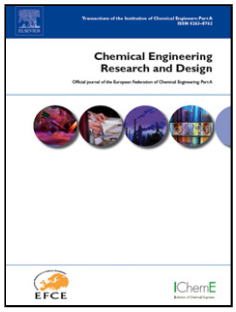
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INFLUENCE OF REAGENTS CHOICE (BUFFER, ACID AND INERT SALT) ON TRIIODIDE PRODUCTION IN THE VILLERMAUX-DUSHMAN METHOD APPLIED TO A STIRRED VESSEL

Carlos Baqueiro[1], Nelson Ibaseta[1,*], Pierrette Guichardon[1], Laurent Falk[2, 3]

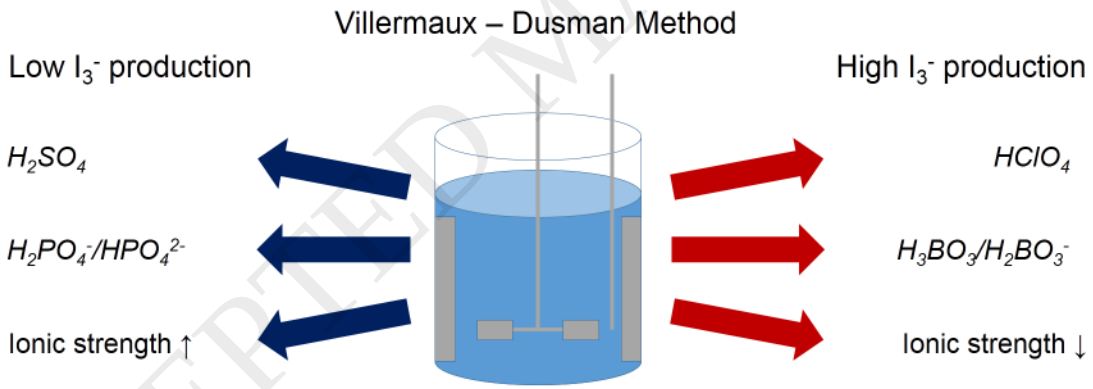
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Graphical abstract



Highlights

- The influence of the reagents choice in the Villermaux Dushman test is studied
- Phosphate buffers lead to lower I_3^- production that borate buffers
- I_3^- production is slightly influenced by the ionic strength
- Both acids and buffers can be used for qualitative studies
- The pK_a of H_2SO_4 and H_3PO_4 should be considered in micromixing time estimations

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Abstract

This work studies how deeply the reagents choice influences micromixing characterisation by the Villermaux-Dushman method, when applying it to a 1 litre stainless steel standard vessel with two baffles, stirred by an inclined blade turbine. For the first time, borate and phosphate buffer are compared on their use in the method. It is observed that triiodide production is higher when borate buffer is used. Moreover, perchloric acid leads to higher triiodide production than sulphuric acid, when injecting the same concentration of both acids. Finally, the influence of the ionic strength is also studied, since there has been a great deal of controversy about it over the last years. The results show that the ionic strength affects triiodide production, although relatively slightly . Advice concerning the choice of the reagents is given in conclusion.

Keywords

Micromixing, Villermaux-Dushman, Iodide iodate method, mixing characterization

1. Introduction

Micromixing (Bałdyga and Pohorecki, 1995) is defined as mixing at the molecular scale, that is, below the Kolmogorov scale. It plays a main role when dealing with fast reactions: polymerization reactions, fast competitive-consecutive and fast parallel reactions, as well as reactive crystallizations (precipitations). In all these applications, the final product obtained depends on the micromixing rate. Hence, a special focus was given to developing micromixing characterization methods at the end of the 20th century (Bourne et al, 1992; Fournier et al, 1996a). The iodide iodate method, also called Villermaux-Dushman method, has probably become the main micromixing characterization method, thanks to a lower cost and easier product manipulation (Guichardon et al, 2001). Since it was proposed by Fournier et al (1996a) and modified by Guichardon and Falk (2000), the method has been widely used for selection of the injection point and comparison of the micromixing quality obtained using new devices or removing baffles (Rousseaux et al, 1999; Assirelli et al, 2002; Assirelli et al, 2005; Assirelli et al, 2008a) and determination of the local dissipative rate (Schaer et al, 1999; Assirelli et al, 2008b; Nouri et al, 2008; Habchi et al, 2014). With the development of micromixers during the 2000s (Hessel et al, 2005), the method has also been adapted for their characterization (Panić et al, 2004; Kölbl et al, 2008; Commenge and Falk, 2011).

This method is based on the competition between two reactions: an instantaneous neutralization reaction (reaction 1, where B^- is a base), and the Dushman reaction (Dushman, 1904), which is a fast (but slower than reaction 1) comproportionation reaction (reaction 2).

$$H^+ + B^- \rightarrow HB \qquad \text{(reaction 1)}$$

$$6H^+ + 5I^- + IO_3^- \rightarrow 3I_2 + 3H_2O \qquad \text{(reaction 2)}$$

When some acid is fed in stoichiometric default in an aqueous basic solution containing an appropriate pre-mixture of iodide, iodate and B^- anions, the products obtained depend on the quality of micromixing. In the case of perfect mixing conditions, all the protons will be consumed by the base according to reaction 1. In the case of imperfect mixing, there will be a local lack of base, protons will react with iodide and iodate anions, and some iodine will be produced.

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Iodine will then be involved in a quasi-instantaneous equilibrium with triiodide (reaction 3), as follows:

$$I^- + I_2 \leftrightarrow I_3^- \qquad \text{(reaction 3)}$$

Hence, triiodide concentration, which can be easily measured by UV-visible spectrophotometry, can be used to characterize the quality of micromixing.

The original method (Fournier et al, 1996; Guichardon and Falk, 2000) used sulphuric acid and borate buffer. However, during the last ten years, different adaptations of the method have been proposed, most of them concerning the use of a different acid and/or buffer. Kölbl and Schmidt-Lehr (2010) proposed replacing sulphuric acid with perchloric acid for quantitative treatment, arguing that sulphuric acid may not be completely dissociated. Hydrochloric acid has even been used (Ehrfeld et al, 1999), despite the catalytic effect of chloride anions on the Dushman reaction (Schmitz, 1999). On the other hand, Pinot et al (2014) proposed using a phosphate buffer ($HPO_4^{-2}/H_2PO_4^-$) instead of the borate buffer ($H_2BO_3^-/H_3BO_3$) because of the toxicity of borate. However, it is worth noting that the influence of these choices (especially the choice of the buffer) have not been deeply analysed. The present work aims at comparing results obtained using both acids and both buffers, and then proposing the most adapted combination for a given application.

2. Materials and methods

The following compounds were used without further purification in the preparation of the solutions: H_2SO_4 (VWR, GPR Rectapur), $HClO_4$ (Fisher chemical, laboratory grade), Na_2SO_4 (Alfa Aesar, ACS reagent grade), $NaClO_4$ (Acros Organics, extra pure), NaOH (Acros Organics, ACS reagent grade), H_3BO_3 (Acros Organics, ACS reagent grade), Na_2HPO_4 (Acros Organics, extra pure), NaH_2PO_4 (Acros Organics, ACS reagent grade), KI (Acros Organics, ACS reagent grade) and KIO_3 (Acros Organics, ACS reagent grade). Acid solutions were obtained by dilution of H_2SO_4 or $HClO_4$ in distilled water, in some cases adding Na_2SO_4 or $NaClO_4$, whereas pre-mixture solutions were prepared by dissolving KI, KIO_3, NaOH and H_3BO_3 (for borate buffer solutions) or KI, KIO_3, Na_2HPO_4 and NaH_2PO_4 (for phosphate buffer solutions) in distilled water. The concentrations for each experiment set are shown in Table 1.

Table 1 : Experimental concentration sets used for acid solutions and pre-mixture solutions. All concentrations are in mol/L. (*): In experiment sets 16 to 19, $NaClO_4$ was added to the pre-mixture solution

	Acid solution				Pre-mixture solution			
Set	$[H_2SO_4]$	$[HClO_4]$	$[Na_2SO_4]$	$[NaClO_4]$	$[NaH_2BO_3]$ & $[H_3BO_3]$	$[Na_2HPO_4]$ & $[NaH_2PO_4]$	[KI]	$[KIO_3]$
1	0.5	-	-	-	0.1 each	-	0.0116	0.00233
2	0.5	-	-	-	-	0.1 each		
3	-	1	-	-	0.1 each	-		
4	-	0.5	-	-	0.1 each	-		
5	-	1	-	-	-	0.1 each		
6	-	1	0.5	-	0.1 each	-		
7	-	1	0.5	-	-	0.1 each		

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8	-	0.5	-	-	-	0.1 each		
9	0.5	-	-	1	0.1 each	-		
10	0.5	-	-	1	-	0.1 each		
11	-	1	-	0.5	0.1 each	-		
12				1				
13				2.5				
14				4				
15				6.5				
16	-	1	-	0.394 (*)	0.1 each	-		
17				0.904 (*)				
18				1.41 (*)				
19				1.92 (*)				

The different sets of concentrations and species were appropriately chosen to examine the influence of sulphuric acid dissociation and the influence of the buffer at constant ionic strength, which is known to have an important influence of the kinetics of reaction 2.

The di-acid H_2SO_4 was then compared to the monoacid $HClO_4$ to study the partial dissociation of sulphuric acid.

Different sodium salts, Na_2SO_4 and $NaClO_4$, were also tested to study the potential basic behaviour of sulphate. And two buffer systems, NaH_2BO_3 and Na_2HPO_4, were also compared.

Experiments were carried out in a 1L stainless steel standard stirred vessel equipped with two baffles and an inclined blade turbine. Stirring speed was controlled with the aid of a Eurostat 20 Digital (IKA), and temperature was maintained at 25.0°C thanks to a double jacket connected to a Ministat 230 (Huber). An amount of 2 mL of acid solution was injected in the mobile discharge area, at the same height as the turbine and a radial distance of 0.8 times the vessel radius from the shaft. Feed was provided by a peristaltic pump (Masterflex L/S Digital Drive with a Masterflex L/S Easy-Load 3 head pump, Cole-Parmer) through an injection tube with an internal diameter of 1 mm. Absorbance at 353 nm, which can be directly correlated to the concentration in triiodide, was measured by UV-visible spectrophotometry (AvaSpec-ULS2048LTEC-USB2, with an AvaLight DH-S-DUV light source, both by Avantes). Samples were taken 5 minutes after the beginning of the injection.

If the injection flowrate is too high, the injection time will be smaller than the characteristic meso- and/or macromixing times (Bałdyga and Pohorecki, 1995). In that case, the reactions will be affected by meso- and/or macromixing, leading to greater triiodide productions for higher injection flowrates. Therefore, the injection flowrate has been gradually increased (Guichardon and Falk, 2000), without any significant variation of the absorbance (Fig. 1). It can therefore be concluded that mixing is only controlled by the last micromixing step. All the experiments were carried out at an intermediate injection flowrate of 0.040 $mL \cdot s^{-1}$.

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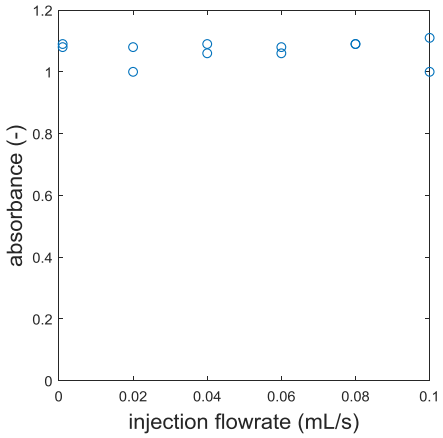


Figure 1: Influence of the injection flowrate on absorbance at 353 nm, for 2 mL of acid. [$HClO_4$] = 1 mol/L; [$H_2BO_3^-$]=0.1 mol/L; [KI]=0.0116 mol/l; [KIO3]=0.0233 mol/l; N=180 rpm

Classical data analysis (Guichardon and Falk, 2000) in the Villermaux-Dushman method includes converting absorption at 353 nm into triiodide concentration by using the molar extinction coefficient at this wavelength, and then determining a segregation index, X_S, and/or micromixedness ratio, α. However, the determination of both X_S and α requires a precise estimation of the proton concentration available in the feed. As it will be seen in section 3.1, sulphuric acid is not fully dissociated when it is injected into the vessel, and the estimation of the proton concentration is not trivial. Hence, only absorbance (which can be directly related to triiodide concentration) will be considered here.

3. Results

3.1. Influence of the acid choice

The influence of the acid solution composition on the triiodide production (and thus, on the absorbance at 353 nm), when using a borate buffer is shown in Fig. 2 (left). In all cases, triiodide production decreases when increasing the stirring speed. As expected, a higher stirring speed increases the rate of energy dissipation and so decreases the micromixing time. Results comparison for concentration sets 1 (0.5 mol/L H_2SO_4) and 3 (1 mol/L $HClO_4$) shows a higher triiodide production for set 3. When comparing experiment sets 1 (0.5 mol/L H_2SO_4) and 4 (0.5 mol/L $HClO_4$), it can be seen that triiodide production is lower for set 4. These results show the occurrence of the second dissociation of sulphuric acid in experiment set, even if it is not complete. They are in agreement with those of Kölbl and Schmidt-Lehr (2010) who were the first to study the influence of the acid choice.

The behaviour of the sulphuric acid solutions can be better understood if we consider that, according to Bałdyga and Bourne (1989), engulfment controls micromixing for moderate viscosities (Sc << 4000). Large blobs of the acid solution are deformed and broken up, becoming long and thin slabs that expand engulfing the vessel fluid (Bałdyga and Pohorecki, 1995). Given the second dissociation constant of the sulphuric acid, pK_a=1.99 (Skoog et al, 1996), the initial composition of these slabs is the following: 0.51 mol/L H^+, 0.49 mol/L HSO_4^-, 0.01 mol/L SO_4^{2-}, at least as a first approximation (the actual pKa value is certainly different at this high electrolyte concentration). As the fluid from the vessel is incorporated, proton concentration decreases through both dilution and consumption (reactions 1 and 2). Thus, pH

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increases, leading to further dissociation of the HSO_4^- anions into protons and finally, further triiodide production.

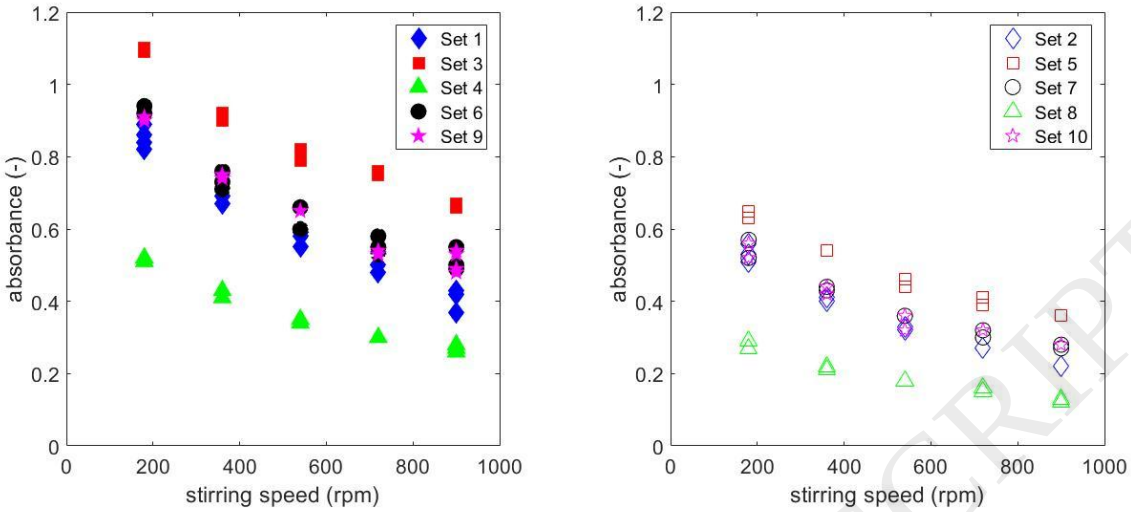


Figure 2: Influence of the stirring speed on absorbance at 353 nm, for different concentration sets using $H_3BO_3/H_2BO_3^-$ (left) or $H_2PO_4^-/HPO_4^{-2}$ (right) as buffer. (The interactive figure is available in the online article)

Let us now compare experiment sets 6 and 9. Both curves closely overlap, showing similar triiodide production. This similar behaviour has been confirmed by using a General Linear Model (Saporta, 2006) described in Appendix B. Given the high p-value of 0.88, the hypothesis that the two curves are actually the same cannot be dismissed. This is consistent with the fact that both experiment sets include the same concentration of each ion, even if they have been introduced in a different way. This means that sulphate anions act as a base in experiment 6, which confirms the observations made by Kölbl et al (2013a).

When comparing experiments 1 and 6, it can be observed that roughly the same amount of triiodide is produced, although slightly lower in experiment 1. This difference is statistically significant, as it can be deduced from the low p-value ($9.4 \cdot 10^{-4}$). Although the initial proton concentrations are the same for both experiment sets (Appendix A), the ionic strengths are different. This seems to indicate a slight influence of the ionic strength, which is confirmed by the comparison of experiments 1 and 9. For both concentration sets, the same acid is at the same concentration, but concentration set 9 includes 1 mol/L of sodium perchlorate. The low p-value ($9.6 \cdot 10^{-5}$) enables us to consider that the difference between both curves is significant.

As Pinot et al (2014) have proposed using a phosphate buffer instead of the borate buffer, the influence of the composition of the acid solution on triiodide production in the case of phosphate buffer use was also studied, and the results are shown in Fig. 2 (right). The trends are the same as when a borate buffer is: triiodide production decreases again when the stirring speed is increased; the hydrogen sulphate dissociation is not complete (experiments 2 and 5), but it is significant (experiments 2 and 8); the triiodide production is the same if the ion concentrations in the solution are the same, no matter how they are introduced (experiments 7 and 10; p-value = 0.65); and finally, sulphate anions have a basic character at low pH values (comparison of experiments 2 vs 10, and 2 vs 7). However, the influence of the ionic strength is not so obvious: experiments 2 and 7 are significantly different (p-value=0.025), whereas experiments 2 and 10 may not (p-value=0.12) Thus, the influence of the ionic strength will be

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further discussed in section 3.2, before considering the influence of the buffer choice in section 3.3.

3.2. Influence of the ionic strength

Comparison between experiments 1 and 9, and experiments 2 and 10, respectively, seems to indicate a slight influence of the ionic strength on triiodide production, with higher ionic strengths leading to slightly higher triiodide productions. To confirm this trend, the ionic strength was modified by adding $NaClO_4$ to the acid solution before injection (Experiments sets 11 to 15), and results are shown in Fig. 3. There is a slight increase in triiodide production for higher ionic strengths. This increase was verified by applying a one-way analysis of variance (ANOVA; Navidi, 2015); the obtained p-value = $2.5 \cdot 10^{-10}$ enables us to confirm that the ionic strength in the acid solution influences the triiodide production. This conclusion opposes that of Kölbl et al (2013a), who did not observe a significant influence of the ionic strength.

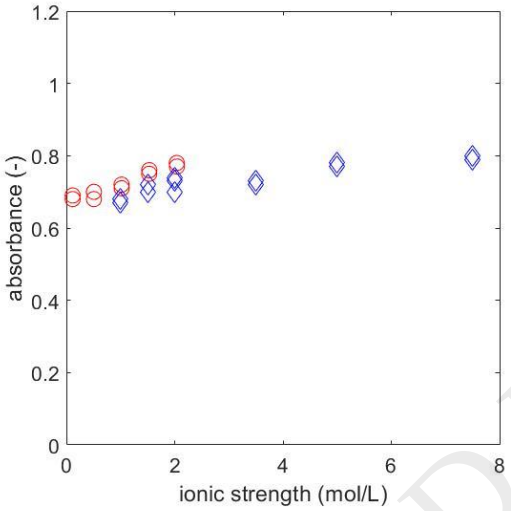


Figure 3: Influence of the ionic strength on absorbance at 353 nm. ◊: Ionic strength change concerns the acid solution; ○: Ionic strength change concerns the pre-mixture solution. (The interactive figure is available in the online article)

When $NaClO_4$ was added to the pre-mixture solution (Experiments sets 16 to 19), a slight increase in triiodide production with increasing ionic strength was again observed. Once again, the one-way ANOVA confirmed this influence of the ionic strength (p-value=$8.3 \cdot 10^{-7}$). This effect was not observed by Kölbl et al (2013a); one possible explanation is that the range of ionic strengths that they tested was narrower than ours.

The influence of the ionic strength might be attributed to two different mechanisms. First, the ionic strength affects the activity coefficients, thus altering both the dissociation constant of the boric acid and the self-ionization constant of the water; therefore, the $H_2BO_3^-$ concentration in the pre-mixture solution might be slightly modified when the ionic strength in this solution is increased. Second, the evolution of the activity coefficients with the ionic strength impacts the Dushman reaction rate, although this influence might be not monotonic (Barton and Wright, 1968). Further comprehension of these mechanisms would thus require a fine modelling of the

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thermodynamics of these solutions and a reliable kinetic law for the Dushman reaction. This will be the purpose of an upcoming paper.

3.3. Influence of the buffer choice

The influence of the buffer choice is shown in Fig. 4. When comparing results for concentration sets 1 and 2, and concentration sets 3 and 5, respectively, it can be seen that triiodide production is significantly higher when a borate buffer is used. This result was actually unexpected since the same buffer concentration was used. Moreover, the $H_2BO_3^-/H_3BO_3$ buffer has a higher pK_a value (9.24, see Table 2); iodine and triiodide are actually thermodynamically unstable in this buffer, although iodine disproportionation is slow enough for the experiments to be free of error (Guichardon and Falk, 2000). On the other hand, $H_2PO_4^-/HPO_4^{2-}$ buffer has a lower pK_a value (7.20, Table 2), which is much closer to the pH^* at which iodine and triiodide are stable (Fournier et al, 1996a). Therefore, iodine and triiodide are much more stable in phosphate buffers, and the difference between both measurements could not be assigned to the thermodynamic stability of iodine.

Table 2: Dissociation constants at 25°C for boric and phosphoric acid (Skoog et al, 1996)

Acid	$pK_{a,1}$	$pK_{a,2}$	$pK_{a,3}$
H_3BO_3	9.24	-	-
H_3PO_4	2.15	7.20	12.35

One explanation might be given by a potential catalytic effect of the buffer. Barton and Wright (1968) observed a catalytic effect of different bases, including HPO_4^{2-} and $H_2PO_4^-$, on the Dushman reaction. Moreover, the catalytic rate constant seemed to follow a Brönsted law, meaning that the catalytic effect should increase when dealing with stronger bases (higher pK_a values). One could then expect a catalytic effect of the $H_2BO_3^-$ anions, stronger than that of the HPO_4^{-2} and $H_2PO_4^-$ anions, since $H_2BO_3^-$ is the strongest base. This would explain the enhanced triiodide production when using borate buffers. However, according to Schmitz (1999), this catalytic effect is owed to a reaction between the base (B^-) and I_2O_2, which is an intermediate species in the Dushman reaction mechanism. This seems unlikely in micromixing experiments, if we consider the mechanism of micromixing (Bałdyga and Pohorecki, 1995): as soon as the base B^- is incorporated in the thin slabs containing the acid solution, the B^- anions are consumed by the neutralization reaction (reaction 1). Thus, the Dushman reaction (reaction 2) can only take place in the case of an excess of protons, when all the B^- has been consumed already. Thus, the catalytic effect of the buffer could probably be neglected in our case.

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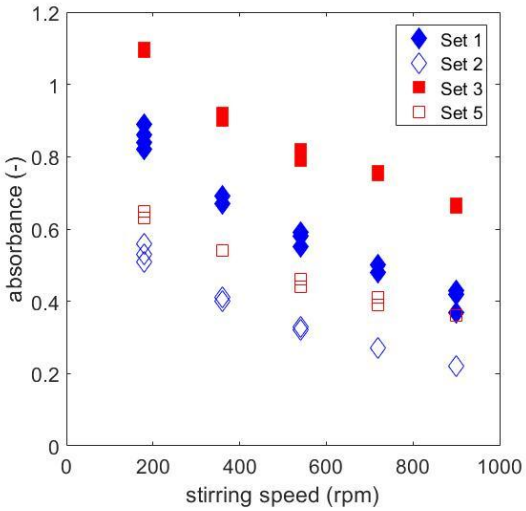


Figure 4: Influence of the buffer choice on absorbance at 353 nm. . (The interactive figure is available in the online article)

Another explanation, which seems to us more likely, is that both $H_2PO_4^-$ and HPO_4^{2-} act as a base. Indeed, when the acid is injected, the local pH is low and smaller than the pK_a for the third dissociation of phosphoric acid (pK_a=2.15, Table 2). Thus, both anions act as a base at the beginning, leading to higher proton consumptions and thus reducing the iodine production (although later, when the pH becomes greater than 2.15 as a consequence of the engulfment, HPO_4^{2-} turns out to be the only base of the system).

4. Discussion

The experiments show that the acid and buffer choice has a great influence on iodine and triiodide production. However, the same trends (decreasing absorbance with increasing stirring speed, i.e., with decreasing micromixing time) are obtained in all cases. Thus, the influence of the acid and buffer choice on triiodide production should not be a criterion of choice when carrying out qualitative studies. Both phosphate and borate buffers could be used, but two considerations should be taken into account. On the one hand, iodine and triiodide are more stable in a phosphate buffer, since its pK_a is closer than the pK_a for borate to the pH^* at which iodine and triiodide are thermodynamically stable. On the other hand, boric acid is reprotoxic. Therefore, a phosphate buffer would probably be a better choice if the Villermaux Dushman method is only used for qualitative studies.

For qualitative purposes, both sulphuric or perchloric acids may be used preferably, since the same trend is obtained for both (Fig. 2). However, it should be pointed out that perchloric acid and perchlorates are oxidants. Their oxidizing power in aqueous solutions is very little at room temperature because of kinetic activation barriers, but they become vigorous oxidants when heated (Greenwood and Earnshaw, 1997). Thus, perchloric acid use in the Villermaux Dushman method should be limited to room temperature, as it could oxidize iodide into iodine and iodine into iodate at higher temperatures.

If the Villermaux Dushman method is used for quantitative purposes (i. e., to estimate the micromixing time), the combination of perchloric acid and borate buffer is probably a more appropriate choice. Indeed, estimating micromixing times needs using a micromixing model (Bałdyga and Bourne, 1989; Villermaux and Falk, 1994; Fournier et al, 1996b; Lemenand et

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al, 2017) and the kinetics of the Dushman reaction. Since sulphuric acid is an incompletely dissociated acid, the micromixing model should take into account its dissociation constant. The same reasoning applies to phosphate buffers: both $H_2PO_4^-$ and HPO_4^{-2} have the role of a base in the first moments, but as long as the acid volume incorporates the vessel solution and pH increases, only $H_2PO_4^-$ will continue to have this role. Therefore, at least the first dissociation constant of phosphoric acid should be considered in the model. This renders the calculations much more complicated. Moreover, the acid solution is quite concentrated (1 mol/L), meaning that the dissociation constants for ideal diluted solutions, which can be easily found in the literature, should not be used. The activity coefficients should be taken into account, rendering calculations even more tedious. A new model taking into account the dissociation constants of the sulphuric and phosphoric acids will be the goal of another paper.

5. Conclusion

The Villermaux-Dushman test for characterising micromixing effects through triiodide production gives qualitatively consistent results, whatever the acid and buffer chosen. In the case of quantitative purposes (micromixing time determination), the precise estimation of the real chemical operating conditions is of prime importance; perchloric acid and borate buffer are probably a wiser choice but a quantitative application also requires reliable kinetics data. The kinetics of the Dushman reaction (reaction 2) obtained by Guichardon et al (2000) is often used in quantitative studies. However, it has been the object of discussions (Bourne, 2008; Kölbl, 2008; Kölbl et al, 2013a, 2013b). Since the strengthening of the Villermaux-Dushman test deserves further investigation into the influence of the acid choice on the kinetics, it will be the main purpose of a next paper.

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Appendix A: Estimation of the proton concentration in solutions containing sulphate and hydrogen sulphate anions

The proton concentration in the sulphuric acid solutions which are being injected can be estimated in the following way (Skoog et al, 1996). First of all, let us consider the case where the injected acid is sulphuric acid. It can be considered as completely dissociated in hydrogen sulphate and protons:

$$H_2SO_4 \rightarrow H^+ + HSO_4^- \qquad \text{(reaction A1)}$$

Hydrogen sulphate can be further dissociated in sulphate anions and protons:

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-} \qquad \text{(reaction A2)}$$

Reaction A2 is actually an equilibrium, with a characteristic equilibrium constant:

$$K_a = \frac{\left[H^+\right]\left[SO_4^{2-}\right]}{\left[HSO_4^-\right]} \qquad \text{(Eq. A1)}$$

The mass balance of each species takes the following form:

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$[HSO_4^-] = c_a - x$ (Eq. A2)

$[SO_4^{2-}] = x$ (Eq. A3)

$[H^+] = c_a + x$ (Eq. A4)

where c_a is the analytical concentration of the sulphuric acid in the solution, and x is the ratio of the extent of reaction to the solution volume. Combining Eqs. A1 to A4, a following quadratic equation is obtained, leading to the final expression of the proton concentration:

$$[H^+] = c_a + \frac{-(c_a + K_a) + \sqrt{(c_a + K_a)^2 + 4K_a c_a}}{2} \quad \text{(Eq. A5)}$$

This solution is independent of a possible presence of perchlorate anions.

When perchloric acid is used, and a sulphate salt is added, the sulphate anions will play the role of a base. In this case, the following mass balances are obtained:

$[SO_4^{2-}] = c_s - x$ (Eq. A6)

$[HSO_4^-] = x$ (Eq. A7)

$[H^+] = c_a' - x$ (Eq. A8)

where c_a' and c_s are the analytical concentrations of the perchloric acid and the sulphate salt. Combining Eqs. A1 and A6 to A8, the following expression for the proton concentration is obtained:

$$[H^+] = c_a' - \frac{(c_s + c_a' + K_a) - \sqrt{(c_s + c_a' + K_a)^2 - 4c_a' c_s}}{2} \quad \text{(Eq. A9)}$$

When comparing experimental sets 1 and 6 (or 2 and 7), it can be seen that $c_a=c_s=c_a'/2$. In this particular case, Eq. A9 reduces to Eq. A5, that is, proton concentration is the same for both experimental sets. The equivalence of the two equations is a consequence of our choice of the acid and salt concentrations, and is independent of the dissociation constant, K_a.

Appendix B: General Linear Model for the comparison of experiments with different concentration sets.

The absorbance is a function of two variables: x_1 (the stirring speed) and x_2, which is a binary variable (for instance, when comparing concentration sets 6 and 9, $x_2=0$ for the former and $x_2=1$ for the latter). If we consider a linear model:

$$y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + e_i \quad \text{(Eq. B1)}$$

where y_i is the absorbance obtained in a given experiment, β_j are the model coefficients and e_i is the error in experiment i.

The following vectors and matrix are defined:

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$$\mathbf{y} = \begin{pmatrix} y_1 & \dots & y_n \end{pmatrix} \quad \text{(Eq. B2)}$$

$$\boldsymbol{\beta} = \begin{pmatrix} \beta_0 & \beta_1 & \beta_2 \end{pmatrix} \quad \text{(Eq. B3)}$$

$$\mathbf{e} = \begin{pmatrix} e_1 & \dots & e_n \end{pmatrix} \quad \text{(Eq. B4)}$$

$$\mathbf{X} = \begin{pmatrix} 1 & x_{1,1} & x_{1,2} \\ \dots & & \\ 1 & x_{n,1} & x_{n,2} \end{pmatrix} \quad \text{(Eq. B5)}$$

where $x_{i,j}$ is the value of the variable x_j in experiment i. Thus, all the n experiments can be summarised in the following equation:

$$\mathbf{y} = \mathbf{X}\boldsymbol{\beta} + \mathbf{e} \quad \text{(Eq. B6)}$$

According to Saporta (2006), the vector

$$\mathbf{b} = (\mathbf{X}'\,\mathbf{X})^{-1}\mathbf{X}'\,\mathbf{y} = \begin{pmatrix} b_0 & b_1 & b_2 \end{pmatrix} \quad \text{(Eq. B7)}$$

can be used as an estimator of β.

If there is not any influence of the concentration set on the absorbance, then $\beta_2=0$ and the statistic

$$t_{n-3} = \frac{b_2}{\sqrt{\frac{\|\mathbf{y}-\mathbf{X}\mathbf{b}\|^2}{n-3}\left[(\mathbf{X}'\,\mathbf{X})^{-1}_{33}\right]}} \quad \text{(Eq. B8)}$$

follows a Student's t distribution with n-3 freedom degrees.

Thus, the p-value can be evaluated as

$$\text{p}-\text{value} = 2\cdot\int_{t_{n-3}}^{\infty} t(z)dz \quad \text{(Eq. B9)}$$

where t(z) is the probability density function of a Student's t distribution.

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