

Iodine and Disinfection: Theoretical Study on Mode of Action, Efficiency, Stability, and Analytical Aspects in the Aqueous System

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Summary

Although they have been in use for nearly 170 years, the mode of action of iodine-based disinfectants is not yet clearly understood, as is manifested, for example, in diverging judgements about the relevance of the individual iodine species. Although studies based on calculated equilibrium concentrations in pure iodine solutions have already been done, there is a lack of knowledge about iodine solutions in the presence of additional iodide which would be of intrinsic importance for disinfection practice. Therefore, a re-calculation was undertaken considering variations of this parameter in the pH range 0–14. The presented calculations concern fresh iodine solutions not affected by disproportionation (iodate formation) and provide information about the equilibrium concentrations of the species I^- , I_2 , I_3^- , I_5^- , I_6^{2-} , HOI , OI^- , HI_2O^+ , IO_2^- , and H_2OI^+ . Additional iodide and the pH value have a very pronounced influence on the individual equilibrium concentrations (several powers of ten); hence, conditions can be indicated where the number of species of virtual importance is drastically reduced. In the most common case with iodine in the presence of additional iodide at pH < 6, only I^- , I_2 , and I_3^- play a role. In the absence of additional iodide, at pH 8–9 and at high dilution ($c(I_2) < 10^{-5}$ M), on the other hand, HOI accounts for over 90% of the oxidation capacity. At high iodide concentration (e.g. Lugol's solution) the species I_5^- and I_6^{2-} make up 8.2% of the oxidation capacity. The iodine cation H_2OI^+ , frequently quoted as an active agent in disinfection, is without any relevance under the conditions occurring in practice, as are IO_2^- and HI_2O^+ which become important only at pH > 10. The stability problem (i.e. rate of iodate formation) arising at pH > 6 can be reduced to hypoiodous acid, as manifested in the simple rate law $d[IO_3^-]/dt = 0.25[HOI]^3/[H^+]$ which allows an estimation of stability under weakly alkaline conditions. The results of this study allow us to deduce general qualities of aqueous iodine solutions, such as reactivity, stability, and analytical aspects, and to estimate major disinfection-orientated properties such as microbicidal activity, irritation, and incorporation effects. Though the calculations consider primarily preparations devoid of polymeric organic compounds capable of complexing iodine species, the results can be largely transferred to iodophoric preparations.

Introduction

One of the oldest and, even nowadays, most important applications of iodine in aqueous solution is its use for disinfection [1]. A reliable understanding of the interactions of a rather complicated system like iodine in water with the material to be disinfected (e.g. innate surfaces, living tissue, blood products) is essentially based on knowledge of the

exact equilibrium concentrations of the reacting iodine species. An exhaustive insight in the trends caused by changing the most important parameters of influence, viz. total iodine, pH, and (additional) total iodide, requires a vast number of analytical data, which can easily be calculated. An experimental approach would require immense labour, quite apart from the fact that no analytical methods are available for some species [2]. Fortunately, the equilibria in aqueous solution have been well studied, with important contributions focussing on the fate of radio-iodine species known to emerge in the course of nuclear accidents having been published in the last 20 years [3].

However, there are two kinds of preparations based on aqueous iodine, i.e. (a) without and (b) with the presence of organic compounds capable of complexing iodine species. The second group includes the iodophores (polyvinyl-pyrrolidone, polysaccharides) but also polymeric additives (alcohols, esters) which act as skin cosmetics. Because no quantitative data concerning their interactions with iodine species are available such calculations are restricted to iodine solutions without complexing polymers.

Among contributions hitherto made on this topic, two deal with the sole influence of pH on the distribution of iodine species. They concern pure iodine solutions (without additional iodide) as used in drinking water disinfection.

One shows the effect of pH on 10^{-6} M iodine (0.25 ppm) regarding the species I^- , I_2 , I_3^- , HOI , OI^- , H_2OI^+ , and IO_3^- [4], while the other concerns solutions with 1–300 ppm iodine

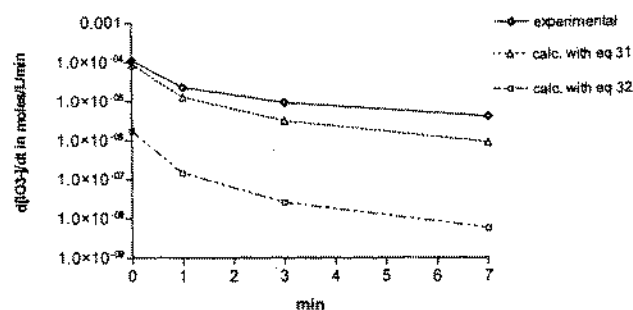


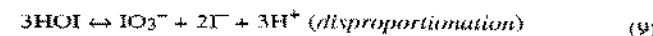
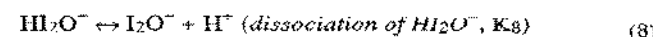
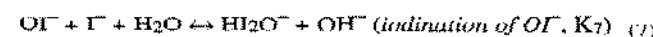
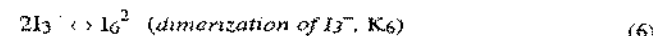
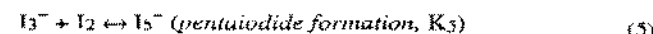
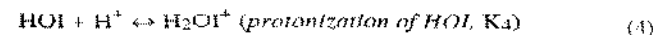
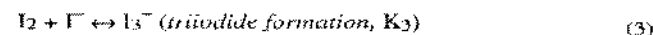
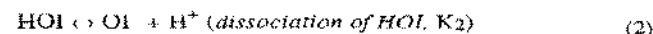
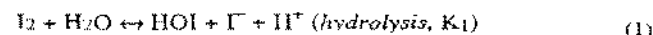
Figure 1. Calculated and experimentally determined rate of iodate formation in an aqueous iodine solution (1.305×10^{-3} mol L $^{-1}$) at pH 7.6. Using the data of the disproportionation experiment described in ref. [2] the rate of iodate formation or the loss of $c(I_2)$ at defined time points was both calculated with eq. (31) and eq. (32), respectively, and graphically derived from the temporal decrease of $c(I_2)$ with $d[IO_3^-]/dt = 1/3 \tan \alpha$ of the tangent of the $c(I_2)/t$ curve (shown in Figure 3 [2]) at these points.

comprising in addition also the species HIO_3 , HI_2O^- , and $\text{I}_2\text{O}_2^{2-}$ [5].

Of greater practical relevance are calculations which also consider additional iodide which, on the one hand, is a major component of most iodine preparations because it has – besides pH – a great influence on the distribution of the species and on stability. On the other hand, iodine-based disinfecting solutions (without additional iodide) which are partly reduced can be calculated like solutions of iodine and iodide.

A rough survey of the influence of pH and iodide on the equilibrium concentrations in aqueous iodine has already been published [1]. However, these calculations judged only the species I_2 , HOI , OI^- , I_3^- , and I^- . Therefore, to acquire a more accurate insight concerning aqueous iodine, a re-calculation of the equilibrium concentrations in aqueous solution regarding additional iodide and pH was done. In addition, the literature contains inconsistent statements on the relevance of the different species for the disinfecting process, mainly concerning hypoiodous acid and iodine cation (HOI , H_2OI^+), which needs to be clarified.

For the system iodine/water nine different equilibria are specified [3] which are producing at least 10 iodine species:



In contrast to the very fast reactions described by eq. (1)–(8), disproportionation to iodate (eq. (9)) proceeds rather slowly. Including iodate in the calculation routine, therefore, would need to consider also the parameter time. This has already been done only for the equilibria eq. (1)–(3) and eq. (9), and where it was found that the rate of iodate formation changes considerably with the prevailing conditions, mainly pH and $c(\text{I}^-)$ [6].

The present calculation, therefore, does not consider iodate formation (eq. (9)), which implies that the calculated values concern initial equilibrium concentrations comprising the species I^- , I_2 , I_3^- , I_5^- , I_6^{2-} , HOI , OI^- , HI_2O^- , I_2O^- , and H_2OI^+ .

Results

To demonstrate the main properties of aqueous iodine solutions and their variation by modifying $c(\text{I}_2)$, $c(\text{I}^-)$, and pH, the equilibrium concentrations were calculated for (1) iodine solutions (10^{-3} – 10^{-6} M) without any additional iodide, (2) 0.001 M iodine in presence of additional iodide, and (3) Lugol's solution (USP XXI, aqueous solution of 5% iodine and 10% KI) and its dilutions. Although in practice strongly acidic and strongly alkaline conditions are of little relevance, the calculations were done in the range pH 0–14 which helps to illustrate the trends caused by pH variation. In order to obtain less complicated graphs equilibrium concentrations of iodide are not shown in Figure 2 and 3.

Iodine without Iodide (Figures 2a–d)

A remarkable feature of pure iodine solutions is the decrease of the number of species which contribute to 99% of oxidation capacity with dilution. At $c(\text{I}_2) = 0.001$ (Figure 2a) there are five species, I_2 , HOI , I_3^- , HI_2O^- , and OI^- , while at $c(\text{I}_2) < 10^{-3}$ (Figure 2c,d) only I_2 , HOI , and OI^- are of importance. Another characteristic concerns the species showing maxima which is the case with HOI , I_3^- , HI_2O^- , I_5^- , and I_6^{2-} , while I_2 , H_2OI^+ , and OI^- are either decreasing or increasing. The maxima lie between pH 8 and pH 10 at $c(\text{I}_2) = 10^{-3}$ M and are broadened at higher dilution.

Influence of Iodide (Figures 3a–d)

The addition of iodide to 0.001 M iodine brings about a drastic change of the shape of the curves. The most important features are: (1) $[\text{I}_2]$, HOI , and H_2OI^+ are diminished and I_3^- , I_5^- and I_6^{2-} are increased, which applies also to the maximum of HI_2O^- . In the pH range 0–7 the amount of bactericidally active free iodine ($= [\text{I}_2] + [\text{HOI}]$) decreases from 254.245 ppm (no iodide) to 170 ppm (0.001 M I^-), 33.3 ppm (0.01 M I^-), and 3.4 ppm (0.1 M I^-). In the same order also the portion of HOI (at pH 7) decreases from 9.2 to 0.82, 0.06, and 0.007%. (2) The pH range where I_2 , I_3^- , I_5^- , and I_6^{2-} are constant is extended from pH 7 to pH 10 when $c(\text{I}^-)$ increases from 0.001 to 0.1 M.

Lugol's Solution and Its Dilutions (Figures 4a–c)

The influence of dilution manifests in two ways, the relative distribution of the species and the pH range where the concentration of the oxidizing species I_2 , I_3^- , I_5^- , I_6^{2-} does not change. In undiluted Lugol the order of these species is $[\text{I}_3^-] > [\text{I}_6^{2-}] > [\text{I}_5^-] > [\text{I}_2]$ and remain constant up to pH 10. In a 1:100 dilution the order is $[\text{I}_3^-] > [\text{I}_2] > [\text{I}_5^-] > [\text{I}_6^{2-}]$ and remains the same up to pH 8 while at a 1:10000 dilution the order is $[\text{I}_2] > [\text{I}_3^-] > [\text{I}_5^-] > [\text{I}_6^{2-}]$ which remains unchanged only up to pH 6. These pH limits apply also, in reverse manner, to HOI and its derivatives OI^- and HI_2O^- which become important only under conditions exceeding these pH values. Their relation also changes, with HI_2O^- dominating in undiluted Lugol, while at 1:10000 dilution it is HOI .

In the pH range 0–7 the amount of bactericidally active free iodine ($= [\text{I}_2] + [\text{HOI}]$) decreases from 155.6 ppm (undiluted), to 116.4 ppm (1:100) and 4.7 ppm (1:10000), respectively.

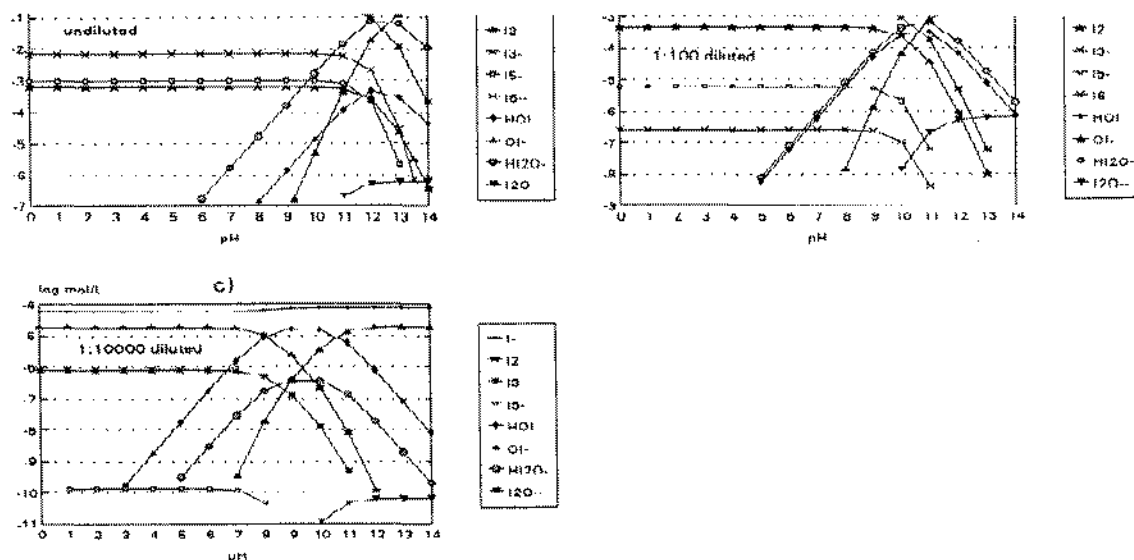


Figure 4. Calculated equilibrium concentrations in Lugol's solution and its dilutions. a) undiluted, b) 1:100 c) 1:10000

Estimated Stabilities

It can be deduced from Figure 5a that the stability of iodine solutions expressed by the rate of decrease of oxidation capacity decreases with pH and increases with dilution. Up to pH 6 the system iodine/water can be considered as completely stable. Figure 5b shows the effect of additional iodide on a 10^{-3} M iodine solution which manifests itself in a shift of the stability curves to higher pH values. Since the curves have the same shape, one can discern that in the case of a 0.001 M iodine solution the pH which is characteristic for a defined stability (rate of iodate formation or loss of oxidation capacity) is increased by 0.1, 0.7, 2.0, and 3.6 units in the presence of 0.0001, 0.001, 0.01, and 0.1 M iodide. With other words, a high iodide level ensures stability also in an alkaline medium (pH < 10).

Discussion

Comparison with Previous Calculations

The already published algorithm^[7] which considers only I₂, I₃⁻, HOI, and OI⁻ delivers sufficiently precise equilibrium concentrations at moderate iodide concentrations and at pH < 8, where the other iodine species occur only at negligible concentrations. For other conditions the new comprehensive algorithm should be used which, however, needs a more sophisticated calculational effort. E.g., at high iodide and iodine concentration, as is the case in Lugol's solution, I₅⁻ and I₆⁻ become important. Up to pH 10 their molar fraction amounts to 3.6% and 0.5% which equals 8.2% of total iodine.

Compared with the previous calculation^[7] this results in a decrease of [I₂] and [I₃⁻]. The correct value for the equilibrium concentration of molecular iodine and triiodide at pH ≤ 8, therefore, is 155.6 ppm and 0.1803 mol L⁻¹ instead of 169.7 ppm and 0.1963 mol L⁻¹ as calculated previously^[7]. Consideration of the species HI₂O⁺ becomes important in the alkaline region where it can amount to ≈42 % of total iodine (Figure 4a, pH 12). The iodine cation H₂OI⁺, on the other hand, is of slight importance only in very acid solutions (see below). For both species the new algorithm is the first approach to estimate their equilibrium concentration.

Conditions for Evaluating Specific Reactivities

On studying disinfection processes, the question arises as to which species play a role in the killing reaction. An unambiguous answer is possible concerning those species which can be investigated in the absence of other iodine species as pure and isolated substances. This is the case only with iodide and iodate which, however, are reported to have no bactericidal power^[8]. Such clear statements are not possible for the other species because the various equilibria mean that they never exist alone.

The calculations presented, however, allow us to answer the quoted questions at least in part. Presuming that a species can be ignored which is present at a level of < 1% of the one with the highest concentration, one can specify pH ranges where virtually only one species prevails and is therefore responsible for a special reaction (e.g. substitution of covalent hydrogen by iodine). However, this concept implies the assumption of similar reactivities of the predominant iodine species and

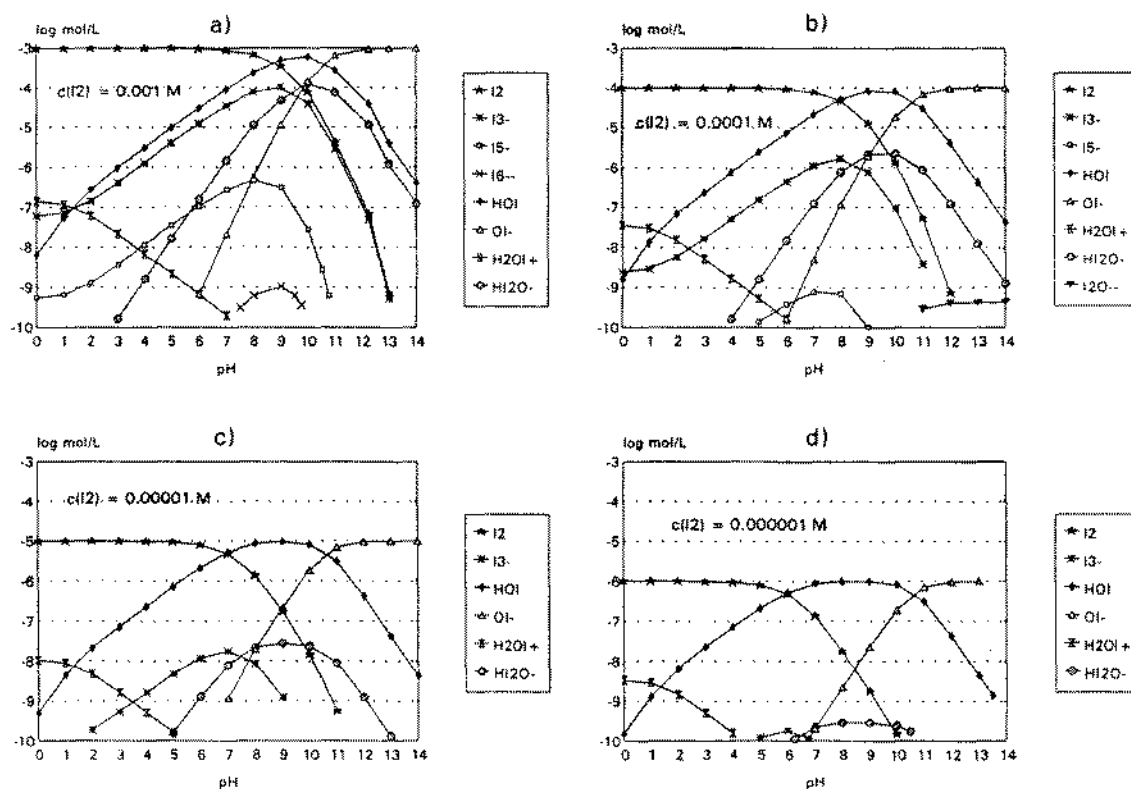


Figure 2. Calculated equilibrium concentrations in aqueous iodine solutions without additional iodide. a) $c(I_2) = 10^{-3}$ mol L⁻¹, b) $c(I_2) = 10^{-4}$ mol L⁻¹, c) $c(I_2) = 10^{-5}$ mol L⁻¹, d) $c(I_2) = 10^{-6}$ mol L⁻¹.

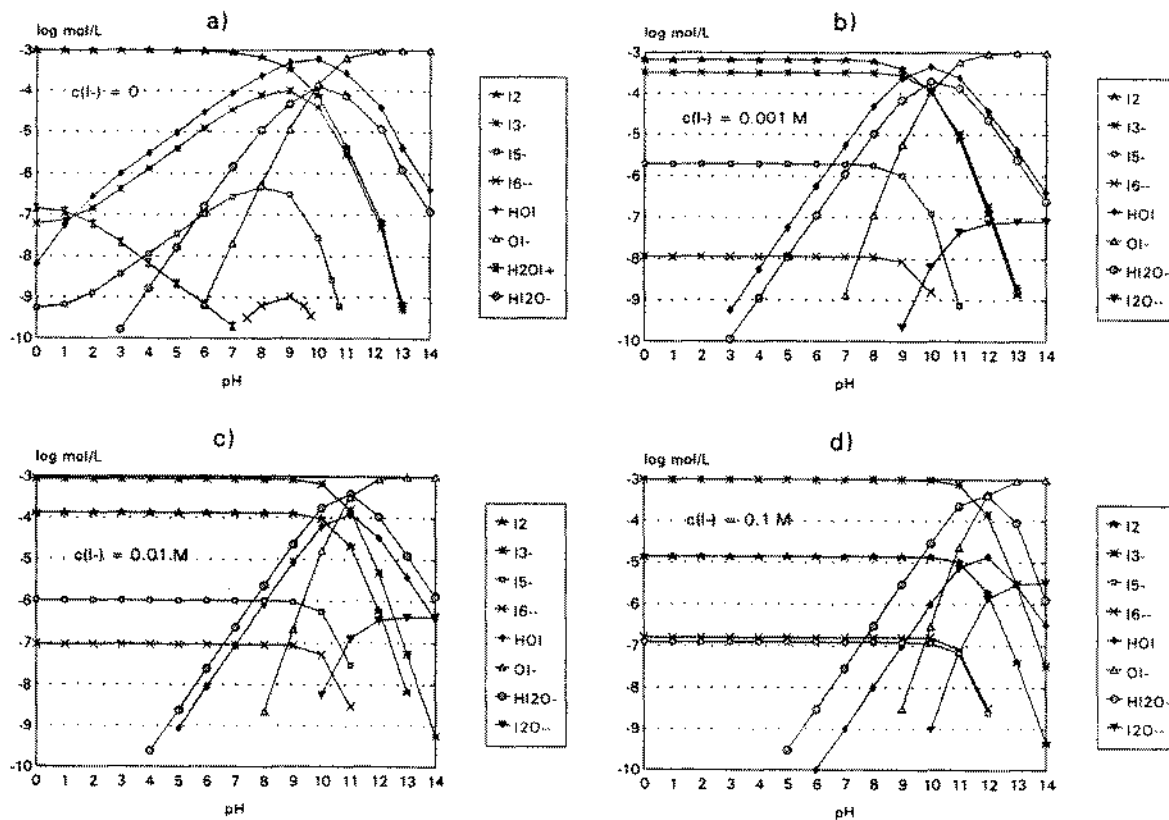


Figure 3. Calculated equilibrium concentrations in aqueous 10^{-3} mol L⁻¹ iodine solutions in presence of additional iodide. a) No additional iodide, b) $c(I^-) = 10^{-3}$ mol L⁻¹, c) $c(I^-) = 10^{-2}$ mol L⁻¹, d) $c(I^-) = 10^{-1}$ mol L⁻¹.

$$d[\text{IO}_3^-]/dt = 0.25 \times [\text{HOI}]^3/[\text{H}^+] \quad (11)$$

The Iodine Cation, H_2OI^+

Many publications assign some relevance to this species as being responsible for disinfection, which can be traced back to a comprehensive and very often cited study dealing with the halogens in disinfection^[11]. The present calculations show that the iodine cation, if at all, is of importance only under very acidic conditions ($\text{pH} < 1$) and in the total absence of additional iodide, where it amounts at most to only = 0.3% of total iodine at high dilution (Figure 2d). Under conditions used in practice, i.e. in the presence of iodide (to regulate the concentration of free molecular iodine and improving stability), however, *the iodine cation is virtually absent* and therefore of no importance. For example, a solution with $c(\text{I}_2) = 0.001$ and $c(\text{I}^-) = 0.01 \text{ mol L}^{-1}$ generates $[\text{I}_2] = 1.31 \times 10^{-4} \text{ mol L}^{-1}$ or 33.3 ppm at $\text{pH} 0-8$ (Figure 3c). The concentration of the iodine cation, however, comes to $[\text{H}_2\text{OI}^+] = 2.15 \times 10^{-13} \text{ mol L}^{-1}$ (not shown in Figure 3c) which is *about 9 powers of ten less than $[\text{I}_2]$* . Even if one attributes a higher reactivity to the iodine cation, which is deemed to play an important role in certain substitutions^[11], this can hardly explain any real contribution to the disinfecting process.

Comparison of Reactivities in View of Killing Microorganisms

A frequently quoted issue is the contribution of free molecular iodine, I_2 , and hypiodous acid, HOI, to disinfection processes and differences in their bactericidal power^[11]. As set forth above, a solution containing predominantly I_2 needs a $\text{pH} < 5$ while in the case of HOI it is $\text{pH} = 8.4$. A comparison of the killing effect of I_2 and HOI would presuppose that the susceptibility of bacteria for the interaction with these iodine species is the same in both pH ranges which can be deemed a coarse simplification. Therefore, a definite differentiation of both species probably will not be feasible.

Analytical Consequences

The presented calculations of equilibrium concentrations are based on a knowledge of the parameters total iodine, $c(\text{I}_2)$, total iodide, $c(\text{I}^-)$, and pH . While pH and $c(\text{I}_2)$ can easily be assessed (glass-electrode and iodometric titration), total iodide is not generally known and a calculation is therefore impossible. As a rule, the solution has to be analysed at which the choice of the method depends on the conditions: In the presence of iodide and $\text{pH} < 7$ a method which detects only I_2 , I^- , and I_3^- will be of sufficient precision because the other species can be neglected (except in very high iodide and iodine concentration as in Lugol's solution, see above). In other words, in this case only the triiodide equilibrium (eq. (3)) is of relevance, which is not influenced by pH . A sufficiently precise evaluation, therefore, can be based on the sole determination of $[\text{I}_2]$ (e.g. potentiometrically^[12] or by dialysis^[13]) and $[\text{I}^-]$ (iodide electrode) while triiodide is calculated from both.

From these assertions it can be deduced that in stable iodine solutions, i.e. in the presence of additional iodide ($\geq 10^{-3} \text{ M}$) and at $\text{pH} < 7$, which effects virtual absence of HOI, and the other species derived therefrom (OI^- , HI_2O^- , I_2O^{2-} , H_2OI^+),

measurement of pH is not needed for analysis. However, if the prevailing conditions allow the formation of measurable HOI then measurement of pH is indispensable and redox-potentiometric methods^[2,14] can be recommended.

Conclusions for Iodophoric Preparations

The already quoted interactions of organic polymeric compounds (povidone, polysaccharides) with iodine species can be described with eq. (12)–(14)^[15].



However, because no quantitative data (mass law constants) are available an exact calculation for iodophoric preparations is not feasible.

In spite of this, qualitative investigations on the interactions with the iodophoric molecule polyvinylpyrrolidone^[16] reveal that K_{I^-} is much less than K_{I_2} or $K_{\text{I}_3^-}$. Considering the normal conditions of use, i.e. presence of appreciable iodide and $\text{pH} < 7$, this has the following consequences:

- (1) HOI and the species derived from (OI^- , HI_2O^- , I_2O^{2-} , and H_2OI^+) can be neglected.
- (2) Since the reactions eq. (12)–(14) reduce the equilibrium concentrations of I_2 , I_3^- , and to a certain degree also of I^- the species I_5^- , I_6^{2-} can be ignored too.

Therefore, for iodophoric preparations only the triiodide equilibrium (eq. (3)) and the interactions of the iodophoric molecules with I_2 , I_3^- and I^- (eq. (12)–(14)) are of importance.

Because HOI is virtually not present stability problems concern only interactions with oxidable components but not the disproportionation to iodate.

Acknowledgement

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Experimental

Definition of mass balances: Regarding the equilibria eq. (1)–(8) the parameter $c(\text{I}_2)$ can be defined by eq. (15):

$$c(\text{I}_2) = [\text{I}_2] + [\text{I}_3^-] + 2[\text{I}_5^-] + 2[\text{I}_6^{2-}] + [\text{HOI}] + [\text{OI}^-] + [\text{HI}_2\text{O}^-] + [\text{I}_2\text{O}^{2-}] + [\text{H}_2\text{OI}^+] \quad (15)$$

$$\text{The total of iodine atoms then comes to} \\ c(\text{I}_{\text{atoms}}) = [\text{I}^-] + 2[\text{I}_2] + 3[\text{I}_3^-] + 5[\text{I}_5^-] + 6[\text{I}_6^{2-}] + [\text{HOI}] + [\text{OI}^-] + 2[\text{HI}_2\text{O}^-] + 2[\text{I}_2\text{O}^{2-}] + [\text{H}_2\text{OI}^+] \quad (16)$$

For a solution made from elemental iodine (I_2) and iodide (e.g. KI) also eq. (17) can be defined.

$$c(\text{I}_{\text{atoms}}) = 2c(\text{I}_2) + c(\text{I}^-) \quad (17)$$

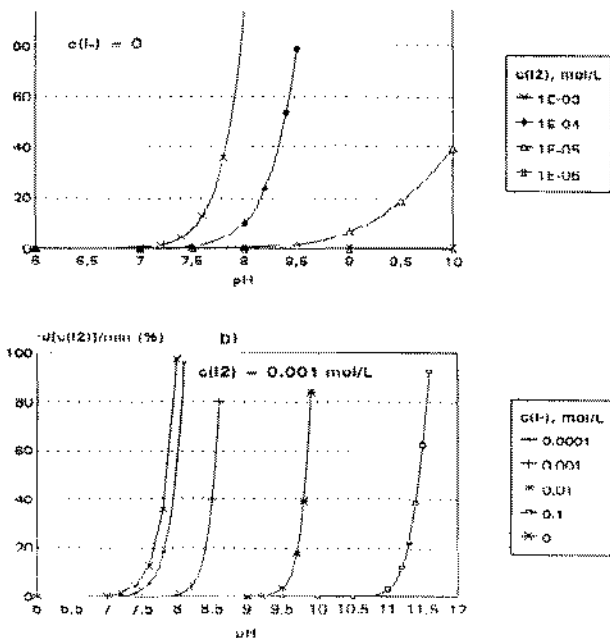


Figure 5. Initial rates of iodate formation expressed as loss (in %) of initial oxidation capacity. a) $c(I_2) = 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6} \text{ mol L}^{-1}$; no additional iodide. b) $c(I_2) = 10^{-3} \text{ mol L}^{-1}$, $c(I^-) = 0, 10^{-3}, 10^{-2}, 10^{-1} \text{ mol L}^{-1}$. From the curves can be settled that, e.g., in a $10^{-4} \text{ mol L}^{-1}$ iodine solution at pH 8 the initial rate of loss of oxidation capacity amounts $\approx 10\%$ of the initial concentration per min.

those occurring at negligible concentrations in the case of a given reaction. In other words, in a substitution reaction such as



the kinetics of these reactions should be similar, i.e.

$$-d[I_2]/dt \sim -d[HOI]/dt \sim -d[H_2OI^+]/dt,$$

in order to make reliable differentiations. However, since such kinetic parameters are not generally available, a clear differentiation with regard to reactivity will be speculative.

Conditions with only I_2 or HOI

For molecular iodine this is the case under acidic conditions in the absence of additional iodide. In a 0.001 M solution it is $pH \leq 5$ which decreases with dilution to $pH \leq 2.3$ in 10^{-6} M (Figures 2a-d).

readily be deduced from eq. (1). As Figure 2b-d shows, there exists only a very small pH range where HOI dominates, i.e. at $pH = 9.3, \approx 9.0,$ and ≈ 8.4 for $10^{-4}, 10^{-5},$ and $10^{-6} \text{ mol L}^{-1}$, respectively. Since unavoidable stability problems arise at these pH values (see Figure 3a) one is forced, when investigating the properties of HOI in detail, to conduct these experiments at low concentrations ($c(I_2) < 10^{-5} \text{ mol L}^{-1}$). At pH 8.3-8.5 HOI amounts $\approx 99\%$ of the total oxidation capacity in a 10^{-6} M iodine solution. Only under this highly diluted condition is a compromise between high portion of HOI and sufficient stability (see Figure 3a) fulfilled.

pH Ranges with Constant Reactivity

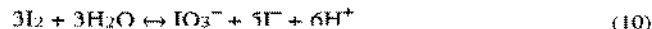
In contrast to chlorine-based disinfectants, which are very sensitive to pH changes [9], there are pH ranges in the iodine/water system where the pH does not influence the equilibrium concentrations of the predominant species. This is the case in the presence of additional iodide, as can be deduced from Figure 3a-d. In 0.001 M iodine solution, adding 0.001, 0.01, or 0.1 M iodide extends the region with a constant concentration of molecular iodine (and therefore also constant reactivity) from pH 5 to pH 7, 8, or 9, respectively. This iodide-effect is still more pronounced in undiluted Lugol's solution where it reaches up to pH 10.

Regulating Microbicidal Activity

There is general agreement that free molecular iodine is the real active iodine species which is based on the frequently observed positive correlation between $[I_2]$ and the rate of microbial kill [11]. Furthermore, it is an important parameter for toxicity related features like skin irritation and incorporation effects [11] while staining of biological material is attributed to $[I_3^-]$ [10]. Knowledge of $[I_2]$ and $[I_3^-]$, therefore, allows us to make predictions concerning these items. On the other hand, using calculated equilibrium concentrations, it is possible to tailor an aqueous iodine-based disinfectant by addition of iodide for a special task, e.g. a low or high level of I_2 .

Iodate Formation and Stability

The disproportionation of aqueous iodine to form iodate causes a decrease of oxidation capacity effective at biological pH ($pH 5-8$) and which comprises all species with the oxidation number 0 to +1. It is usually described by eq. (10) which is a combination of eq. (1) and (8).



Since the oxidizing properties of iodate become apparent only at acidic pH (in form of HIO_3 , $pK_a = 0.77$) it is of no practical relevance. A knowledge of the conditions under which aqueous iodine is stable (i.e. negligible iodate formation), therefore, is obligatory. This can easily be settled using eq. (11) which is derived from eq. (31) and the mass law expression for eq. (1). It reveals the relevance of HOI and pH for the kinetics of iodate formation and stability.

From eq. (15) (17) follows for the concentration of (additional) iodate eq. (18):

$$c(\Gamma) = [\Gamma] + [I_3^-] + [IO_3^-] + 2[I_6^{2-}] - [HOI] - [OI^-] - [H_2OI^+]$$
 (18)

Development of the algorithm: Using the symbols

$C = c(I_2) = c(I_2^{(2)} \dots I_2^{(1)})$, $D = c(F)$, $x = [I_2]$, $y = [I^-]$, $z = [I_3^-]$, $p = [HOI]$, $r = [F^-]$, $s = [I_5^-]$, $t = [I_6^{2-}]$, $k = [H_2OI^+]$, $q = [HF_2O^-]$, $j = [F_2O^{2-}]$, $H =$ proton activity, $f_a =$ activity coefficient of the single charged species, $f_s =$ activity coefficient of I_6^{2-} and I_2O^{2-} , the following set of ten equations (eq. (19)–(28)) with ten unknowns ($x, y, z, s, t, p, r, q, j$, and k) can be established:

$$C = x + z + p + r + 2s + 2t + q + j + k$$
 (19)

$$D = y + z + s + 2t - p - r - k$$
 (20)

$$K_1 = ypf/f_a/x$$
 (21)

$$K_2 = rH/f_p$$
 (22)

$$K_3 = z/y$$
 (23)

$$K_4 = z/f_s$$
 (24)

$$K_5 = s/y$$
 (25)

$$K_6 = tf_j/z^2 f_s^2$$
 (26)

$$K_7 = q/rH$$
 (27)

$$K_8 = j/f_j q f_s H$$
 (28)

where eq. (19) and (20) are mass balances, and eq. (21)–(28) the mass-law expressions for eq. (1)–(8).

The equations (19)–(28) can be transformed to the polynomial of eq. (29):

$$F_1(y) - F_2(y)$$
 (29)

where

$$F_1(y) = x(C - y)$$

$$F_2(y) = x(K_3 y^2 + B + Qy) + 2x^2 y^2 (N + Py)$$

$$x_{1,2} = \frac{-(K_3 y^2 + B)/(2(2Py^2 + Ny^2)) \pm \{[-(K_3 y^2 + B)/(2(2Py^2 + Ny^2))]^2 - (y^2 - D_3)/(2Py^2 + Ny^2)\}^{0.5}}{2(2Py^2 + Ny^2)}$$

$$B = K_1(1/H + K_2/H^2 + K_4), O = K_1 K_7 K_8 (1 + K_8/H)/H, N = K_5 K_6, P = K_5^2 K_6,$$

$$K_1 = 5.44 \times 10^{-13} [17], K_2 = 2.5 \times 10^{11} [118], K_3 = 723 [19],$$

$$K_4 = 22.2 [27], K_5 = 9, K_6 = 0.1 [21], \text{ and } K_7 = 1.3 \times 10^{13} [18].$$

The root of eq. (29), i.e. y or $[X^-]$, respectively, was found by iteration between the boundaries $0 < y < 2C+D$ and also delivers x or $[I_2]$, respectively. The other components were found with

$$p = K_1(x/y)H, r = pK_2/H, z = K_3x, s = K_5x, t = K_6z^2 f_s^2 / f_a, q = K_7 r / f_a,$$

$$j = K_8 q f_s H / f_a, k = K_8 p H / f_a.$$

The calculation of the activity coefficient is merged in the same iteration process using eq. (30) which is valid for 25 °C [21].

$$\log f_a = 0.509e^2 f^{0.5} / (1 + 0.328df^{0.5})$$
 (30)

$e =$ charge of the iodine species

$$J = y + z + r + k + s + 3t + 3j + J_{add}$$

As an approximation, $d = 3$ which is valid for Γ^- was also taken for the other univalent species, while $d = 4$ was taken for I_6^{2-} and F_2O^{2-} . Therefore $f_y = f_z = f_r = f_k = f_s = f_q = f_j$ which agrees with the previously published approach [21]. The activity coefficients of the non-charged species x and p were assumed to be unity. J_{add} refers to additional ionic strength coming from buffers or other ionic compounds not interfering with the equilibria of eq. (1)–(8).

Estimating Stability: The kinetics of the disproportionation described with eq. (10) is very complex and, though investigated nearly a century, is still not known clearly [23]. The presented approaches discuss the participation of HOI [24] and, at higher pH also HOI_2^- and OF^- [25].

However, for weakly alkaline conditions the rate law eq. (31), which was derived from the basic research of Abel and Hiltferding [26], proved to be a useful tool for estimating stability based on reaction times which were gained by a purely analytical calculation [6].

$$d[I_2]_0 / dt = 4 \times 10^{-28} [I_2]^3 / [\Gamma^-]^3 [H^+]^4$$
 (31)

Since this study considered only the equilibria (1)–(3) a recalculation based on the equilibria (1)–(8) was performed. However, considering the rather complicated algorithm eq. (29) in this case an iterative procedure was used to calculate reaction rates. As shown in Figure 1, there is a satisfactory correspondence between measured rates and those calculated with eq. (31) which, however, is not the case using rate law eq. (32) as reported by Bell and Gelles [26].

$$d[IO_3^-] / dt = 8 \times 10^{-44} [I_2]^3 / [\Gamma^-]^4 [H^+]^4$$
 (32)

The rates of iodate formation calculated with eq. (31) are shown in Figures 5a and b. To indicate the influence of pH on stability the results are presented as the rate of decrease of $c(I_2)$, which was calculated from

$$-d[c(I_2)] / dt = 1/3 \times d[IO_3^-] / dt.$$

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