On the Use of the Iodide Iodate Reaction Method for Assessing Mixing Times in Continuous Flow Mixers

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It is demonstrated experimentally by example of simple, commercially available T-junctions and by "unsymmetrical" V-type micromixers that mixing times cannot be derived by applying the Iodide Iodate Reaction Method without considering the specific mixer geometry. Experimental results differ depending on the orientation of the feeds with respect to the inlets. An explanation for the observed effects is suggested. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 835–840, 2011
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Introduction

Competing chemical reaction schemes

Competing chemical test reactions are popular means for chemical engineers for the characterization of mixing processes.[1] Most of the test reactions described in the scientific literature are parallel competing reaction schemes, where a very fast reaction (Eq. 1) competes with a fast reaction (Eq. 2) for a common reactant (B).

$$A + B \rightarrow C \quad (1)$$

$$C + B \rightarrow D \quad (2)$$

The rate of reaction (1) is considered to be instantaneously fast compared with the rate of the physical mixing process, whereas the rate of reaction (2) is comparable with the rate of the mixing process when mixing-sensitive product yields are obtained. Generally, both reactions occur in parallel during mixing. In case of an instantaneous mixing process, the product selectivities in the resulting mixtures are solely governed by the kinetics of the chemical reactions involved and virtually no product D is found. In practice, the product selectivities are determined by the hydrodynamics of the mixing process and the kinetics of the chemical reactions involved. The more effective the mixing process, the more C is found in the resulting mixtures. Thus, mixing processes can be characterized by the concentrations of the chemical compounds in the resulting mixtures.

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The Iodide Iodate Reaction Method

The most popular chemical reaction method for the characterization of mixing processes is the Iodide Iodate Reaction Method. The reaction that is considered to be infinitely fast compared with the mixing process is the neutralization reaction of dihydroboric acid ions with protons to form orthoboric acid (Eq. 3). The slower reaction is the comproportionation of iodide ions and iodate ions to form iodine (Eq. 4), sometimes referred to as the Dushman reaction.

$$H_2BO_3^- + H^+ \rightarrow H_3BO_3 \quad (3)$$

$$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (4)$$

Iodine further reacts with excess iodide to form triiodide (Eq. 5).

$$I_2 + I^- = I_3^- \quad (5)$$

Triiodide can be easily monitored photospectrometrically in the UV range. It exhibits two distinct maxima centered at 282 and 353 nm. Applying Beer's law, triiodide concentrations can be derived from the optical densities of the resulting solutions.

The Iodide Iodate Reaction Method was originally developed for the characterization of mixing processes in stirred laboratory vessels,[2,3] where a small quantity of a rather concentrated aqueous solution of sulfuric acid is injected in the stirred tank. Byproduct (triiodide) selectivities depending on various parameters were observed. Among those are the concentration of the acid injected,[2,4] the acid feed point,[2,4,5] the acid feed time,[2,4] the geometry of the mixing accessory,[4] and the stirrer speed.[2,4–6] Later, the reaction scheme was applied for characterizing mixing in continuous flow devices,[7] where two flows were combined in the device in a flow ratio of 1:1. One feed contained sulfuric acid in a rather low concentration; the other feed contained the other reactants.

Evaluation of the experimental results reported in scientific literature

A simple way to evaluate the experimental results is plotting the optical densities over the parameters of interest (e.g., the mass flow or the pressure drop). Thus, different mixers can be compared[7] or parameter studies on structural details of specific types of devices can be given, as shown by the authors in a recent publication by example of microstructured V-type mixers.[8]

In studies on stirred laboratory tanks, a "segregation index," X_S, is typically derived from the experimental results.[2,4–6] The segregation index takes into account that the faster neutralization reaction always occurs in parallel. The index aims to relate the iodine yield (in form of iodine and triiodide) to the yield of iodine for an infinitely slow mixing process. Thus, the segregation index should yield values between 0 (perfect mixing) and 1 (worst case scenario) and should therefore be comparable with classically defined selectivities. The derived segregation index is a function of the reactant concentrations applied. For a wide range of experimental conditions, there is direct proportionality between the optical density of the resulting solutions and the segregation index derived. Plotting segregation indices over the parameter of interest instead of optical densities is thus basically just a rescaling of the ordinate.

"Mixing times," t_m, from simple mixing models have been derived from experimental results applying the Iodide Iodate Reaction Method to mixing processes in stirred vessels and in continuous flow mixers. It should be kept in mind that those "mixing times" are parameters of the respective models. They are reported to be independent of the reactant concentrations[9,10] (as opposed to the segregation indices). An experimental verification of this assumption has not been provided yet, except for varying H^+ concentrations in stirred laboratory vessels by Assirelli et al.[11]

For the case of stirred laboratory vessels, numerous "mixing times" have been derived from the incorporation model, mainly by the working group in Nancy, which developed the experimental method and the mixing model.[3,4] To get from the experimentally determined optical densities of the resulting solutions to the corresponding "mixing times," a stiff system of coupled, first-order differential equations needs to be solved. The resulting functions describe the development of the concentrations of the involved species over time. The "mixing time," t_m, is assumed to be the characteristic time for the incorporation of one fluid into the other.[3] The comparison of the model predictions for $t = t_m$ with the experimentally determined product selectivities yields the "mixing time" for a given mixing process.

Another model, the IEM model, can also be used to derive mixing times. As opposed to the incorporation model (acronym for **I**nteraction by **E**xchange with the **M**ean[12]), where one fluid incorporates the other, the two fluids remain distinct in the IEM model. The solution of the differential equation system describes the mass exchange between the fluids.

In recent contributions Falk and Commenge reviewed work on continuous flow mixers.[9,10] They derived "mixing times" from measurements utilizing the Iodide Iodate Reaction Method based on the IEM model. In case of the IEM model, a set of two differential equations has to be solved for each reacting compound (Eqs. 6–8).

$$\frac{dc_{k,1}}{dt} = \frac{\langle c_k \rangle - c_{k,1}}{t_m} + R_{k,1} \quad (6)$$

$$\frac{dc_{k,2}}{dt} = \frac{\langle c_k \rangle - c_{k,2}}{t_m} + R_{k,2} \quad (7)$$

$$\langle c_k \rangle = \alpha c_{k,1} - (1-\alpha) c_{k,2} \quad (8)$$

Equation 6 refers to the stream containing H^+, Eq. 7 to the stream containing the other reactive species (I^-, IO_3^-, I_2, I_3^-, $H_2BO_3^-$). $c_{k,1}$ represents the concentration of species k in stream 1; $c_{k,2}$ represents the concentration of species k in stream 2. $\langle c_k \rangle$ represents the mean concentration of species k (α is fraction of the stream containing H^+), whereas $R_{k,1}$ and $R_{k,2}$ represent the change of the concentrations of the reactive species (k) in the respective streams (1 or 2) due to chemical reactions. The solution of the set of differential equations yields functions describing the evolution of the concentrations of the reactive species over time, depending on a single parameter t_m, the "mixing time."

One experimental work reviewed by Falk and Commenge is the work of Schneider et al.,[13] who examined an "unsymmetrical T-mixer." This T-mixer is "unsymmetrical" with respect to the orientation of the feed streams, where one stream is fed perpendicularly to another that lies on the same axis than the mixing chamber. A change of the feed streams with respect to the mixer inlays might result in different iodine concentrations of the resulting mixtures and thus to different optical densities of the resulting solutions. Falk and Commenge are relating "segregation indices" to "mixing times" graphically by means of the IEM model for a specific set of concentrations. In this graph, the segregation index is proportional to the mixing time. As the segregation indices are also roughly proportional to the iodine yields and the optical densities, there is also roughly a linear relationship between the optical densities of the resulting solutions and the "mixing times" determined with the IEM model. Thus, any experimental differences observed, when

Table 1. Concentrations of the Reactants in the Feed Streams Used for Applying the Iodide Iodate Reaction Method to Mixing Devices

	Standard Concentration "1SC"	Twice the Standard Concentration "2SC"
Solution 1		
Sulfuric acid H_2SO_4	0.015 Mol/L	0.03 Mol/L
Solution 2		
Potassium iodide KI	0.016 Mol/L	0.032 Mol/L
Potassium iodate KIO_3	0.003 Mol/L	0.006 Mol/L
Sodium hydroxide NaOH	0.045 Mol/L	0.090 Mol/L
Hydroboric acid H_3BO_3	0.045 Mol/L	0.090 Mol/L

switching the orientations of the feed streams to the mixer inlets, would yield different "mixing times" despite unchanging hydrodynamics of the mixing process.

Simple mixing models like the incorporation model and the IEM model promise one specific mixing time from UV spectra of the resulting mixtures (achieved with a specific set of concentrations) regardless of the mixing device from which the mixtures were obtained. To test this assumption experimentally, mixing experiments were carried out on commercially available T-junctions and microstructured V-type mixers.

Experimental Conditions

Experimental setup and reactant concentrations

Details on the experimental setup can be found in a recent publication by the authors.[8] In addition, a long tube was attached downstream of the mixer to avoid an influence from the collecting vessel upon the product distribution in the resulting mixtures, which is crucial for the T-junctions as they exhibit a comparatively poor mixing performance. The authors verified experimentally in previous work[8] that the reactant concentrations need to be carefully chosen to achieve maximum sensitivity. For that purpose we have chosen a "standard concentration" (abbreviated 1SC) and applied multiples of this set of concentrations. The concentration sets are, for instance, abbreviated 2SC and 3SC for sets of concentrations containing two times and three times the concentration of each chemical compound with respect to the "standard concentration" 1SC, respectively. The T-junctions were characterized with the concentration set 1SC, the microstructured V-type mixers with the concentration set 2SC. The reactant concentrations are detailed in Table 1.

The optical densities of the resulting solutions at a wave length of 353 nm were determined in a 1 cm quartz cell (Hellma, Germany) using a UV-spectrometer (Agilent Technologies, USA, HP 8453).

Mixing devices

T-Junctions. Three T-junctions commercially available from the Swagelok company were characterized with the Iodide Iodate Reaction Method. (1) A T-junction for tubing of 6-mm outer diameter (SS-6MO-3), (2) a T-junction for tubing of 3-mm outer diameter (SS-3MO-3), and (3) a T-junction for two tubes of 6-mm outer diameter and one tube of 3-mm outer diameter (SS-6MO-3-3MJ-6M, Figure 1). All T-junctions were used in a similar way: the inlets for the feeds coincide at an angle of 180° and the outlet forms an angle of 90° with each inlet. Figure 1 shows a photograph (a) and a schematic (b) for the "unsymmetrical" T-junction (Table 2).

V-Type Mixers. V-type mixer inlays have been described in detail in previous publications.[8,14,15] Mixing is achieved according to the multilamination principle. The inlet feeds are subdivided into several small fluid streams and recombined in the mixing chamber. Thus, the diffusion path lengths for the species are shortened and mixing is therefore enhanced. Typically, those devices possess for each feed the same number of channels. In this study, two V-type mixers were characterized, each with a different number of channels for multilamination for each inlay. Other than that, the geometry of the single channels is identical (100 μm $\times$ 70 μm cross-section and 14-mm length). The numbers of channels in the mixers used for this study are given in Table 3.

Mixer V30/20 was constructed by stacking a foil with 10 channels (inlet 1), followed by a second foil with 10 channels (inlet 2) and a third foil with 10 channels (inlet 1).

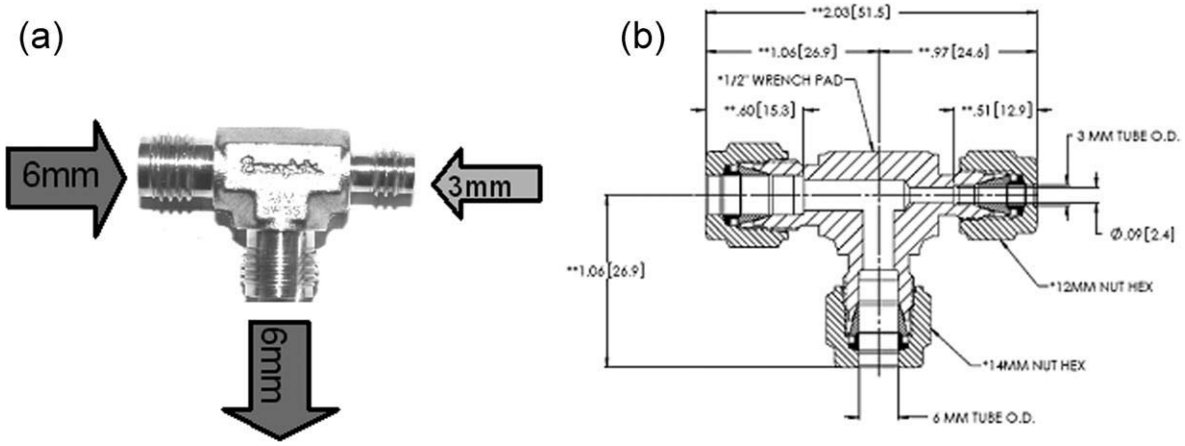

Figure 1. Photograph (a) and schematic (b) of a T-junction which was characterized as a mixing element.

The reactants are fed over tubing of different diameter. Courtesy of Swagelok.

Table 2. Dimensions of Inlet and Outlet of T-Junctions

Mixer	Inlet 1	Inlet 2	Outlet
T6mm	4.8 mm	4.8 mm	4.8 mm
T3mm	2.4 mm	2.4 mm	2.4 mm
T6mm3mm	4.8 mm	2.4 mm	4.8 mm

Table 2 summarizes the inner diameter of the inlets and the outlet of the three T-junctions characterized for their mixing properties.

Furthermore, unstructured foils at the bottom and top completed the stack. After a diffusion bonding step, the stack was fitted in an adapter flange constructed from stainless steel (for further details see Ref. 8).

Mixer V50/5 was similarly constructed by stacking a foil with 25 channels (inlet 1), followed by a foil with 5 channels (inlet 2), and a foil with 25 channels (inlet 1).

Experimental Results and Discussion

Experimental results

T-Junctions. Simple mixing models like the IEM model promise the derivation of mixing times without considering the specific geometry of the mixing device. Hence, it should have no influence on the experimental results whether solution 1 is fed to inlet 1 and solution 2 to inlet 2 or vice versa, as long as the solutions fed into the mixing device are diluted enough to avoid an influence of their viscosities on the mixing process (mixing of water with water). Any observed differences in the optical densities of the solutions would then indicate different mixing times, when calculated from simple mixing models, although the hydrodynamic situation would be the same for both cases.

By switching the feeds, the assumption of the IEM model that ''mixing times'' could be obtained without considering the geometry of the specific device is tested by example of the T-junctions described in section above. For the case of the symmetrical T-junctions T6mm and T3mm, no differences in the experimental results are expected when switching the feeds to different inlets. Any differences observed in the experimental results can be attributed to the accuracy of the method. The characterization of the ''unsymmetrical'' T-junctions T6mm3mm serves for questioning the assumptions of the IEM model. The results obtained are depicted in Figure 2.

As expected, the optical densities of the resulting mixtures decrease with higher mass flow for all examined cases, indicating better mixing at higher mass flow rates. This experimental finding is explained with higher energy dissipation at higher mass flow rate.

As further expected, the resulting mixtures obtained with the T3mm contain less triiodide than those obtained with the mixing element T6mm at the same mass flow rates. At constant mass flow, mixing in tubes of narrower diameter leads to higher energy dissipation and thus to lower concentrations of triiodide. Lower concentrations of triiodide indicate more efficient mixing processes.

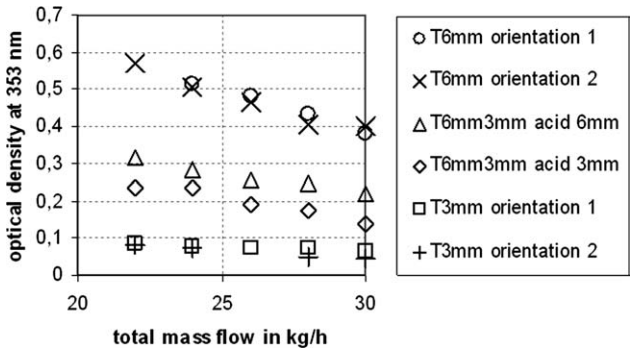

Figure 2. Experimental results for the characterization of commercially available T-junctions as mixing elements achieved with the Iodide Iodate Reaction Method.

The experimental data show that the both orientations of the inlets with regard to the feed streams produce comparable experimental results for symmetrical T-pieces. The small differences observed reflect the accuracy of the method and indicate altogether a reliable characterization method.

As opposed to the findings for the symmetrical T-pieces, the experimental results for the ''unsymmetrical'' T-junction T6mm3mm show an influence of the orientation of the feeds to the respective inlets on the experimental results. Lower triiodide concentrations are found when feeding the acid through the tubing with smaller inner diameter, which means that the feed containing the acid is entering the mixing zone at a higher linear velocity. The observed differences cannot be caused by deviating hydrodynamics because this should be the same for both orientations as long as the reactant concentrations do not influence the viscosity of the feeds noticeably. The differences must therefore be attributed to a deviation of the concentration pattern in the mixing zone created by the changed feed configuration.

V-Type Mixers. To further elucidate the orientation effect observed with the T-junctions, mixing experiments were carried out with V-type mixers described above. Corresponding to the better mixing capability of V-type mixers compared with the T-junctions, the V-type mixers were characterized with doubled concentration of the respective species (2SC). Thus, the results for the V-type mixers are not directly comparable with the results achieved with the T-junctions. The better mixing results obtained with the V-type mixers compared with the T-junctions at the same mass flow rates are obtained at the cost of higher pressure drop. Therefore, the V-type mixers had to be operated in a lower mass flow range due to the restrictions of the pumps employed. The experimental results for the mixer V30/20 and for the mixer V50/5 are given in Figure 3.

The mixer V50/5 shows better mixing performance than mixer V30/20 at the same mass flow rate. As with the T-junctions, better mixing results are observed at higher mass flow rates, corresponding to higher energy dissipation rates. In turn, lower optical densities of the resulting

Table 3. Number of Microchannels of the Examined V-Type Mixers

Mixer	Inlet 1	Inlet 2
V30/20	30	20
V50/5	50	5

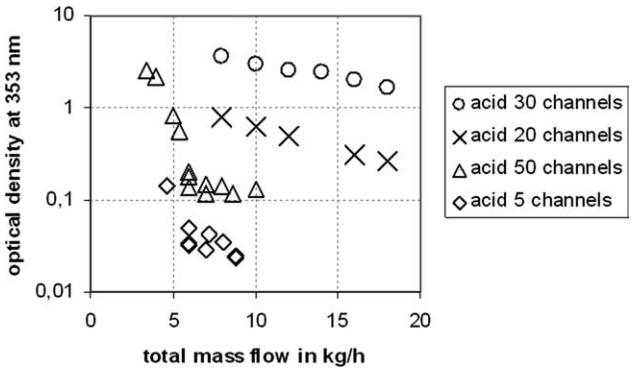

Figure 3. Characterization of the V-type mixers V30/20 and V50/5.

solutions corresponding to lower triiodide concentrations are observed when feeding the acid solutions through the inlet at higher flow velocity.

Discussion

A possible explanation of the observed effect of the connection of the two feeds to the different inlets is given by the expectation that feeds with higher velocity offer higher local energy dissipation rates. Triiodide is only produced in areas with excess H^+. In areas with a stoichiometric deficiency in H^+, H^+ is totally consumed by the neutralization reaction and thus the Iodide Iodate Reaction Method is ''blind'' to the hydrodynamics in these regions as no triiodide can be formed. Hence, less triiodide is observed when feeding H^+ in regions of higher energy dissipation rate. This effect can be understood through an analogous phenomena occurring in stirred laboratory vessels known as ''local energy dissipation rates.'' Higher triiodide yields are observed when feeding H^+ close to the liquid surface as opposed to feeding close to the impeller. The change of the feed location in a stirred laboratory tank implies a change in the hydrodynamics of the mixing process, and the observed differences in the experimental results can be attributed to differing hydrodynamics of the mixing process. The typical experimental protocol for the characterization of continuous flow mixers uses a flow ratio of 1/1. Therefore, the differences in the optical densities of the resulting solutions obtained from unsymmetrical mixers at the same flow conditions cannot be attributed to the hydrodynamics of the mixing process but to the shortcomings of the simple mixing models.

Conclusions

As demonstrated experimentally by example of simple T-junctions and microstructured V-type mixers, mixing times cannot be derived from chemical test reactions by applying simple mixing models that do not take the specific geometry of the device into account.

This conclusion was drawn based on data from mixing experiments with ''unsymmetrical'' mixers with different inlet geometries. By feeding the acid stream through different inlets, different compositions of the resulting mixtures were achieved. This would indicate different ''mixing times'' when applying simple mixing models like the IEM model for the interpretation of the experimental data.

Unsymmetrical mixers were characterized with the Iodide Iodate Reaction Method by other research groups.[13,16] These data are also likely to be influenced by the effects of the feed orientation with regard to different inlets.

It is suggested that the observed effect of the orientation of the feeds is due to the question whether H^+ is fed in regions with high or low energy dissipation. Iodine is only produced in areas with local excess of H^+. If H^+ is fed into regions of high energy dissipation, comparatively low amounts of iodine are detected in the resulting mixtures.

The experimental findings were achieved by applying the Iodide Iodate Reaction Method, but most likely they apply to other characterization methods as well as for mixing in regions with a large stoichiometric deficiency in B (the reactant both reactions are competing for: H^+ in the Iodide Iodate Reaction Method), only the faster reaction occurs. The comparison of experimental results and the results of numerical simulations will be a subject of further investigations.

The Iodide Iodate Reaction system is a reliable method for parameter studies but might also be used for the quantitative evaluation of the experimental results when comparing the experimental results to model predictions as recently shown in scientific literature.[17] However, for the successful application of this approach, reliable kinetic data on the Dushman reaction must first be obtained.[18,19]

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