^{3/4} / \varepsilon^{1/4}$. The engulfment parameter E can be easily related to the time constant, τ_M, for decay of the concentration variance, by simple relation $E = 1/\tau_M$. The model was used to interpret experimental data in many types of equipment, which will be presented in Section 4 of this paper.

3.2. The Interaction by Exchange with the Mean (IEM) model

The model was proposed independently by Harada et al. (1962), Villermaux and Devillon (1972), and Costa and Trevissoi (1972a, 1972b). If we consider the fluid as a set of phenomenological points, then according to this model the change of concentration of any component α in any phenomenological point results from a chemical reaction proceeding with rate r_α and mass exchange between this point and the neighbouring phenomenological points (fluid elements) of local mean concentration $\overline{c}_\alpha$.

$$\frac{dc_\alpha}{dt} = k_m \left(\overline{c}_\alpha - c_\alpha \right) + r_\alpha \tag{57}$$

The linear rate expression for mass transfer looks convincing, especially that the exchange coefficient or micromixing parameter k_m can be easily related to the time constant for decay of the concentration variance, τ_M, given by simple relation $k_m = 1/(2\tau_M)$. Eq. (57) is used very often in chemical engineering applications to describe local mixing in composition space; notice that the effect of molecular diffusion on spatial transport requires other methods of modelling, such as Fickian gradient diffusion in space. Consider the application of Eq. (57) to simulation of micromixing effects on the course of the competitive-consecutive second order reactions.

Bałdyga and Bourne (1990, 1999) performed simulations with the IEM model for the competitive-consecutive reactions assuming the first reaction instantaneous and the second reaction fast. Predicted product distribution showed opposite to observed in experiments effect of volume ratio of reactants, $X_{A0}/(1 - X_{A0})$ on the product distribution X_S, when the limiting reactant B has been fully consumed.

$$X_S = \frac{2c_S}{c_R + 2c_S} \tag{58}$$

Moreover, for relatively slow mixing, so that the second reaction was controlled by mixing, the product distribution, X_S, tended to an asymptote significantly smaller than 1 and R was formed as well. Of course, as discussed already by Levenspiel (1972), the correct asymptote corresponds to $X_S = 1$.

It is interesting that the same equation as Eq. (57) was proposed by Dopazo (1975) and Dopazo and O'Brien (1976) and applied subsequently afterwards by many researches to simulate combustion. It was called then Linear Mean Square Estimation (LMSE). Namely, in the transport equation of joint-scalar PDF or joint-scalar velocity PDF (Probability Density Function) the term representing transport in composition space by molecular diffusion is described by Fick's law with molecular diffusion coefficient, D_α

$$\left\langle D_\alpha \frac{\partial^2 Y_\alpha}{\partial x_i^2} \Big| \vec{\Psi} \right\rangle = -\frac{1}{2} \frac{\Psi_\alpha - \langle Y_\alpha \rangle}{\tau_m} = -\frac{1}{2} R_Y \omega \left(\Psi_\alpha - \langle Y_\alpha \rangle \right) \tag{59}$$

where $\vec{\Psi}$ is composition space, Y_α mass fraction of α, R_Y is the ratio of the mechanical and scalar mixing rates, usually $R_Y = 2.0$, and ω represents frequency of turbulence

$$\omega = \varepsilon / k \tag{60}$$

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where ε is the rate of dissipation of kinetic energy of turbulence, k. The form of time constant in Eq. (59) or frequency turbulence, Eq. (60), show that it is characteristic for gases of the Schmidt number $Sc \approx 1$ and describes inertial convective mixing; for liquids with $Sc \gg 1$ also viscous-convective and viscous-diffusive effects can be of considerable importance.

For stochastic (conditional) particles that are of course different than real particles (fluid elements), their one-point statistics are identical,

$$\frac{dY_\alpha^{(p)}}{dt} = -\frac{1}{2} R_Y \omega \left(\Psi_\alpha^{(p)} - \langle Y_\alpha \rangle \right) \tag{61}$$

where $\langle Y_\alpha \rangle$ is the weighted mean.

Pope (1985) has shown that the general behavior of Eqs. (59) and (61) is incorrect as any modeled PDF that is initially not Gaussian, does not relax to the Gaussian distribution. In non-homogeneous systems this effect can be less important due to turbulent diffusion of fluid elements from regions of various compositions (Bałdyga and Bourne, 1999). Also Fox (2003), after several critical remarks about the IEM model, gave some arguments in defense of this model arguing that for inhomogeneous scalar fields, turbulent velocity fluctuations should generate a Gaussian PDF even in absence of a model for molecular mixing. From the point of view of a chemical reaction this effect can compensate weaknesses of the IEM model for processes that are rather controlled by turbulent diffusion (mesomixing) than micromixing and more for gases, where scales of turbulent fluctuations are close to scales of molecular mixing than to liquids, where the scale of molecular mixing is much smaller than the scales of turbulent fluctuations.

It is good to illustrate how the IEM model is related to chemical reactions in the limit, when reaction rate is mixing controlled. Consider at first competitive–consecutive reactions, with $k_1 \ggg k_2$ carried out in the diffusion controlled regime in a batch reactor, and simulate it using the IEM model. The product distribution is shown in Fig. 1 for $\overline{c}_{A0} = c_{A0} X_A = \overline{c}_{B0} = c_{B0} (1 - X_A)$. Notice that the proper value is $X_S = 1$. This illustrates the effect of incorrect structure of the IEM model. This happens not only when $k_1 \ggg k_2$; Figure 1 shows a similar effect for $k_1 = k_2$.

The IEM model is often used to interpret experimental data; Figure 1 shows that the range of variation of X_S can be reduced but the trends of variation with increased agitation power still can be correct. This explains why, when X_A is kept constant, correct rank of different mixers or different operating conditions can be obtained.
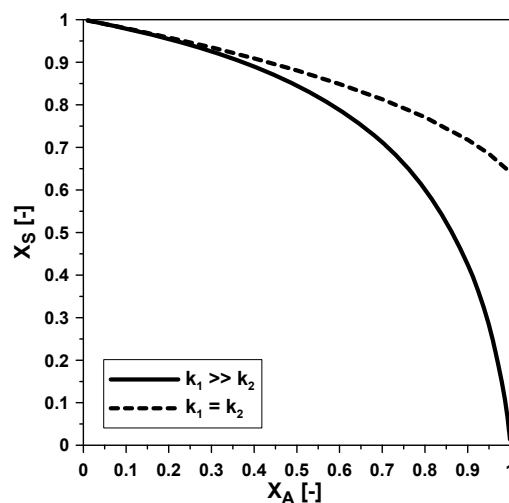

Fig. 1. Predictions of IEM model for both reactions controlled by mixing, $\tau_{R1} \gg \tau_m$, $\tau_{R2} \gg \tau_m$
$\overline{c}_{A0} = c_{A0} X_A = \overline{c}_{B0} = c_{B0} (1 - X_A)$ for $k_1 \ggg k_2$ and $k_1 = k_2$

The equation for IEM model and Eq. (53) for E model have a similar mathematical form and both describe micromixing. This similarity is, however, superficial; the models do not give the same results. The reason is related to the model structure. In the case of E-model the reaction is localised only in B-rich zone (growing in time but finite), whereas IEM model assumes the reaction in the whole reactor, once B is introduced. Since it is not possible for reaction to proceed in the whole interior of a reactor (the reaction can proceed only locally, in the part of reactor where B reactant is present), the application of the IEM model to the whole reactor and assuming that the process is controlled by micromixing gives not proper limits of X_S.

4. EXAMPLES OF APPLICATION OF REACTIVE TRACER METHOD

The complex chemical test reactions, described in detail in Section 2 of this review, when applied together with an appropriate mixing model, for example one of models presented in Section 3, can be used to identify efficiency of micromixing or mass transfer in various devices of industrial importance. In recent years test reactions were applied to characterise mixing in many mixers and reactors. Among them one can find those which recently became very popular such as microreactors or rotor-stator mixers, as well as those which belong to the group of traditional equipment, such as impinging jet reactors, stirred vessels or tubular reactors. In fact, the method based on chemical, complex reactions is very universal and can be used to describe mixing and/or mass transfer in any apparatus encountered in chemical and related industries. In what follows I am going to present literature examples of the application of this method to interpret mixing experiments in various devices.

4.1. Microreactors

Microreactors were frequently investigated using complex, test chemical reactions in order to evaluate mixing time and mixing efficiency. Studies on the performance of microreactors became very popular in a past few years. Many new designs of microreactors have been presented recently in the literature. Microreactors have also found practical applications in industry and laboratory.

In order to demonstrate a good mixing performance of a newly-designed apparatus, several researchers used a method based on the application of test reactions together with micromixing models. In the vast majority, the Villermaux-Dushman reaction together with IEM model was applied. There are also papers on the application of diazo-coupling reaction and neutralisation/estrification reaction, together with E-model of mixing. Below I am going to present a short overview of the results on investigation of mixing efficiency in microreactors.

Some of the first who applied a system of test chemical reaction to study mixing in microdevices were Falk and Commenge (2010) and Commenge and Falk (2011). They extended a method of using iodine/iodide reaction system together with IEM mixing model to study microreactors. The method has become very popular and since then frequently applied to examine all kinds of microreactors, see for example (Guo et al., 2013; Kashid et al., 2011; Su et al., 2011) and (Aubin et al., 2010; Kölbl et al., 2008; Panic et al., 2004) for earlier applications of Villermaux-Dushman reaction.

Falk and Commenge (2010) have shown how to identify mixing time, and how to relate it to operating parameters such as Reynolds number of the flow and the specific power (dissipation of mechanical energy per unit mass of fluid). Finally they presented mixing efficiency of different mixers.

In order to calculate mixing time, it is at first important to identify the controlling step. In the case of large segregation scales laminar flow mixing is controlled by stretching, whereas at fine segregation scales, diffusion in deformed fluid elements controls mixing.

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To describe these phenomena, they applied the relation proposed by Bałdyga and Bourne (1986):

$$t_{\text{diff+shear}} = \frac{1}{2\dot{\gamma}}\text{arcsin}\,h\left(\frac{0.76\dot{\gamma}\delta_0^2}{D}\right) \tag{62}$$

where δ_0 represents initial thickness of striations. Eq. (62) has been modified by Falk and Commenge (2010) to describe mixing in microchannels. Introducing the shear rate given by $\dot{\gamma} = \left(\dfrac{\varepsilon}{2\nu}\right)^{0.5}$ for tubular microchannels, with ε defined by $\varepsilon = \dfrac{Q\Delta P}{\rho V}$, they simplified further Eq. (62) to:

$$t_{\text{diff+shear}} \cong \frac{1}{\sqrt{2}}\left(\frac{\nu}{\varepsilon}\right)^{0.5}\ln(1.52Pe) = \frac{(d^2/D)}{8Pe}\ln(1.52Pe) \tag{63}$$

with $Pe = \bar{u}d/D$ being the Péclet number and, $\bar{u}$ representing a mean velocity in the channel of diameter *d*.

Analysis of Eq. (63) shows that mixing time does not depend much on the Péclet number, which is well seen when Eq. (63) is transformed to $t_{\text{diff+shear}} \cong \dfrac{d}{8\bar{u}}\ln(1.52Pe)$, and therefore weakly dependent on the molecular diffusivity but strongly dependent on the rate of deformation that in this simple flow is proportional to $\bar{u}/d$. Figure 2 illustrates this feature of the time constant.
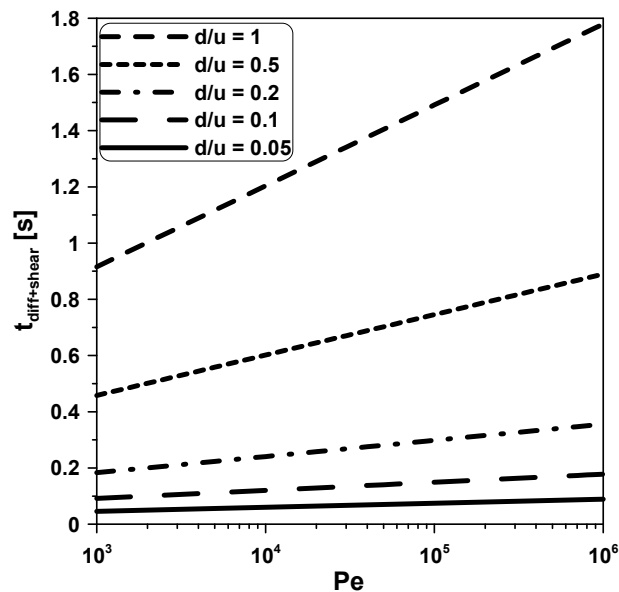

Fig. 2. Effect of the Péclet number on mixing time for aqueous solution and *Sc* = 1000.

Eq. (63) predicts small values of the mixing time in microreactors. However, Eq. (62) was transformed to Eq. (63) assuming 100% of energy efficiency, which means that Eqs. (13) to (17) were not applied. In reality the formation of lamellar structure requires time and energy because orientations of intermaterial surfaces in relation to deformation tensor are neither perfect nor stable. As a result not all mechanical energy that is used to achieve the flow and dissipated has a positive contribution to mixing.

Hence, the authors applied definition based on Eq. (15). They used the average mixing efficiency, $\overline{\text{eff}}$ that was denoted by η in (Falk and Commenge, 2010), to introduce mixing efficiency into the expression for the mixing time scale,

$$t_{\text{diff+shear}} = \frac{d}{8\bar{u}\eta}\ln\left(1.52 Pe\,\eta\right) \tag{64}$$

which for $Pe\,\eta \gg 1$ results in a simple proportionality $t_{\text{diff+shear}} \propto \frac{d}{\bar{u}}Pe^{0.15}\eta^{-0.85}$, and shows that the mixing time is almost inversely proportional to the mixing efficiency. This shows that one should increase efficiency for a given energy input to reduce the mixing time.

In the paper (Falk and Commenge, 2010) the efficiency of mixing was identified based on experimental data. The methodology enabling one to extract the intrinsic mixing time from the experimental results was based on using the Villermaux–Dushman reaction (see Section 2.3) in combination with the IEM model (Section 3.2) assuming a plug flow in the system. Using a theoretical plot (calibration curve) relating the mixing time to the segregation index and the value of the segregation index from experimental data (Eq. 47) the mixing time was estimated. By substituting this mixing time into Eq. (64) the mixing efficiency can be identified.

It must be emphasised that authors of the paper are aware of the disadvantages of this method. They mention that the objective of such a model is to deliver the order of magnitude of mixing time for practical applications and not to properly propose a detailed description of mixing phenomena. The authors' experience of the complete method of mixing time determination is that the accuracy cannot be better than $\pm 30\%$.

Based on numerous results of experimental investigations of the performance of micromixers carried out with the Villermaux–Dushman reaction, their own and taken from the literature, a comparison of micromixers efficiency was established in the paper. Falk and Commenge (2010) have shown that the energy efficiency of mixing in considered micromixers is not higher than 3%. This means that high values of energy dissipation that can be achieved in micromixers, often much larger than those used in conventional mixers with turbulent flow, are not very useful because of low energy efficiency. In other words, only a small fraction of the total mechanical power transmitted to the fluid is effective for mixing. The results are disappointing because whatever the internal geometry of the mixer is, based on results from this paper, the energy dissipation seems to be the only relevant parameter to design an efficient mixer.

The authors (Falk and Commenge, 2010) also pointed out that a direct comparison of the segregation indices in order to characterise performance of the studied micromixers should not be recommended since the obvious sensitivity of selectivity to concentration of reactants.

Another paper which considers a concept of mixing efficiency applied to classify various types of microractors is the one by Malecha et al. (2009), see also (Bałdyga et al., 2012; Jasińska et al., 2011; Jasińska and Bałdyga, 2014) for further applications. In this case the reactions of azo-couplings between 1- and 2-naphthols and diazotized sulphanilic acid were used to characterise the performance of two micromixers, of the meander and serpentine type. This is another, in fact earlier example of quantitative application of the test, complex chemical reactions for the identification of mixing efficiency.

The procedure for the determination of mixing efficiency that has been applied in the paper by Malecha et al. (2009) is as follows. It is based on experimental determination of product distribution for diazo-coupling reaction giving values of the product distribution: X_S and X_Q as defined by Eqs. (25) and (26). X_S should be then used to systems with not very fast mixing, and X_Q to fast mixing cases.

Figure 3 shows some measured X_Q values versus the rate of energy dissipation calculated from measured pressure drop, $\varepsilon_{\Delta P} = Q\Delta P/(\rho V_R)$, and theoretical curve relating product distribution with the

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rate of energy dissipation, ε. Figure 4 illustrates the procedure applied to identify efficiency of mixing from Eq. (17) using ε and $\varepsilon_T = \varepsilon_{\Delta P}$.

To construct a theoretical calibration curve, the E-model of micromixing was used. In this model micromixing is controlled by viscous-convective engulfment process, and the engulfment parameter, E, represents the maximum rate of stretching of vortices or very short material line elements. Such effective mixing was considered as a reference mixing performance with a clear physical meaning. As one can see mixing becomes more effective with increasing mixing power; of course this results from more effective destabilisation of the flow and resulting development of stretching and folding mechanisms. Results confirm that the serpentine micromixer is much more effective than the meander micromixer (Table 1). However, also the efficiency of serpentine micromixer is not very high, in fact not very different from its values reported by Ottino for classical mixers (Ottino, 1980).
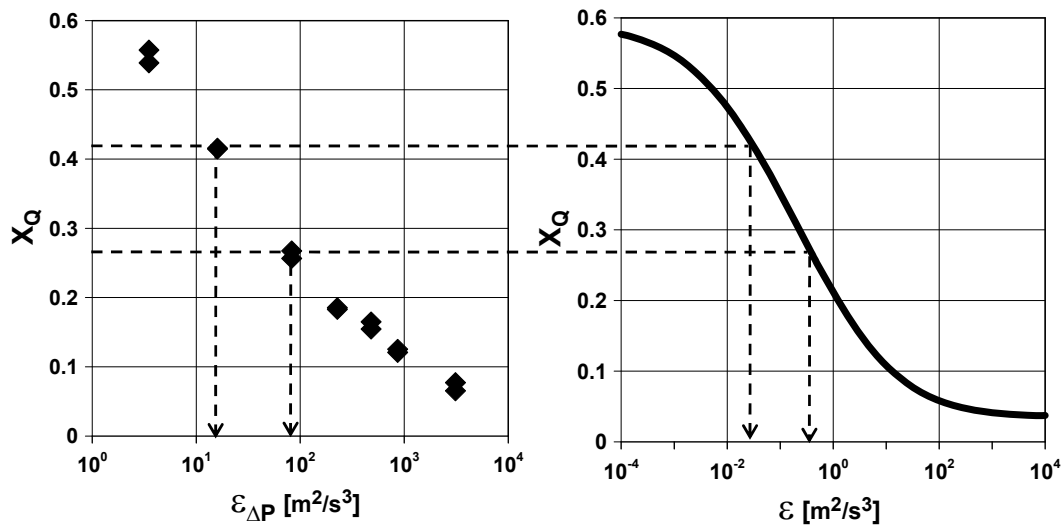

Fig. 3. X_Q characterising the serpentine micromixer: (left) experimental data (Malecha et al., 2009), (right) predictions of E-model.
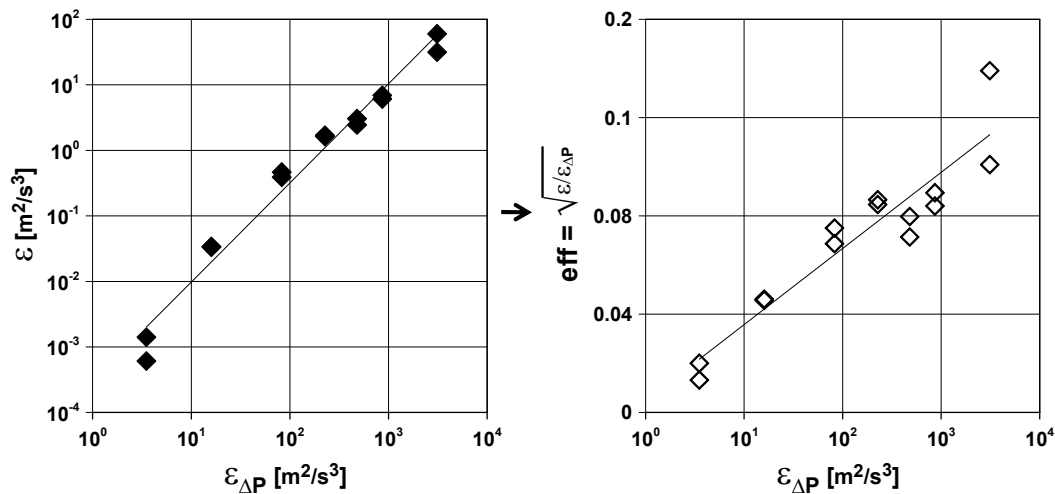

Fig. 4. Energy necessary for mixing in serpentine mixer: theoretical (left) against experimental rate of energy dissipation, (right) effectiveness of mixing as a function of applied energy.

Finally, results presented in the paper have shown that the Péclet number defined by $Pe = ud/D$ does not characterise mixing accurately. Pe should be interpreted in the considered case rather as a ratio of the diffusion time $\tau_D = \delta^2/D$ and the convection time $\tau_c = d_h/U$. Notice that the characteristic time of diffusion should be calculated based on the striation thickness, δ, rather than hydraulic diameter, d_h.

Taking into account that $\delta = a_v^{-1}$, a_v being the intermaterial surface area, one gets for the modified Péclet number, *Pe*:

$$Pe^* = \frac{\delta^2 u}{D d_h} = Pe \frac{1}{\left(a_v d_h \right)^2} = Pe \left(\frac{\delta}{d_h} \right)^2 \qquad (65)$$

Such modified Péclet number takes into account not only general flow conditions and molecular diffusivity but also the local structure of mixtures and related efficiency of mixing.

Table 1. a, b. Efficiency of micromixers: a) serpentine micromixer, b) meander micromixer

a)

Q [cm³/h]	ΔP [Pa]	$\varepsilon_{\Delta P}$ [m²/s³]	ε [m²/s³]	$eff = \varepsilon / \varepsilon_{\Delta P}$	$eff = \sqrt{\varepsilon / \varepsilon_{\Delta P}}$
13.6	1.31×10^3	3.61	9.0×10^{-4}	2.49×10^{-4}	1.58×10^{-2}
20.4	2.08×10^3	8.61	9.5×10^{-3}	1.10×10^{-3}	3.32×10^{-2}
27.2	2.96×10^3	16.3	3.5×10^{-2}	2.14×10^{-3}	4.63×10^{-2}
81.8	1.37×10^4	228	1.6	7.02×10^{-3}	8.38×10^{-2}
136.4	3.10×10^4	859	6	6.99×10^{-3}	8.36×10^{-2}

b)

Q [cm³/h]	ΔP [Pa]	$\varepsilon_{\Delta P}$ [m²/s³]	ε [m²/s³]	$eff = \varepsilon / \varepsilon_{\Delta P}$	$eff = \sqrt{\varepsilon / \varepsilon_{\Delta P}}$
13.6	1.66×10^3	4.58	-	not satisfactory as mixer	
20.4	2.51×10^3	10.4	-	not satisfactory as mixer	
27.2	3.37×10^3	18.6	-	not satisfactory as mixer	
81.8	1.09×10^4	181	1.5×10^{-3}	8.28×10^{-6}	2.88×10^{-3}
136.4	1.98×10^4	549	4.1×10^{-2}	7.47×10^{-5}	8.64×10^{-3}

where $\varepsilon = Q \cdot \Delta P / (\rho \cdot V)$, $V = 1.37$ mm³.

4.2. Rotor-stator mixing devices

Rotor-stator mixing devices have become very popular in the last few years. This results from the fact that these devices are capable of delivering very high values of energy dissipation rates that are concentrated in some specific regions of the apparatus. As a result rotor-stator devices have found many applications in processes of industrial importance such as chemical, biochemical, agricultural, cosmetic and food processing for homogenisation, dispersion, emulsification, grinding, dissolving, chemical reaction, cell disruption, shear coagulation and many more (Atiemo-Obeng and Calabrese, 2004; Chu et al., 2007; Cooke et al., 2011; Hall et al., 2011a, 2011b; Özcan-Taşkın et al., 2011; Schönstedt et al., 2015).

Fewer papers compared to reports on microreactors are devoted to the investigation of rotor-stator devices from the point of view of mixing efficiency and mixing time. For instance, Atiemo-Obeng and Calabrese (2004) in their textbook have focused much of their attention to rotor-stator devices but mainly in the context of the flow filed and power characteristics. Investigation of the rotor-stator devices with the test chemical reactions appeared in a paper by Bourne and coworkers (Bourne et al., 1992) and in the PhD thesis of Lenzner (1991). They reported very high intensity of mixing in rotor-stator devices (very small X_S) in comparison to stirred tank reactors and concluded that the rotor-stator devices should become very popular in the next few years.

The rotor-stator geometry is very complex so even at present simulations involving chemical reactions together with the flow, mixing and mass transfer models are considered as difficult. However, rotor-stators mixers are widely used, which includes the creation of emulsions (Bałdyga and Jasińska, 2011;

Hall et al., 2011a; Hall et al., 2013; Jasińska et al., 2012; Jasińska et al., 2013b; Jasińska et al., 2013c; Jasińska and Bałdyga, 2014; Jasińska et al., 2014b) and suspensions (Bałdyga et al., 2008).

One of the most up-to-date works on the intensity of mixing probed with Villermoux-Dushman reaction can be found in Chu et al. (2007). Villermoux-Dushman reaction has been used to show the effect of process variables and apparatus geometry on mixing quality and estimation of mixing time. Chu et al. (2007) presented a new rotor-stator reactor (RSR) and their goal was to achieve the highest possible micromixing efficiency. They started from the basic structure shown in Fig. 5 and afterwards they were introducing changes in geometry for different process conditions and charactersising mixing using the iodide–iodate reaction system. In addition, applying the incorporation model (Villermaux and Falk, 1994) the micromixing time of RSR was estimated based on experimental data.
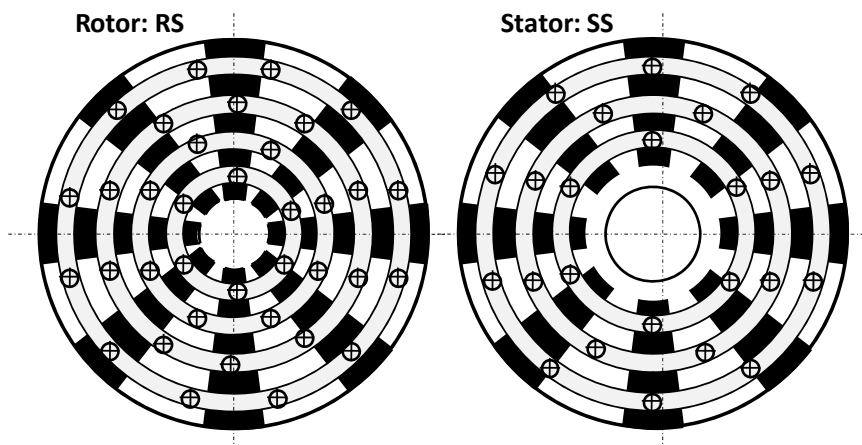

Fig. 5. Schematic presentation of rotor and stator configuration applied in experiments, Chu et al. (2007).

Three different rotors with straight, curve slots or holes around the circular of rotor-rings were used in experiments, named RS, RC and RH, respectively, as well as two different stators with straight and curve slots around the circular of stator-rings named SS and SC. Therefore, they investigated six rotor–stator combinations (RS–SS, RS–SC, RC–SS, RC–SC, RH–SS, RH–SC). They have assessed the best rotor-stator combination based on the smallest value of X_S.

Another attempt made by Chu et al. (2007) was an estimation of mixing time based on combination of experimental data with IEM model following Falk and Commenge (2010) approach. The correlation was obtained through linear regression with correlation coefficient of 0.99983 and standard deviation of 0.05422. This relationship is given by:

$$\log \tau_m = -2.84 + 1.015 \log X_S \tag{66}$$

and is valid for the set of concentrations and volume ratio of reactant solutions applied by Chu et al. (2007). They have shown that the test reactions can be very helpful in mixing apparatus design.

Rotor-stator mixers were extensively investigated by the author of this review, including the application of test reactions. In-line Silverson continuous-flow rotor-stator devices (Bałdyga and Jasińska, 2011; Bałdyga et al., 2007a, 2007b; Bałdyga et al., 2012; Jasińska and Bałdyga, 2014; Jasińska et al., 2010; Jasińska et al., 2013a) and batch rotor-stator devices (Jasińska et al., 2012; Jasińska et al., 2013b) were considered. In the first case the authors were mainly interested in micromixing efficiency in homogenous systems, while in the second case a system of complex test reactions was used to study the efficiency of mass transfer in biphasic liquid-liquid systems.

In the case of a homogeneous system the performance of the Silverson double screen 150/250MS inline rotor-stator mixer (shown in Fig. 6.) was investigated using extended diazo-coupling between 1- and 2-naphtols and diazotized sulphanilic acid as presented in Section 2.3.
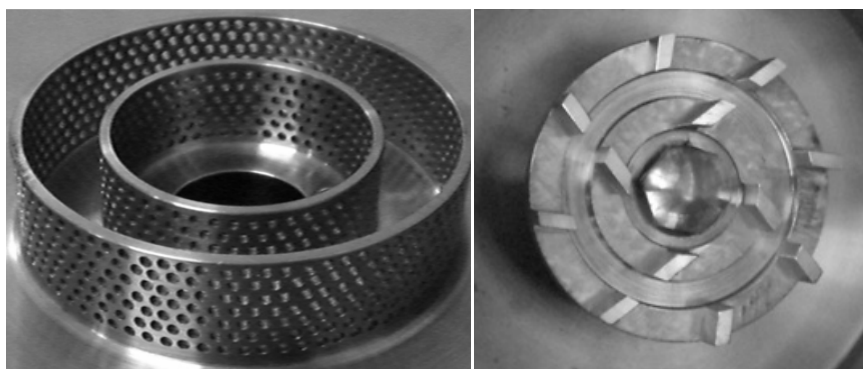
Fig. 6. Silverson 150/250 MS rotor-stator mixer: Silverson screens (left)
and Silverson blades (right) (Bałdyga et al., 2007a, b)

To describe the effect of mixing on the course of chemical reactions at high mixing intensity two approaches were used in these works. The first one, based on the application of extended 3D model allowed one to predict the effect of flow structure on the extent of a chemical test reaction and thus on mixing quality in the system, and the second based on the application of the E-model, following the method presented in Section 4.1.

The 3D simulations of the hydrodynamics were carried out using the standard k-ε model of Fluent-Ansys and the multiple-reference frame of reference. The results of simulation of the flow field are presented by velocity vectors and the energy dissipation rate as shown in Fig. 7. One can see that within the holes placed behind the blades there are strong circulations, whereas in front of a moving blade strong jests are emerging. A fast flow through the holes creates elongation, which is very effective for both phenomena, mixing on the molecular scale and drop breakage. The highest value of the rate of energy dissipation, where also the highest rate of micromixing is expected, is observed close to the blades and in the vicinity of screens, and increased dissipation of kinetic energy created by jets is observed as well.
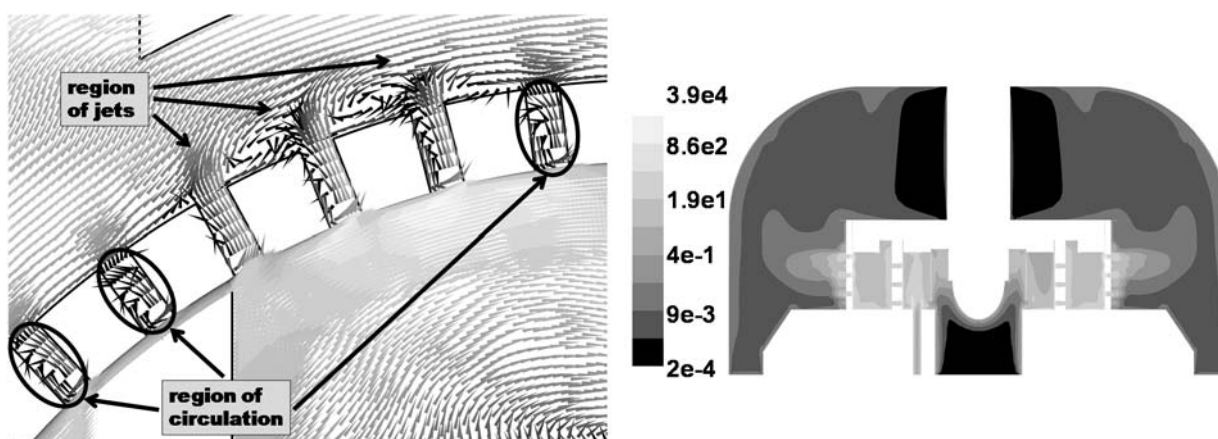

Fig. 7. Results of simulations of the flow in the rotor-stator mixer. The rotor moves clockwise. a) Velocity [m/s] vectors for $Q = 1.67 \times 10^{-3}$ m^3/s, $N = 100$ s^{-1}. Outer screen. b) Rate of energy dissipation [m^2/s^3] distribution for $Q = 1.0 \times 10^{-4}$ m^3/s, $N = 16.7$ s^{-1} (Jasińska et al., 2013a)

To follow the course of mixing in the system the method based on concept of mixture fraction f was applied (Bałdyga and Bourne, 1999).

$$f = \frac{c_A^0}{c_{A0}}$$ (67)

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where c_{A0} represents the feed concentration and c_A^0 is the local instantaneous concentration of the passive scalar tracer. Distributions of the mean mixture fraction $\overline{f}$ and its variance σ_s^2 were calculated in (Jasińska et al., 2013a) using the turbulent mixer model. Typical results of simulations are presented in Fig. 8 (a) and (b).

One can see that mixing is localised close to inlet B, which explains why test reactions are often used as a probe for identification of the local value of the rate of energy dissipation.

To model the course of chemical reactions the presumed probability density function (PDF) of the mixture fraction f, was used (Bałdyga and Bourne, 1999). The presumed PDF (the interdiffusion model by Patterson (1985)) was based on two moments: the mean mixture fraction $\overline{f}$ and the variance about this mean $\sigma_S^2 = \overline{(f')^2}$.

Fig. 8. Results of simulations of mixing in the rotor-stator mixer. $Q = 1.0 \times 10^{-4}$ m³/s, $N = 16.7$ s⁻¹.
a) Mixture fraction distribution, b) Mixture fraction variance distribution. (Jasińska et al., 2013a)

The simulation results of distribution together with results of experiments are shown in Fig. 9. One can see that the experimental conditions have been chosen properly, namely, product distribution represented by X_Q is sensitive to mixing in the considered range of process parameters. The applied method predicts well the product distribution without any fitting; some differences between model predictions and experimental data result most probably from the underestimated rate of energy dissipation by the k-ε model.
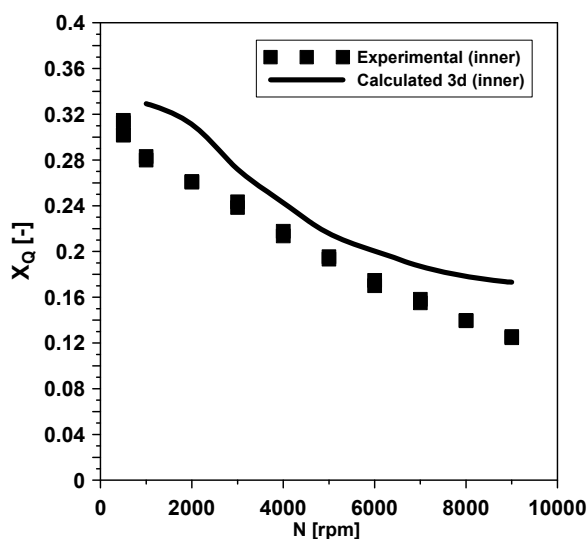

Fig. 9. Effect of rotor speed on the product distributions, $\overline{X_Q}$ (Jasińska et al., 2013a)

In the paper (Jasińska et al., 2013a) also the efficiency of mixing in a rotor-stator mixer has been evaluated in a similar manner as it was done in the case of meander- and serpentine-type microreactors. In fact the method has a universal character and can be applied to examine mixing efficiency of any reactor of industrial importance. One comment is necessary. The engulfment model is used as the model of reference in this method, and the model describes viscous-convective mixing. With increasing Reynolds number, the effect of inertial-convective mixing increases. Inertial-convective mixing requires both time and energy consumption, so one can expect a decrease of mixing efficiency with increasing *Re* when mixing has turbulent character. This means that the faster turbulent mixing, the lower energy efficiency is to be expected. Fig. 9 confirms this observation.

In a rotor-stator system the total rate of energy dissipation depends on both the rotor speed N and the flow rate Q, so the observed value of energy dissipation rate should be expressed as $\varepsilon_T = \varepsilon_{N,Q}$ (Jasińska et al., 2013a). The rate of energy dissipation, $\varepsilon_{N,Q}$, can be calculated using the method presented in (Jasińska et al., 2014a, Jasińska et al., 2015).

Figure 10 shows that the mixing efficiency of homogeneous system in the rotor-stator, where micromixing controls the course of chemical reactions, has the value between 6% and 35%. It decreases with increasing the rotor speed, which results from the Reynolds number mentioned above. Another reason for such a large decrease of efficiency is the fact that for smaller rotor speeds the reaction zone is localised closer to the screen in the region of high dissipation rate, whereas for higher rotor speed the reaction zone shrinks and its localisation is closer to the feeding point, where the rate of energy dissipation is smaller. Predicted efficiency, based on CFD is smaller than that obtained from experiments because of the underestimated rate of energy dissipation by the k-ε model.
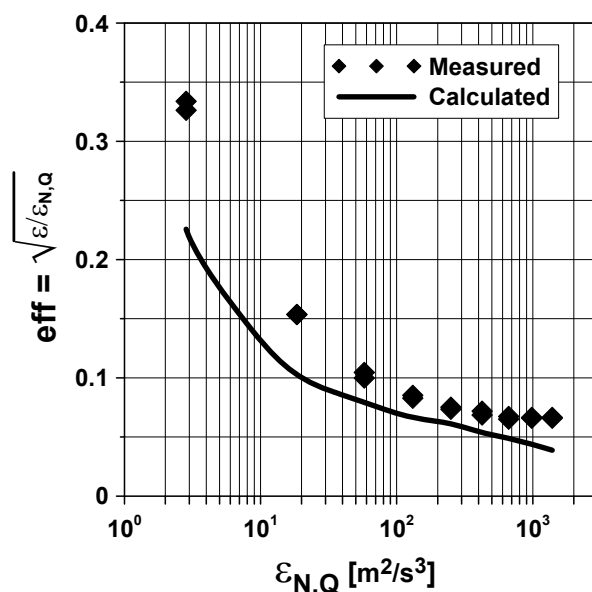

Fig. 10. Efficiency of mixing as a function of the average rate of energy dissipation observed in experiments, $\varepsilon_{N,Q}$.

Another application of test chemical reactions, as mentioned earlier, is to study the effects of mass transfer rate in biphasic liquid-liquid systems (Jasińska et al., 2013b). The idea is similar to that applied for homogenous systems (Jasińska et al., 2013a) and the method to relate mass transfer rate to product distribution was described in section 2 of this review.

In experiments carried out in a batch unbaffled reactor the continuous phase was an aqueous solution of sodium hydroxide (A) and the dispersed phase was a solution of benzoic acid (B) and ethyl chloroacetate (C) in toluene. During experiments the reaction between sodium hydroxide and either

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benzoic acid (instantaneous) or ethyl chloroacetate (fast) was localised in the aqueous phase. The reactor was equipped either with the six-blade paddle or with the Silverson rotor-stator mixer (Fig. 11).
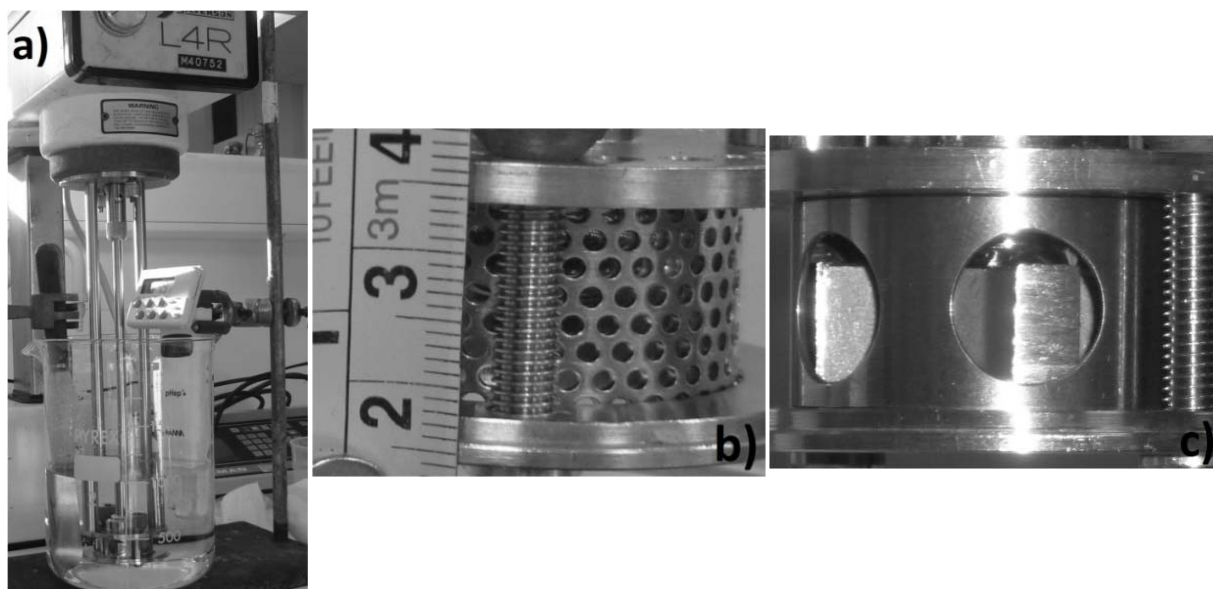

Fig. 11. Experimental setup: a) rotor-stator in batch system, b) standard emulsor screen (SES), c) general purpose disintegrating head (GPDH), (Jasińska et al., 2013b)

In the case of the Silverson rotor-stator mixer two stator geometries were investigated: standard emulsor screen (SES) and general purpose disintegrating head (GPDH). The concentration of ethyl chloroacetate and the drop size were measured after the experiment while pH was recorded during experiment.

To interpret the process and construct a "calibration curve" of product distribution, Eq. (52) versus the rate of energy dissipation or/and mass transfer coefficient, the model of mass transfer with chemical reaction was applied using film theory as described by Doraiswamy and Sharma (1984). It was assumed that the neutralisation reaction between benzoic acid (B) and NaOH (A) is instantaneous. The rate constant for alkaline ethyl chloroacetate hydrolysis is equal to $k_2 = 23$ dm^3/(mol·s), k_La was calculated from Eq. (11c) so for conditions applied in experiments the Hatta number, $Ha = \sqrt{k_2 C_{A0} D_{CB}}/k_{L1}$ took the values between 10^{-6} and 0.1, which means that the regime of this reaction is between slow and very slow.

To include internal resistance in toluene one can use the Sherwood number defined for rigid sphere

$$Sh_i = \frac{k_{LT_i} d}{D_{Di}} = \frac{2}{3}\pi^2 \cong 6.6 \qquad (68)$$

where D_{Di} denotes the molecular diffusivity of i in the dispersed phase. Then, for ethyl chloroacetate, C, one gets

$$\tau_{MC} = \frac{1}{K_{LC}a} \qquad (69)$$

$$K_{LC} = \left(\frac{1}{k_{LTC}\cdot P} + \frac{1}{k_{LC}}\right)^{-1} \qquad (70)$$

The partition coefficient P is relatively high, which means that the external resistance dominates mass transfer of ethyl chloroacetate.

Of course both resistances should be connected when following progress of a chemical reaction.

$$\frac{dC_{BT}}{dt} = ak_{LTB}\left(C_{BT} - C_{BT}^*\right) = aEk_{LWB}C_{BW}^* \qquad (71)$$

Figure 12 shows typical effects of agitation on pH and the product distribution for agitation with rotor-stator mixers equipped with both stators.
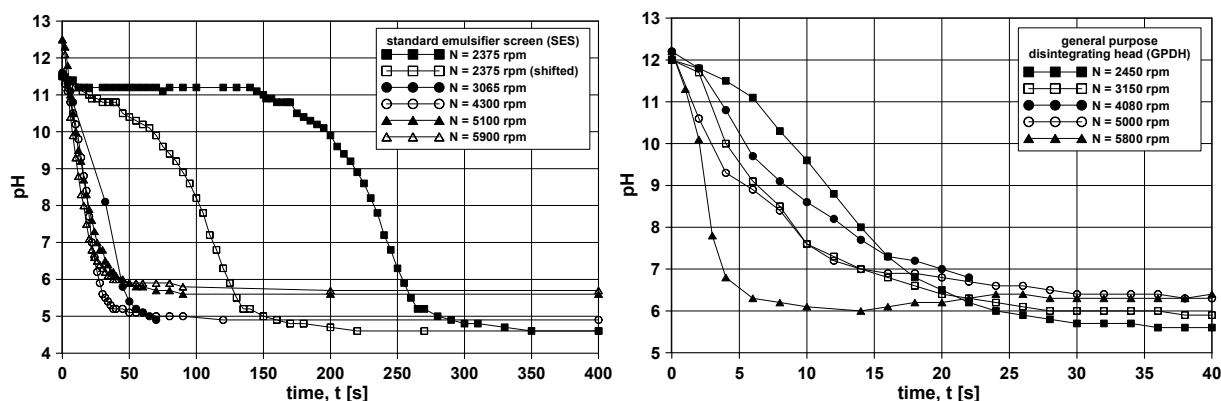

Fig. 12. Effect of rotor speed on variation of pH. Silverson batch system. Vessel equipped with rotor-stator homogeniser with: a) the standard emulsor screen (SES), b) the general purpose disintegrating head (GPDH) (Jasińska et al., 2013b)

One can see that in each case the rate of decreasing pH increases with increasing the stirrer or rotor speed due to increase of the rate of benzoic acid transfer and faster neutralisation of sodium hydroxide. Moreover for faster agitation the final asymptotic values of pH are higher, which results from the fact that at slower agitation ethyl chloroacetate has more opportunity to react with NaOH before the base is consumed and more benzoic acid is left after the process. Both the rate of pH variation and the final value of pH can be used to identify the rate of mixing; Fig. 12 shows that it is higher when the general purpose disintegrating head (GPDH) is applied. The results of modelling presented in (Jasińska et al., 2013b) confirm this interpretation.

Figure 13 shows the effects of agitation rate with the 6-blade paddle and the Silverson mixer equipped with the standard emulsor screen (SES) on the product distribution X_S.

The product distribution, X_S, can be used for direct comparison of effects of agitation in different systems as a segregation index for characterising mass transfer in two-phase liquid-liquid systems. Figure 13 proves that the Silverson rotor-stator batch mixer is less effective for mass transfer than the six-blade paddle. Of course, there is fast mass transfer within the Silverson mixer but most of the time the fluids are out of the mixer, in the bulk, where agitation is very weak.

The product distribution, X_S, can be also used to characterise the energy efficiency of mass transfer, similarly to homogenous systems. Figures 14 a) and b) reveal that the Silverson rotor-stator batch mixers are not effective for mass transfer. An agitation with the classic stirrer results in a more effective mass transfer as shown by a higher effective rate of energy dissipation than that observed in the high-shear Silverson mixer. The real agitation power of the rotor-stator mixers is in fact about 2 orders of magnitude higher than the six-blade paddle agitation power.

The main conclusion is that the focused supply of energy characterising Silverson mixers that is effective for drop breakage, is not effective for mass transfer that takes place mainly in the bulk, where

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agitation is very weak. Results show that the effective supply of agitation power to a mixer is not the same for all processes and is in fact process dependent.
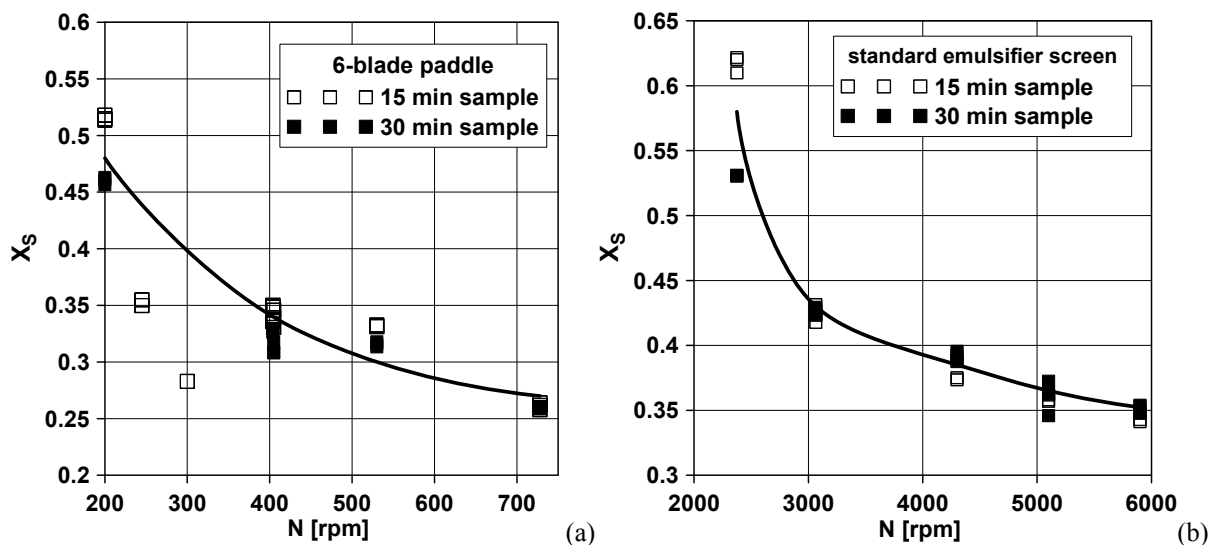

Fig. 13. Effect of agitation (a) with the 6-blade (b) with the rotor-stator homogenizer equipped with the standard emulsor screen (SES) on the product distribution, X_S, in the batch reactor (Jasińska et al., 2013b)
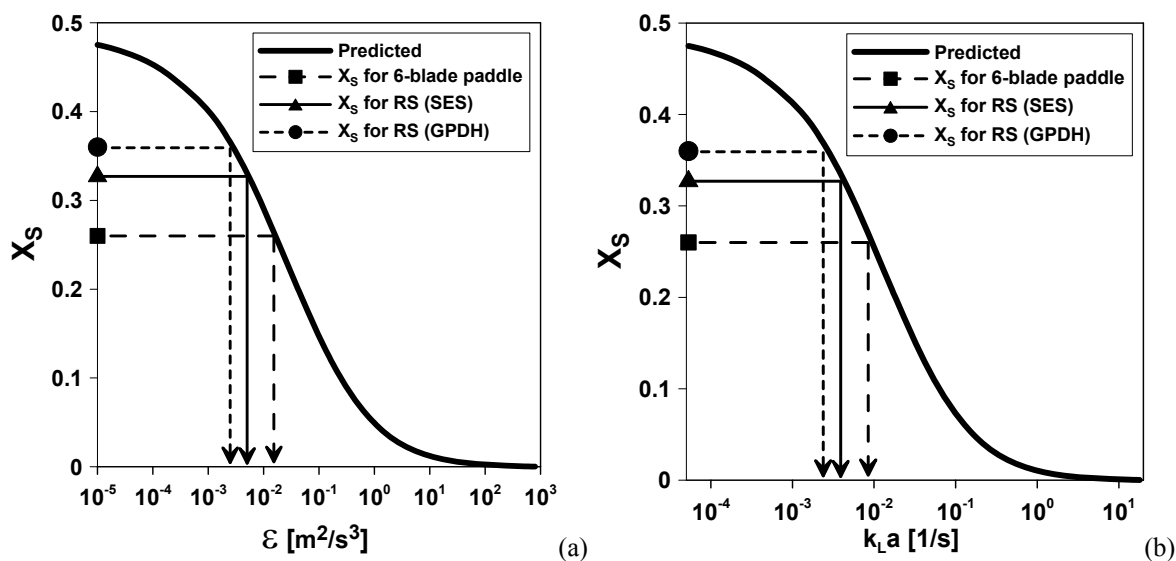

Fig. 14. The results of modelling applied as a calibration curve X_S versus: a) ε, b) k_La. The smallest values of the product distribution X_S for three systems considered are applied to present the smallest: a) energy, b) k_La, that is required to obtain the measured X_S, (Jasińska et al., 2013b)

4.3. Impinging jests

A complex, test, chemical reaction has been also used with success to describe mixing in other kinds of high-efficient mixing devices, called impinging jets. Similarly to rotor-stator devices, impinging jets work in most cases in turbulent regime and are characterized by very high values of the rate of energy dissipation (up to 10^5 W/kg). They require thus the application of fast or very fast test reactions under such process conditions in order to properly characterise mixing. Johnson and Prud'homme (2003) applied to this end a scheme based on DMP reaction, as described in Section 2.3. They investigated

Confined Impinging Jets (CIJ), with two, high-velocity linear jets of fluid colliding in a small chamber where the chamber size can have a significant effect on the mixing process performance.

A high energy dissipation rate results from converting kinetic energy of each jet stream into the energy of turbulent or turbulent-like motions. The process is localised in a very small volume referred to as the mesomixing volume. Jet collisions in this small volume result in a very high rate of energy dissipation. All the fluid passes thus through the region of high rate of energy dissipation. The geometry for CIJ mixer studied in paper by Johnson and Prud'homme (2003) is presented in Fig. 15.

The aim of investigations was to find a proper expression for the mixing time as well as expression for the Damköhler number that correlates well with selectivity, and finally a scale-up criterion.
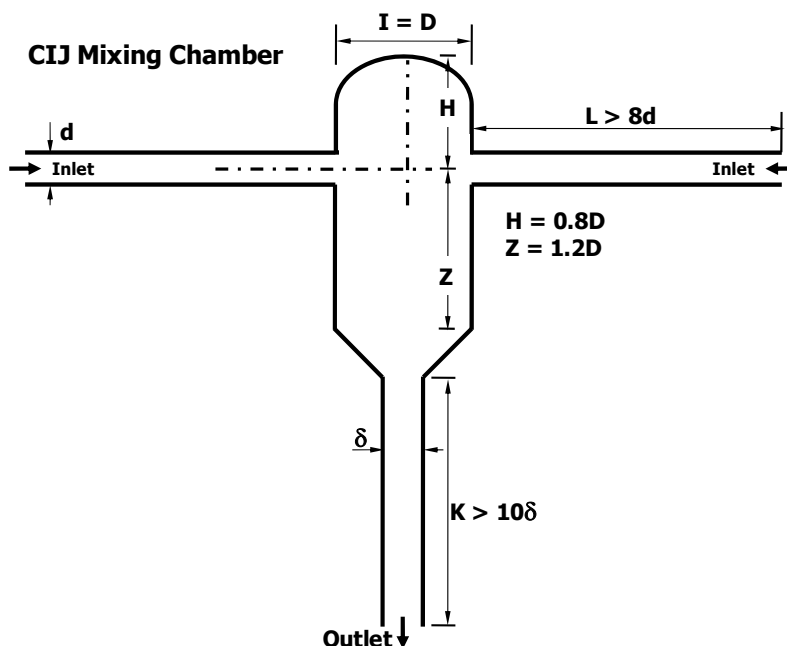

Fig. 15. Basic CIJ mixer geometry (Johnson and Prud'homme, 2003)

The procedure applied by Johnson and Prud'homme (2003) can be summarised as follows. A fraction of the undesired product formed, X_Q, defined by Eq. (39) is measured and is considered to be a unique function of the Damköhler number, $X_Q = f(Da) = f(\tau_m/\tau_R)$ where $\tau_R = 1/(k_2 c_{B0})$. Based on measured X_Q, and calculated τ_R, the time constant for mixing, τ_m can be determined. This has been done by applying a similar procedure as described earlier in this review:

- identification of relation $X_Q = f(Da)$ based on experiments and the engulfment theory of micromixing,
- identification of the mixing time as a function of CIJ geometry and process conditions,
- identification of scale-up rules for turbulent confined impinging jets, including the velocity, viscosity, and geometric dependencies.

The authors started from the following definition of the mixing time

$$\tau_m = \tau_{\text{diffusion}} = \frac{\left(0.5\lambda_K\right)^2}{\text{diffusivity}} \tag{72}$$

with λ_K being the Kolmogorov length scale, $\lambda_K = \nu^{3/4} / \varepsilon^{3/4}$. Two hypotheses regarding diffusivity definition to be applied in Eq. (72) were considered:
- either molecular diffusivity of reactants, leading to $\tau_m \propto \nu^{3/2}$

- or molecular diffusivity of momentum, equal to the kinematic viscosity, leading to $\tau_m \propto \nu^{1/2}$. Momentum diffusion is related to fluid deformation and resulting engulfment in turbulent mixing.

Experimental data obtained by applying the test reaction system: hydrochloric acid competing for sodium hydroxide neutralization and 2,2-dimethoxypropane acid catalysed hydrolysis (DMP reaction), show that only the relation $\tau_m \propto \nu^{1/2}$ is correct in this case. Assuming further that the mesomixing volume is proportional to the internozzle spacing cubed, Eq. (73) has been derived.

$$\tau_m = K_{CIJ} \frac{\nu_3^{1/2} \Delta^{3/2} d_1^{1/2}}{u_1^{3/2} \left(\frac{\rho_1}{\rho_3}\right)^{1/2} \left(1 + \frac{m_1}{m_2}\right)^{1/2}} \tag{73}$$

with dimensionless internozzle separation $\Delta = I/d_1$, K_{CIJ} being the reactor constant, $d_1 = d_2 = d$ denote jet diameters, u_1 denotes the average velocity of stream 1, and m_i denoting the mass-flow rate of stream i. ρ_3 and ν_3 represent kinematic viscosity and density of effluent (stream 3). Eq. (73) can be used to scale-up CIJ mixers.

An important conclusion, based on the form of Eq. (73), is that the mixing process has little dependence on the diffusion coefficient of the reagents in the system, which means that when applying Eq. (73) to other chemical systems, it is not necessary to accurately measure the molecular diffusion coefficient of the reactants to determine the characteristic mixing time. The use of Eq. (73) is limited to the Reynolds number (based on jet diameter of the acid stream, d_1) between 150 and at least 3000 for low viscosity fluids and the Schmidt number near 1000.

For $K_{CIJ} = 1470$ as identified by Johnson and Prud'homme (2003) the competitive reactions in a CIJ mixer can be represented by

$$X_Q = 0.04 Da = 0.04 \frac{\tau_m}{\tau_R} = 0.84 \frac{\tau_M}{\tau_R} \tag{74}$$

where τ_m is the mixing time and τ_M the time constant for viscous-convective engulfment. Eq. (74) can be interpreted using the concept of mixing efficiency. The ratio $\tau_m/\tau_M = 21.1$ for mixing in the viscous subrange of turbulence shows that the fraction of the rate of stretching useful for creation of the intermaterial area that represents the efficiency of mixing according to Eqs. (13) to (17) is equal to $\overline{eff} = 1/21.1 = 0.047$.

Regarding scale-up rules for turbulent confined impinging jets, including the velocity, viscosity, and geometric dependencies, Eq. (73) defines a standard level of mixedness that can be characterised by $X_Q = 0.04$ for $Da = 1$ for the DMP reaction system. The authors regarded this as the key result of the article.

It should be noticed that the results of experimental investigations obtained by Johnson and Prud'homme (2003) were used by other authors to validate some CFD based mixing models (Liu and Fox, 2006). Other examples of the application of test reactions to study impinging jets include diazo-coupling reactions (Mahajan and Kirwan, 1996; Nunes et al., 2012) and Villermaux-Dushman reaction (Hu et al., 2009; Schaer et al., 1999; Siddiqui et al., 2009).

4.4. Stirred tanks

A popular application of complex test reactions is to study mixing performance in stirred tanks operated either in continuous or semibatch modes. There were two main reasons for these investigations:

- either to find process conditions that enable selective creation of products of fast chemical reactions,
- to validate models of micromixing.

In the first case one can look for a proper combination of stirrer speed, feed point position, rate of feeding and number of feeding points. For example, for the feed point placed in the discharge stream from the impeller, and for high stirrer speed one can expect fast micromixing and selective product formation. However, feed rate should be small enough to exclude mesomixing and remain in the micromixing controlled regime. Feeding rate can be then increased only by increasing the number of feed points. A distance between feed points should be large enough to avoid interaction of reaction zones, so the number of feed points is limited.

The effects of backmixing to feeding pipe were studied as well. All these effects were investigated using test reactions (Bałdyga and Bourne, 1999). However, slow feeding means long feed time in the case of the semibatch reactor or long mean residence time in the case of CSTR. This leads to very low efficiency of mixing because in the case of slow feeding the reaction zone is very small and the majority of the tank volume is chemically passive, but still agitated, so there is fast dissipation of energy without any direct effect on mixing. Hence, one should point out that energy efficiency of mixing in stirred tanks is very low when fast and very fast chemical reactions are considered and thus stirred tanks will not be discussed here from the point of view of mixing efficiency, which is the main subject of this paper. However, test reactions are carried out in stirred tanks to validate models of mixing. At long feed times or mean residence times the product distributions become independent of feeding rate and then the models of micromixing in the viscous-convective and viscous-diffusive subranges can be validated as proposed in (Bałdyga and Bourne, 1999).

Of course, depending on process conditions a proper reaction scheme should be chosen. This can be illustrated by the application of either ethyl chloroacetate or ethyl dichloroacetate (both presented in Section 2.3) to study micromixing in the stirred tank reactor (Bałdyga et al., 2012). Ethyl dichloroacetate was introduced to replace chloroacetate and extend the range of application to higher stirrer speeds.
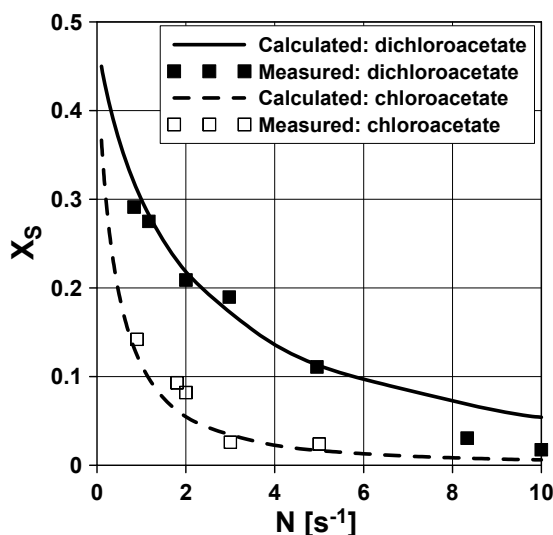

Fig. 16. Effect of agitation rate on selectivity X_S for ethyl chloroacetate and ethyl dichloroacetate: c_B=1M, c_{A0} = c_{C0} = 0.02 M, α = 50, feeding position close to the impeller (Bałdyga et al., 2012)

Simulations were carried out using the model of engulfment (E-model), and results show that the application of ethyl chloroacetate is limited to smaller rates of agitation offering slightly higher sensitivity to agitation rate. Clearly, a much wider range of agitation rates is covered when ethyl

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dichloroacetate is applied, so the new system is better for studying the effects of agitation on mixing and will be used in what follows.

At short feed times or mean residence times (high feed rates) the product distributions X_S and X_Q steadily rise as the feed rate increases, signaling progressively more segregation and increasing effects of the inertial-convective mixing and turbulent diffusion. This gives opportunity to validate macro- and mesomixing models that are based on different approaches to modelling, starting from discrete multi-region or multi-zone models, finishing with CFD simulations. Different models of turbulence and different closure schemes for interaction of mixing with chemical reaction kinetics were investigated, see for example (Bałdyga et al., 2001).

4.5. Other systems

Complex, test chemical reactions have been used with success to examine other reacting systems encountered in chemical and related industrial branches. The most interesting ones include: tubular reactors (Bałdyga and Henczka, 1997), static mixers (Fang and Lee, 2001; Jasińska and Bałdyga, 2010), jets (Baldyga et al., 1994), centrifugal pumps (Bolzern and Bourne, 1985), membrane reactors (Baccar et al., 2009; Jia et al., 2006), sonoreactors (Faryadi et al., 2014; Lee et al., 2014; Monnier et al., 1999; Monnier et al., 2000; Parvizian et al., 2011; Parvizian et al., 2012), reactors with torus shape (Nouri et al., 2008), reactors for polymerisation (Kunowa et al., 2007). Diazo-coupling reactions, ester hydrolysis reactions, and Villermaux-Dushman reaction were applied in these investigations. One should point out that the Villermaux-Dushman reaction is the simplest one to use. However, the results obtained with this reaction should be used with care, as interpretation of results is not always clear, due to some problems with kinetics and IEM modelling, both mentioned earlier in this paper.

5. DISCUSSION AND CONCLUSIONS

Chella and Ottino (1985) proposed to compare flows in terms of their mixing efficiency based on earlier work of Ottino (1981). Their idea was to express mixing efficiency by the efficiency of stretching of area elements. Such efficiency depends on the deformation tensor and the orientation of area elements but does not depend on molecular diffusivity. It is expressed by the ratio of the actual specific rate of area stretching to its upper bound that can be achieved by keeping permanently the optimum orientation of area elements. Of course in real apparatus this is not possible, so the stretching efficiency is smaller than unity. When there is mixing on the molecular scale in a system, there is molecular diffusion as well, so the area elements need to be defined by the maximum gradient of diffusing species. In the case of reactive mixing the reaction front of instantaneous reactions can serve as the area to be stretched. One can thus argue that in such systems there can be some effect of molecular diffusion expressed by *Sc* or *Pe* on mixing efficiency; presented results show that this effect is between negligible and small.

Any direct determination of mixing efficiency when using definitions expressed by Eqs. (13) to (16) for complex mixers and reactors is close to impossible, as it would require a very detailed identification of all material areas and their orientation in relation to deformation tensors. One needs then to carry out either experimental investigations with extremely high resolution of measurements in time and space or Direct Numerical Simulation down to Batchelor microscale when the flow is turbulent. Afterwards results should be integrated over the whole reactor or mixer.

The application of test reactions as a mixing probe that is described in this paper makes this procedure simpler. For fast complex reactions the final product distribution contains integrated effects of the relation between orientation of material surfaces and stretching. From experiments one should also be

able to derive the mixing power. Further, a simple modelling is necessary; using some reference micromixing models one can construct the calibration curve, representing the product distribution for the most effective use of energy to accelerate reactive mixing. One compares then for the same, measured value of the product distribution, the energy observed in experiments with the energy read from the calibration curve.

Results presented in this paper show that this procedure is very effective and enables one to compare the performance of different reactors, for example the performance of microreactors can be easily compared with the peformance of rotor-stator mixers and confined impinging jet reactors. The procedure can be further improved by introducing new, better test reactions and micromixing models.

SYMBOLS

a	characteristic surface per unit volume, m^{-1}
a_v	intermaterial area per unit volume, m^{-1}
c_α	concentration of component α, mol/dm^3
D_α	molecular diffusivity of α, m^2/s
d_d	drop size, m
d_i	jet diameter, m
E	engulfment parameter, s^{-1}
E	reaction enhancement parameter
f	mixture fraction
K_{CIJ}	CIJ reactor constant
K_{LC}	total mass transfer rate coefficient, m/s
k	kinetic energy of turbulence, m^2/s^2
k_i	second order rate constant, dm^3/(mol·s)
k_L	mass transfer coefficient, m/s
k_m	micromixing parameter, s^{-1}
m_i	mass-flow rate of stream "i", kg/s
P	partition coefficient
r_α	reaction rate for formation of α, mol/(dm^3·s)
u_i	velocity of stream "i", m/s
$w_{(p)}$	numerical weight of fluid particle P
X_A	volume fraction of solution containing reagent A
X_S, X_Q	product distribution, selectivity
Y_α	mass fraction of α

Greek symbols

Δ	dimensionless internozzle separation
δ_0	thickness of the stritations, m
ε	rate of energy dissipation, m^2/s^3
$\dot{\gamma}$	rate of deformation/elongation, s^{-1}
$\lambda_B = \left(\nu D_\alpha^2 / \varepsilon\right)^{1/4}$	Batchelor microscale, m
$\lambda_C = \left(D_\alpha^3 / \varepsilon\right)^{1/4}$	Corrsin microscale, m
$\lambda_K = \left(\nu^3 / \varepsilon\right)^{1/4}$	Kolmogorov microscale, m
ν	kinematic viscosity, m^2/s
$\vec{\Psi}$	composition space
ω	frequency of turbulence, s^{-1}

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ρ_i	density of stream "i", kg/m^3
σ_s^2	variance of mixture fraction
τ_D	diffusion time, s
τ_C	convection time, s
τ_R	reaction time constant, s
τ_M	mixing/mass transfer time constant, s

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