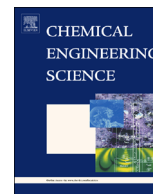




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Kinetic investigation of the Dushman reaction at concentrations relevant to mixing studies in microstructured cyclone type mixers



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HIGHLIGHTS

- Kinetic examinations closest possible to the corresponding mixing experiments.
- The suggested reaction orders are close to the classical assumptions, justifying the examination method.
- No influence of the ionic strength found.
- Previous examination neglected the role of sulfate as a base.

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ABSTRACT

In this contribution we report on kinetic investigations of the Dushman reaction at concentrations relevant to mixing studies in microstructured cyclone type mixers. The investigations were carried out under incomplete mixing. With this approach the kinetic investigations are as close as possible to the conditions of the corresponding mixing investigations, but no information on the absolute rate of the Dushman reaction is obtained.

Our data suggest reaction orders (I^- : **2**; IO_3^- : **1**; H^+ : **1.3**) close to those, typically assumed for mixing studies.

No significant influence of the ionic strength could be found. Previous assumptions on the influence of the ionic strength neglected the basic nature of the sulfate ion.

The use of perchloric acid instead of sulfuric acid, commonly employed in mixing studies, yields far higher optical densities of the resulting solutions, suggesting higher local H^+ concentrations for the perchloric acid case.

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1. Introduction

Mixing processes can be investigated by competing chemical reaction methods. The most popular test reaction method is the so-called iodide iodate reaction method (Villermaux et al., 1994; Guichardon et al., 2000; Panić et al. 2004; Kölbl et al., 2008). It is based on the competition of a neutralization reaction (Eq. (1)) and the Dushman reaction (Eq. (2)), which can serve as a time measure for the investigated mixing process. Iodine formed via the Dushman reaction further reacts with excess iodide to form triiodide (Eq. (3)), which is typically quantified by its UV absorbance at a wave length of 353 nm.



Thus, qualitative comparison of mixers and mixing processes is possible.

1.1. Motivation

Any quantitative measures derived from the experimental results (such as mixing times) depend on the reliability of the kinetic data available for the Dushman reaction (Dushman, 1904).

In a recent submission to this journal a method for the kinetic investigation of the Dushman reaction under incomplete mixing, applied to mixing processes in stirred laboratory tanks was suggested (Kölbl et al., 2013). Incomplete mixing implies the parallel use of the neutralization reaction (Eq. (1)). Iodine is formed in a state of incomplete mixing in acid rich regions. With this approach the conditions of the kinetic investigations are as close as possible to the conditions of the corresponding mixer characterization, but only the relative influence of reactive and non-reactive components can be investigated. No information on the absolute rate of the Dushman reaction can be obtained. In order to obtain quantitative kinetic information the reactants

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need to be mixed fast enough, so that no significant reaction occurs during mixing. No neutralization is applied with this approach. After mixing, the UV absorbance is monitored time- or space resolved, which will be reported in detail elsewhere. Preliminary results have been published already in a recent conference contribution Kölbl et al. (2012).

In this contribution we report on the kinetic investigation of the Dushman reaction in a microstructured cyclone type mixer under incomplete mixing.

1.2. Previous assumptions on the kinetics of the Dushman reaction at concentration relevant to mixing studies

In scientific research on mixing examinations, both in stirred laboratory vessels and continuous flow mixers, the kinetic model published by Guichardon (1996) and Guichardon et al. (2000) has been widely used to derive 'mixing times' using the IEM model (Villiermaux, 1986) and the incorporation model (Villiermaux and Falk, 1994) as simple mixing models (Fournier et al., 1996; Rousseaux et al., 1999; Fang and Lee, 2000, 2001; Guichardon et al., 2000, 2001; Bertrand-Andrieu et al., 2006; Nienow et al., 2007; Assirelli et al., 2008; Hu et al., 2009; Falk and Commenge, 2010; Commenge and Falk, 2011). The kinetic model suggested is detailed in Eqs. (4) to (7).

$$r = kc^2(\text{H}^+)c^2(\text{I}^-)c(\text{IO}_3^-) \quad (4)$$

$$\log k = 9.28 - 3.66\sqrt{I} \quad \text{for } I \leq 0.16 \text{ M} \quad (5)$$

$$\log k = 8.38 - 1.51\sqrt{I} + 0.23I \quad \text{for } I \geq 0.16 \text{ M} \quad (6)$$

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad (7)$$

The rate r of the iodine formation (Eq. (4)) depends on the rate constant k and the concentrations of the reactants I^- , IO_3^- , and H^+ . The corresponding reaction orders are **2** (I^-), **1** (IO_3^-), and **2** (H^+). The rate constant k (Eqs. (5) and (6)) is assumed to be a function of the ionic strength (Eq. (7)), which shows a spatial distribution due to the different ionic strengths of the feeds.

1.3. Recent findings on the kinetics of the Dushman reaction at concentrations relevant to mixing studies

With an approach similar to the one applied in this study the kinetics of the Dushman reaction was investigated at concentrations relevant to mixing studies in stirred tank reactors (Kölbl et al., 2013). Similarly the investigations were carried out under incomplete mixing with parallel neutralization.

No verifiable influence of the ionic strength on the rate of the Dushman reaction was found. It is assumed that previous examinations neglected the role of sulfate as a base. Thus, with the use of perchloric acid instead of the frequently employed sulfuric acid higher triiodide yields are obtained in the resulting solutions. These differences are higher than assumed in a previous publication (Kölbl and Schmidt-Lehr, 2010). With the method described, new reaction orders for the conditions of mixing experiments in stirred laboratory vessels were suggested: H^+ : **0.6**; IO_3^- : **0.6**, I^- : **1.4**. The odd numbers for the reaction orders obtained (as opposed to the classical assumptions, Eq. (4)) led to some discussions on the validity of the approach. The experimental findings further suggest that the Dushman reaction occurs in areas with a large acid surplus, into which small amounts of I^- and IO_3^- diffuse. Concentrations relevant to mixing studies in semibatch stirred tank reactors are thus high acid concentrations with correspondingly low concentrations of iodide and iodate.

2. Materials and methods

2.1. Examined concentration sets

Continuous flow mixers are typically investigated with a concentration set suggested by Panić et al. (2004). Effective mixing processes are indicated by small byproduct (I_3^-) yields and correspondingly low optical densities of the resulting solutions. With this concentration set, highly effective mixing processes yield no detectable quantities of triiodide. By raising the concentrations of the reactants, the velocity of the Dushman reaction is raised. Thus, mixing sensitive results are obtained for highly effective mixing processes. In scientific literature on mixing investigations in stirred vessels and continuous flow mixers, it is typically suggested to raise only the H^+ concentration (Guichardon et al., 2000; Panić et al., 2004). With this approach the ratio of 'iodide active' (local surplus of H^+) and 'iodine inactive' compartments (local surplus of H_2BO_3^-) is altered, and the experimental results achieved for different concentration sets are not directly comparable. For this reason the IMVT has suggested a standard set of concentrations (abbreviated IMVT-1SC) and to raise the concentrations of all components by the same factor. This leads e.g. to concentration sets denoted IMVT-2SC and IMVT-3SC when doubling or tripling the concentrations of all components (Kölbl et al., 2008). As highly effective mixers, microstructured cyclone type mixers are typically characterized with five times the standard concentration, abbreviated IMVT-5SC. This concentration set is given in Table 1, along with the ionic strength I of the feeds.

The composition of the combined feeds (after the total consumption of H^+) for a typical mixing experiment (see Section 3, Fig. 5), resulting in an optical density of 1 A.U. is given in Table 2. It has to be kept in mind that each feed concentration (without chemical reactions) is reduced by a factor of 0.5 due to the dilution.

The conversion degree of the key component IO_3^- is approximately 0.15%.

2.2. The mixer

The kinetic investigations described in this contribution were carried out in a microstructured cyclone type mixer similar to a metallic mixer described in a previous contribution (Kölbl et al., 2011). Fig. 1 shows characteristic details of the mixer.

The inner structure of the PEEK (poly(etheretherketone)) disk is given in Fig. 2 along with the mixing principle.

The fluids to be mixed are fed tangentially into the mixing chamber. Thus, a swirl motion is created which enhances mixing.

2.3. Experimental set-up

A sketch of the experimental set-up is given in Fig. 3.

Mixing is achieved by pumping (mzr type 7206, HNP Mikrosysteme GmbH, Parchim, Germany) the solutions (Section 2.1) through the mixer described above (Section 2.2). The flow is monitored with Coriolis flow meters (Promass 63, Endress und Hauser, Reinach, Switzerland). The pressure is measured with electric pressure transducers (E913, Baumer Bourdon-Haenni AG, Jegenstorf, Switzerland). The resulting mixtures are collected at

Table 1
Concentration set IMVT-5SC.

	NaH_2BO_3	KI	KIO_3	H_2SO_4	I
Feed 1	0.22735 M	0.07975 M	0.01597 M		0.32307 M
Feed 2				0.075 M	0.075 M

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