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Short communication

Comments on the iodide/iodate method for characterising micromixing

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Abstract

Qualitatively the iodide/iodate method, in which the iodine yield is measured, has provided reliable results for assessing the extent of micromixing of miscible reagents. Quantitative treatment requires however a robust kinetic model. Comparison of published models shows large differences due to the complexity of the iodine-forming reaction. The kinetics needs to be re-determined employing modern techniques for fast reactions and under the conditions (concentrations, ionic strength, etc.) used in mixing studies.

Keywords: Iodide/iodate method; Reaction kinetics; Quantitative models

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1. Introduction

Several sets of rapid multiple chemical reactions, having mixing-sensitive product distributions, are in use to characterise the extent of mixing on the molecular scale (micromixing) [1]. For example, when the rates of a pair of competitive reactions differ by many orders of magnitude, the yield of the slower reaction will be (a) almost zero if mixing is perfect, so that reaction kinetics controls the progress of both reactions, but (b) comparable with the yield of the faster reaction if mixing can not be completed before significant reaction has already occurred.

The iodide/iodate method, introduced in the 1990's and described in more detail in 2000 [2,3], is based upon measuring the mixing-sensitive yield of iodine in the competition between the neutralisation of an acid Eq. (1) and its role in liberating iodine through the Dushman reaction Eq. (2).

$$H_2BO_3^- + H^+ \rightleftarrows H_3BO_3 \quad (1)$$

$$5I^- + IO_3^- + 6H^+ \rightleftarrows 3I_2 + 3H_2O \quad (2)$$

$$I_2 + I^- \rightleftarrows I_3^- \quad (3)$$

Before mixing, the two aqueous solutions contain: (a) sulphuric acid, which is the limiting reagent and (b) iodide, iodate and borate ions, which also act as buffer [2]. Liberated iodine complexes with iodide to form triiodide Eq. (3), whose concentration is determined photometrically. This measurement together with the equilibrium constant for Eq. (3) and the initial quantities of all reagents allows the iodine yield to be found [2].

When mixing is much faster than Eq. (2), the acid will be almost totally consumed in Eq. (1). When, however, micromixing is slower than reaction (2) or of similar rate, iodine forms and its yield is a measure of segregation on the molecular scale and incomplete micromixing.

2. Application of method to studying micromixing

Extensive details of experimental procedures for studying mixing are available [2] including achievement of a suitable alkaline pH and solution concentrations for operation in semi-batch or continuous modes. Table 1 gives concentrations used for reactions (1) and (2) with semi-batch addition of sulphuric acid to stirred tank reactors [2,4,5]. Note that the iodide to iodate ratio was 5 as in Eq. (2). For the competitive Eq. (1) the concentrations of ortho-boric acid and borate in the tank were both 0.0909 M giving a pH of 9.14 [3]. Concentrations can be changed to match mixing rates in other mixer types [2]. When measuring reaction kinetics [3] the ionic strength (μ) was varied by addition of potassium sulphate.

Although a narrower range of operating conditions has been covered with the iodide/iodate method than with alternative reac-

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Table 1
Reagent concentrations (M) for Eq. (2)

H^+	I^-	IO_3^-	μ	Ref.
0.25–4[a]	0.0117	0.00233	0.11	[2,4,5]
0.01–0.08	8×10^{-4}–2×10^{-3}	10^{-5}–7×10^{-5}	0.01–1.8	[3]
6×10^{-6}–10^{-4}	0.003–0.03	2×10^{-4}–10^{-3}	0.2	[7]
0.01–0.09	5×10^{-8}–5×10^{-6}	0.005–0.029	0.2	[8]
0.1–0.49	6×10^{-5}–6×10^{-4}	4.5×10^{-4}–4.5×10^{-3}	–	[9]
0.01–0.21	0.03–0.5	5.3×10^{-5}	0.5	[10]

[a] Concentration *before* mixing.

tion sets [1], the method has given results which are qualitatively consistent with these alternatives. They can be understood by considering how operating conditions such as feed location, stirrer speed, reagent concentrations, etc. influence the time scales for mixing and reaction. Any reduction of iodine yield reflects either more rapid mixing or slower reaction and vice versa. Examples include:

- Faster micromixing – lower iodine yield – with faster stirring and when relocating the feed point to a more turbulent region of a stirred tank [2,4,5].
- Faster reaction – higher iodine yield – with increasing acid concentration whilst reducing the acid volume to maintain a constant acid quantity [2,4,5].
- Decreasing iodine yield when reducing the acid feed rate stepwise in a series of runs until the yield reaches an asymptotic minimum value, indicating micromixing as the sole mixing mechanism [2,4].

3. Reaction kinetics

3.1. Measurements directed at mixing investigations

When the kinetics of Eqs. (1)–(3) are known and a micromixing model is employed, iodine yields can be processed to give a micromixing time and possibly an energy dissipation rate in the region where mixing and reaction occur [2,4,5].

The rate constant of Eq. (1) is about $10^{11}\,M^{-1}\,s^{-1}$ so that neutralisation is almost instantaneous. The equilibrium in Eq. (3) is also much faster than the Dushman reaction-kinetics are available [3]. For mixing studies the kinetics of Eq. (2) was measured in a spectrophotometer cell, the mixing time being “smaller than 3 s”, whilst the Dushman reaction needed some 100 s for completion [3]. The longer mixing time in the cell relative to a stirred tank {10–100 ms} necessitated much lower concentrations in the spectrophotometer than are used in mixing studies (Table 1).

The resulting kinetic model for the rate of the Dushman reaction $\{r\,(Ms^{-1})\}$ was

$$r = k[H^+]^2[I^-]^2[IO_3^-] \tag{4}$$

where the rate constant k $(M^{-4}\,s^{-1})$ decreased with increasing ionic strength. After the effect of temperature on the equilibrium constant of Eq. (3) had been included, k was independent of temperature in the range 283–308 K [3].

The temperature-independence of k and the high kinetic order {five} indicate a multistep reaction mechanism. Its rate-determining step could change when employing widely different concentrations in kinetics measurements and in mixing studies (Table 1). Consequently the applicability of Eq. (4) to mixing investigations seems to be in doubt.

3.2. General kinetic and mechanistic studies of the Dushman reaction

Since Dushman’s work in 1904 many mechanistic and kinetic studies of Eq. (2) have appeared, but no complete agreement has yet emerged [6]. Some complexities will now be briefly cited.

A review [6] presents many characteristics including (a) catalysis by bromide, chloride, phosphate and acetate ions; (b) a kinetic order in iodide varying from 1 at low iodide concentrations to 2 at higher values and less than 2 at still higher values; (c) effects of buffer nature and concentration on rate; and (d) decreasing rate with increasing ionic strength. When several measurements [7] at iodide concentrations from 3.34×10^{-3} to 1.67×10^{-2} M were fitted [6] to Eq. (4), k decreased from 9.56×10^{8} to $5.19\times10^{8}\,M^{-4}\,s^{-1}$, indicating an order smaller than 2 if k is to be independent of kinetic order as it should be. A possible reaction mechanism gave the following kinetic model [6]

$$r = 10^9[IO_3^-][H^+]^2[I^-]^2\left(0.32 + \frac{0.39}{0.28 + 10^2[I^-]}\right) \tag{5}$$

at 298 K and an acetate concentration 0.192 M. Table 1 gives the ranges of reagent concentrations employed. The iodide order in Eq. (5) decreases gradually below 2 with rising iodide levels.

The authors of the data used to establish Eq. (5) found orders of 1 for iodate and 2 for hydrogen ions, as in Eq. (4), but for iodide it varied from 1.51 at 293 K to 1.85 at 308 K [7]. At 298 K their kinetic model was

$$r = [IO_3^-][I^-][H^+]^2(2.62\times10^6 + 4.23\times10^8[I^-]) \tag{6}$$

which with rising iodide concentration implies an increasing order from 1 to 2. This disagrees with the trend in Eq. (5).

The following limits for the variation of iodide order with iodide concentration have been given: $<5\times10^{-7}$ M, order = 1; $5\times10^{-6}/10^{-3}$ M, order = 2; $>10^{-3}$ M, order <2 in non-buffered solutions [8]. A mechanism accounting for some of these changes was proposed. Experiments in a CSTR [8] using low iodide levels (Table 1) were correlated with the following rate expression at 298 K

$$r = [IO_3^-][H^+]^2(1200[I^-] + 4.2\times10^8[I^-]^2) \tag{7}$$

The models in Eqs. (5)–(7) are based on kinetic runs where one or more reagent concentrations were much lower than those used in mixing studies (Table 1). Some results of employing fast mixing techniques and therefore higher concentrations (Table 1) are however available [9,10].

Large excesses of iodate and acid permitted study of the order with respect to iodide [9]. The suitability of the stopped-flow method is evident when employing the highest concentrations in Table 1, where the measured half-life of the Dushman reaction was approximately 10 ms. Mixing experiments however use much higher iodide levels (Table 1). The reaction was second order in iodide (the limiting reagent), but its rate increased more slowly than the square of the acid concentration as this was increased. Not only could the order in acid fall below 2, but in the most acidic solutions it tended to zero. A reaction mechanism, consistent with these results, was given and was reduced to alternative kinetic models when either iodide or iodate was in excess. This latter case corresponded to the experimental conditions using perchloric acid in high excess, giving

$$r = 1.6\times10^8[HIO_3]_0[HClO_4]_0[I^-]^2 (1 + 990[HIO_3]_0[HClO_4]_0)^{-2} \tag{8}$$

Again using a technique suited to rapid reactions having time scales on the order of 10^{-4} to 10^{-3} s and the concentration ranges in Table 1, a kinetic and mechanistic study [10] gave kinetic orders for both acid and iodide less than 2. A mechanism led to the following kinetic model at 298 K for an ionic strength of 0.5 M

$$r = 2.8\times10^8[IO_3^-][H^+]^2[I^-]^2(1 + 2.53[H^+])^{-1} (1 + 2.3[I^-])^{-1} \tag{9}$$

The source of hydrogen ions in the experiments leading to Eqs. (7)–(9) was perchloric acid, which is so strong ($pK = -9$) that complete ionisation may be assumed. In some mixing studies sulphuric acid might not fully ionise ($pK_1 = -3$, $pK_2 = 1.94$) and its dissociation equilibria together with that of water should also be considered in kinetic modelling.

Differences between the kinetic Eqs. (4)–(9) could be due to the widely different reagent concentrations used in their determinations (Table 1). The ionic strengths and the buffers and anions also vary between these investigations. No rigorous comparison of kinetic equations can be made. Some order-of-magnitude results can possibly be obtained using the correlation for k in Eq. (4) at ionic strengths of 0.2 and 0.5 M. When $\mu > 0.166$ M, k at 298 K is given by [3]

$$\log k = 8.383 - 1.5112\mu^{0.5} + 0.2369\mu \tag{10}$$

and so $k = 5.68\times10^7\ M^{-4}\,s^{-1}$ ($\mu = 0.2$ M) and $k = 2.71\times10^7\ M^{-4}\,s^{-1}$ ($\mu = 0.5$ M). Neither ionic strength equals that used in mixing work (0.11 M) for which $k = 1.16\times10^8\ M^{-4}\,s^{-1}$ [3]. The rate constant is very sensitive to ionic strength. The ionic strengths of added acid and bulk solution would only be matched when the acid concentration was approximately 0.04 M. This is less than frequently used values (Table 1).

Table 2
Reaction rates calculated from kinetic equations

μ (M)	0.2	0.2	0.2	0.2	0.5	0.5
Equation	(4)	(5)	(6)	(7)	(4)	(9)
r (Ms^{-1})	73	751	825	536	35	57
Ref.	[3]	[6]	[7]	[8]	[3]	[10]

3.3. Application of kinetics to mixing studies

In a typical mixing experiment [2,4,5] one part by volume of sulphuric acid solution is gradually added to approximately one thousand parts by volume of the iodide, iodate, borate solution whose composition is given above (Table 1 and text). Acid concentration decreases from a high value (Table 1) towards zero as mixing and reaction with the tank contents occur. Reagent concentrations in the tank hardly change. An initial acid concentration of 2 M will be considered for the results in Table 2, which gives the initial reaction rate r at 298 K calculated from various kinetic expressions.

Eqs. (5) and (6) are based on the same set of measurements [7]. Eq. (8) shows a much weaker dependence on acid concentration than Eq. (4). This is also seen in Eq. (9) for both acid and iodide, where the reaction order in each decreases from 2 to 1 as concentrations rise. This contradicts Eqs. (6) and (7) as far as iodide is concerned: concentrations (Table 1) are however very different. Table 3 compares Eq. (4) and (9) for $\mu = 0.5$ and various initial acid concentrations. Rates are initial values after adding acid of given concentration. However, because bulk concentrations hardly change during reaction, these values also approximate the decreasing reaction rates as the mixing of any one acid addition proceeds and its concentration gradually decreases.

The term in the denominator of Eq. (9) greatly reduces the dependence of initial reaction rate on the acid concentration relative to the quadratic term in Eq. (4). Neither of these equations is based on kinetic measurements using the same concentrations as in mixing experiments: Tables 2 and 3 do not accurately simulate such experiments. Problems with reaction kinetics might be responsible for discrepancies observed when simulating these reactions [11]. The importance of kinetics increases with increasing mixing rate and, if discrepancies also increase, difficulty with the kinetics is indicated.

Table 3
Reaction rates using different acid concentrations

$[H^+]$ (M)	0.5	1.0	2.0	3.0	4.0
r (4) (Ms^{-1})	2.2	8.7	35	78	138
r (9) (Ms^{-1})	9.6	25	57	91	125

4. Conclusions

The iodide/iodate method for characterising the extent of micromixing through the iodine yield gives qualitatively consistent and intelligible results. It is, for example, suitable to rank different mixers or different operating conditions, whereby the lower the iodine yield, the better the mixing on the molecular scale.

Quantitative application requires the kinetics of Eqs. (1)–(3) to be fully known under the conditions – especially reagent concentrations and ionic strength – used in mixing experiments. None of the kinetic models of the Dushman reaction Eqs. (4)–(9) satisfies this requirement and the models show little mutual agreement. There is need for a kinetic study of the Dushman reaction Eq. (2), employing modern techniques for fast reactions and concentrations relevant to mixing investigations.

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