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Modeling drinking water chlorination at the breakpoint: I. Derivation of breakpoint reactions

Khadidja Driss*, Mohammed Bouhelassa

Faculty of Pharmaceutical Processes Engineering, LIPE Laboratory, Constantine 3 University, Algeria
Email: Idrisskhadija@hotmail.fr

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ABSTRACT

From a bibliographic synthesis on the reactions that can occur during breakpoint chlorination. We carry out the stability study of produced entities under the applied conditions in the potable water production, where the pH range 6.5–8.5, and the initial weight ratio Cl/N including in 10/1–15/1 at ambient temperature. The choice of dominant species and reactions that have been taken into account must be based on data of the thermodynamics and the kinetics governed by pH and temperature. Through this selection appears a large disagreement in results of researches between the rate expressions of the kinetics and observed and even with the empirical results, especially for reaction the monochloramine formation and for equilibrium the formation-hydrolysis of trichloramine. Then, the nature of identified intermediate and the observed rate of its formation reaction were not agree in different published works, as well the possibility of destruction of the free chlorine residual by this intermediate is not confirmed yet. Through this study, we obtain a representative selected group of reactions during breakpoint chlorination process, this identified group of reactions is compared with other models of breakpoint reactions proposed in the literature, where some differences appear.

Keywords: Drinking water; Chlorination; Breakpoint; Modeling; Set reactions

1. Introduction

Most of civilizations had recognized the importance of adequate and wholesome water supplies. One criterion among many for technological development of a country is the quality of drinking water produced. Generally, the ultimate purification step of potable water is the disinfection process [1]; this process means the operation of killing most bugs. The disinfection step of treatment water is the critical process to protect the public health, although the majority of pathogens (99–99.9%) are removed by coagulation, flocculation, sedimentation and filtration [2].

The potent germicide qualified to accomplish this task is chlorine. LEAL in (1909) listed its qualities “it is so cheap, so easy and quick of application, so certain in its results and so safe …” Furthermore, it has been called a “tremendous boon” in the safeguarding of public health [3]. The studies ensure that the most important characteristic of chlorine is its ability to maintain a biocidal residual for a long period. This residual helps to protect water from microbial

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*Corresponding author.

contamination, along its path to the consumer tap providing an indicator of water contamination in the distribution system [4]. The needed chlorine quantity during the disinfection phase serves to guarantee the hygienic quality and the adjustment of their organoleptics parameters [5].

The reached concentration of chlorine residual in water of the consumer taps must be about 0.5 mg/l after contact time equal to 30 minutes at pH inferior to eight [6]. Then, the investigations reveal that an overdose of chlorine in presence of dissolved organic matters leads to form chlorine organic compounds, like trihalomethanes, haloacetic acids, etc. [7], that are responsible of several serious illnesses [8,9] and can cause corrosion problems in the network pipes [10].

Previously, the discovery of the breakpoint reaction in the period of 1939–1940 allowed just elimination of ammonia from water that is naturally formed in water sources [11]. In general, one of three conditions involving breakpoint chlorination will occur in disinfection part. The easiest reactions to understand and the condition that usually predominates are a high ammonia concentration in the wastewater plant effluent treatment. The reaction results in the formation of the monochloramine. The second condition is at very low ammonia concentrations (inferior or equal to 1 mg/l) in treated effluent [12]. In this fact, breakpoint will probably be complete. With this condition, it may be difficult to maintain free chlorine residual, because of the potential for side reactions that consume free chlorine. The third condition is most difficult from a process control view. If the effluent ammonia concentration varies, either seasonally or diurnally, from 1 to 5 mg/l as NH_3–N, the disinfection mechanism will vary between the monochloramine and the free residual chlorine. The control system must be able to supervise both chemistries and detected when the transition from one the other occurs [13].

The main task of this study is to identify a model of reactions for breakpoint chlorination when the initial molar ratio chlorine–ammonia exceeds the value 1.5, a controversial chlorination process at the breakpoint takes place. To find the breakpoint reactions, it is important to examine the stability of resulted products from chlorination of the ammoniacal water. Then, the bibliographic researches provide a lot of reactions that can really occur at the breakpoint among all presented reactions during chlorination of the ammoniacal water. The selection of breakpoint reactions is leaning on the stability of generated entities that is deduced from data of the thermodynamics and the kinetics at pH and temperature conditions involved in the production of drinking water. Finally, our deducted model of reactions is compared with those proposed in the literature and will be discussed.

2. Breakpoint reactions

The breakpoint shows the quantity of chlorine that must be added to treated water contains the ammonia requiring for the formation of free chlorine residual. Breakpoint reaction is defined as the point, where the total quantity of ammonia nitrogen has disappeared and the amount of free chlorine residual is minimum, through this process, the active chlorine species (combined chlorine) are reduced to chloride ion, and ammonia is oxidized to molecular nitrogen [14–16], this process requires generally a theoretical molar ratio chlorine–ammonia equal to 1.5 according to a complex mechanism that we can summarize by each of these reactions [17–20]:

$$\begin{cases} 2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl \quad (a) \\ \qquad\qquad \text{Or} \\ 2NH_3 + 3HOCl \rightarrow N_2 + 3H^+ + 3Cl^- + 3H_2O \quad (b) \end{cases} \tag{1}$$

Really, the breakpoint reaction has several versions that depend on several factors: The chlorine dose, pH, the contact time, and temperature [21]. Another interesting stoichiometry which links two disinfectant agents: chlorine and monochloramine, so in this case, another reaction is envisaged at the breakpoint though the following generalized reaction [14,19,22]:

$$2NH_2Cl + HOCl \rightarrow N_2 + 3HCl + H_2O \tag{2}$$

This reaction is also called breakpoint, where the chlorine in large dose oxidizes the monochloramine, and free chlorine may become the predominant species [18]. In the case contrary, when there is lack in chlorine, reaction (15) preferentially takes place [15]. This reaction generates the dichloramine that is the source of alteration of the produced water quality [23] also it is devoid of the disinfectant force. For this reason, it is very important to ensure an enough dose of chlorine to avoid the quantitative formation of chloramine. In this regard, Hand and Mergerum [24] confirm that the reaction of the dichloramine with the trichloramine in the presence of base is the main source formation of gaseous nitrogen during the breakpoint. In other respects, we can specify that each molar ratio involves the appearance of specific end-products such as N_2, NO_3^-, NO_2^-, N_2O, etc. [19,25]. In addition, Ward et al. [26] reported that the concentration of 99% inactivation is higher when pH is decreased and the initial Cl/N is increased. For example, under acidic conditions and a molar ratio Cl/N equal to 4/1 implies production of nitrate ions according to the new breakpoint stoichiometry:

$$NH_4^+ + HOCl \rightarrow NO_3^- + 4Cl^- + 6H^+ + H_2O \tag{3}$$

This reaction demands more quantity of added chlorine and produces especially nitrate ions, which are neither stable nor harmless and referring as nuisance residuals [23]. Therefore, according to the previous data, in order to optimize the chlorination process at the breakpoint, it is appropriate to minimize the chlorine demand, provide an initial molar ratio Cl/N ranging in 2/1–3/1 and ensure the formation of stable end-products. All these criteria are meeting in the breakpoint reaction (3).

3. Model development

3.1. Chlorine and ammonia ionization

When the liquid chlorine is used, it is added as gas, this latter will dissolve in water to generate mixture of hypochlorous and hydrochloric acids [27]. The hydrolysis reaction of chlorine is as following:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{4}$$

The equilibrium constant expression and K_H value corresponding to this reaction at 25°C is [28]:

$$K_H = \frac{[HOCl][H^+][Cl^-]}{Cl_2} = (3.94 \pm 0.02) \times 10^{-4} (mol/l)^2 \tag{5}$$

As knows, the hydrochloric acid is always completely dissociated into proton ion (H^+) and chloride ion (Cl^-). Whereas the hypochlorous acid is only partially dissociated into proton ion and hypochlorite ion (OCl^-) [17] thus:

$$HOCl \rightleftharpoons H^+ + OCl^- \tag{6}$$

The pK_{a1} value for this reaction is 7.537 at 25°C [29] and the ionization constant expression:

$$K_{a1} = \frac{[H^+][OCl^-]}{[HOCl]} \tag{7}$$

It is clear from reactions (5) and (7) that the amount of various oxidized chlorine species are function of pH as shown in Fig. 1. Chlorine, hypochlorous acid, and hypochlorite ion are called the free chlorine residual. Moreover, at pH value 7.5, there is only a mixture of hypochlorous acid and hypochlorite ion. The main advantage of the simultaneous presence of both species expressed by the acid/basic couple ($HOCl/OCl^-$) in equal amounts is to effectively destroy of bacteria and virus at the same time [21,30].

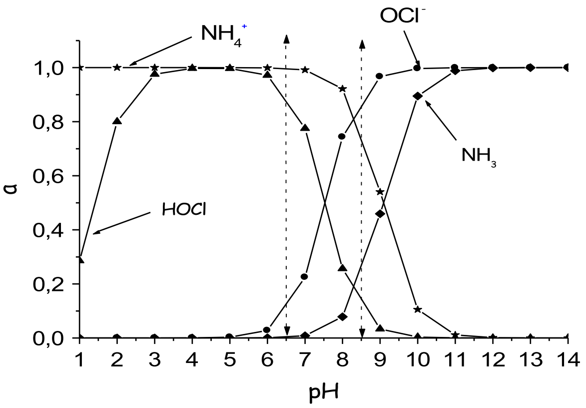


Fig. 1. Distribution diagram of chlorine and ammonia species, at 25°C, and $[Cl^-] = 10^{-3}$ M.

Aqueous ammonia is a weak base, in water, it forms ammonium ion. The deprotonation of ammonium ion is showed in the following acid/base reaction:

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \tag{8}$$

The equilibrium constant expression for this reaction at 25°C is [31]:

$$K_{a2} = \frac{[NH_3][H^+]}{NH_4^+} = 5.70 \times 10^{-10} mol/l \tag{9}$$

In this respect, the ammonia amount depends on pH as in Fig. 1. Moreover, it is recommended to express the fractions α of the chlorine and the ammonia concentrations respectively in terms of pH, as follows:

$$\alpha HOCl = \frac{[H^+]}{[H^+] + K_{a1}} \tag{10}$$

$$\alpha OCl^- = \frac{[K_{a1}]}{K_{a1} + [H^+]} \tag{11}$$

$$\alpha NH_4^+ = \frac{[H^+]}{[H^+] + K_{a2}} \tag{12}$$

$$\alpha NH_3 = \frac{K_{a2}}{[H^+] + K_{a2}} \quad (13)$$

Thus,

$$\alpha_{HOCl} + \alpha_{OCl^-} = 1 \quad (14)$$

And

$$\alpha_{NH_4^+} + \alpha_{NH_3} = 1 \quad (15)$$

3.2. Formation of chloramines

The addition of chlorine to water supply containing ammonia, hypochlorous acid reacts in a stepwise to form chloramines [18,32,33]. Inorganic chloramines include monochloramine, dichloramine, and trichloramine, that each one is referred as combined chlorine. In water treatment practice, the recommended amount of chloramine is usually 0.5–2.0 mg/l [34]. Then, the substances with which chlorine combines increases a demand on the chlorine that must be satisfied before the free chlorine residual is formed [22].

3.2.1. Monochloramine

First, the hypochlorous acid reacts with ammonia to yield the monochloramine as follows [35]:

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \quad (16)$$

The thermodynamics of the monochloramine formation proves its spontaneity; it is shown by its formation constant that is in order of size $2.01 \times 10^{11}\,M^{-1}$ at 25°C. Whereas its hydrolysis reaction can be neglected and it is equal to 5.0×10^{-12} mol/l at 25°C [36]. Concerning the kinetics law of the formation reaction of monochloramine, the reaction is second order with respect to concentrations of reactants, and usually, the rate is expressed in neutral species [37]. Table 1 shows the values of kinetics rate constant at 25°C found in the literature that we can see a big discrepancy of the authors' researches. These differences of K_c values are probably due to the ionic strength, buffer concentrations, the instrumentation and experimental design [38]. Furthermore, ammonia pKa ≈ 9.5 confirms that ammonium ion is alone, without ammonia at pH range 6.5–8.5 of the drinking water (Fig. 1), and we may rewrite the rate expression such:

$$r_1[\text{mol/l s}] = K_{c1}[HOCl][NH_4^+] \quad (17)$$

3.2.1.1. Potable water pH. HOCl and NH_4^+ can be written as function of pH, C_0, and N_0, Where C_0 and N_0 are the initial concentrations of chlorine and ammonia, respectively, and the rate may be rewritten as follows:

$$r_1[\text{mol/l s}] = k_{c1}\frac{C_0[H^+]}{K_{a1} + [H^+]} \times \frac{N_0[H^+]}{K_{a2} + [H^+]} \quad (18)$$

Or,

$$r_1[\text{mol/l s}] = k_{c1}\alpha_{HOCl}\, C_0\, \alpha_{NH_4^+} N_0 \quad (19)$$

Moreover, it is suitable to put:

$$k_{o1} = k_{c1}\alpha_{HOCl}\alpha_{NH_4^+} \quad (20)$$

It is apparent that the observed rate constant depends on pH. In fact, Fig. 2 illustrates the graphic variation of k_{o1} vs. pH. The fact is that Fig. 2 shows that the maximum rate of the monochloramine formation occurs at the pH_M, where the product of HOCl and NH_4^+ is the highest; which is the midpoint of the both values of pka 8.4 [18], and so the monochloramine formation is rapidly accomplished in a few seconds and it is the predominant species in potable water pH including in 6.5–8.5. The hydrolysis of monochloramine is very slow and follows kinetics law of order one [35]:

Table 1
Arrhenius expressions of monochloramine

Authors	Arrhenius expression (k_c, $M^{-1}\,s^{-1}$)	k_c ($M^{-1}\,s^{-1}$) at 25°C	References
Morris (1967)	–	5.11×10^6	[19]
Wei and Morris (1972) and Selleck and Saunier (1976)	9.70×10^8 exp (−1,509.8/T)	6.11×10^6	[50]
Morris and Issac (1985)	6.60×10^8 exp (−1,510/T)	4.20×10^6	[39]
Qiang and Adams (2004)	5.40×10^9exp (−2,237/T)	3.07×10^6	[38]

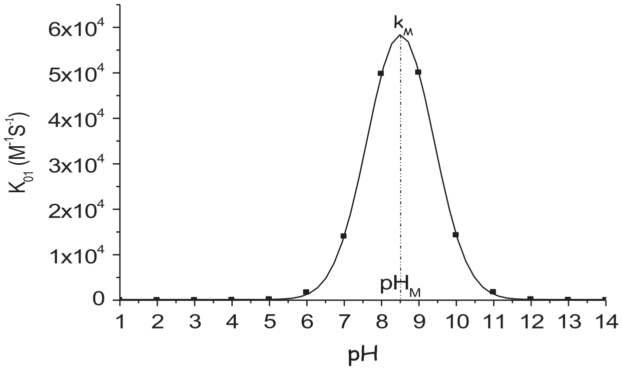


Fig. 2. The dependence of the observed rate constant of monochloramine as a function of pH at 25˚C.

$$NH_2Cl + H_2O \rightarrow HOCl + NH_3 \tag{21}$$

The rate expression was reported at 25˚C [39] as follows:

$$r_{-1}[S^{-1}] = 1.38 \times 10^8 \exp(-8,800/T)\ [NH_2Cl] \tag{22}$$

It is clear that the monochloramine hydrolysis does not depend on pH.

3.2.1.2. Side reactions of monochloramine in basic and acidic solutions. However, the shift of pH value of neutrality range prevents the substitution reaction chlorine-monochloramine involving a new reaction stoichiometry for the monochloramine.

At first, a basic solution favors the formation of hydroxylamine (NH_2OH) from NH_2Cl as follows [40]:

$$NH_2Cl + OH^- \rightarrow NH_2OH + Cl^- \tag{23}$$

This reaction is slowest than the hydrolysis reaction of the monochloramine and has not influence on chlorination process [36].

Secondly, a low-pH solution leads to the protonation of the monochloramine as shown [33,41]:

$$NH_2Cl + OH^+ \rightarrow NH_3Cl^+, \quad K = 28\ M^{-1} \tag{24}$$

This product will react with monochloramine to produce dichloramine and the ammonium ion thus [20]:

$$NH_3Cl^+ + NH_2Cl \rightleftharpoons NHCl_2 + NH_4^+ \tag{25}$$

The sum of reactions (24) and (25) gives the following equilibrium [18]:

$$\begin{aligned} &2NH_2Cl + H^+ \rightleftharpoons NHCl_2 + NH_4^+, \\ &K = 6.7 \times 10^5 \mathrm{l/mol\ at\ } 25^\circ\mathrm{C} \end{aligned} \tag{26}$$

According to Montgomery [20], reactions (23) and (24) are disfavored, other studies precise that the resulting reaction (26) cannot occur only at pH near to three [25,42]. Therefore, it is clear that both reactions (23) and (26) are suspected absents at pH relatively neutral, where it is easy the domination of the monochloramine formation reaction (16).

3.2.2. Dichloramine

The second generated entity is the dichloramine; it is the product of the reaction between hypochlorous acid and monochloramine thus [43]:

$$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O \tag{27}$$

Its thermodynamics constant is 4.54×10^8 l/mol at 25˚C. That confirms its completion contrary to the hydrolysis reaction. This latter is disfavored according to its constant value 2.2×10^{-9} mol/l at 25˚C [36]. Regarding its formation kinetics, it is elementary reaction of second order and its rate expression is [19,39]:

$$\begin{aligned} r_2[\mathrm{mol/l\ s}] = {}& 3.00 \times 10^5 \exp(-2,010/T)[HOCl] \\ & \times [NH_2Cl] \end{aligned} \tag{28}$$

$$r_2[\mathrm{mol/l\ s}] = k_{c2}[HOCl][NH_2Cl] \tag{29}$$

$$r_2[\mathrm{mol/l\ s}] = k_{c2}\frac{C_0[H^+]}{K_{a1} + [H^+]}[NH_2Cl] \tag{30}$$

And,

$$r_2[\mathrm{mol/l\ s}] = k_{c2}\alpha_{HOCl}\ C_0[NH_2Cl] \tag{31}$$

where

$$K_{o2} = k_{c2}\alpha_{HOCl} \tag{32}$$

One can notice that the formation rate of dichloramine depends upon pH, as long as the hypochlorous acid constitutes member of the rate expression. Fig. 3 shows graphically this relation. However, the hydrolysis reaction of dichloramine is independent of pH as its rate expression shows. Besides the hydrolysis reaction of ammonia is a first order [39]. So, hydrolysis dichloramine reaction can be omitted vs. its formation.

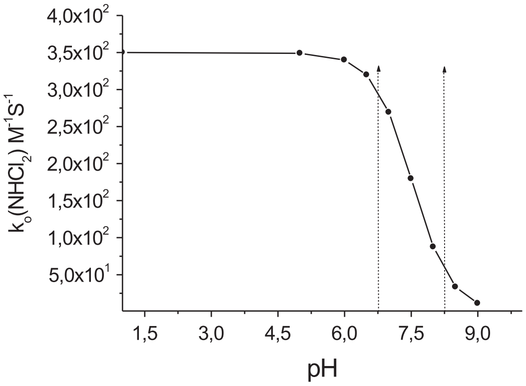


Fig. 3. Variation of the observed rate constant of the dichloramine formation with pH at 25˚C.

$$r_{-1}[S^{-1}] = 7.6 \times 10^{-7}[\mathrm{NHCl_2}] \text{ at } 25^{\circ}\mathrm{C} \tag{33}$$

Dichloramine is relatively stable at pH 4–5 in the presence of monochloramine and ammonium ion also it decomposes easily in the presence of hypochlorous acid and nitrogen trichloride [24].

3.2.2.1. Influence of proportions of chlorine and ammonia. In one instance, Jafvert and Valentine [44] proved that deficit in chlorine concentration leads to the reaction of the remainder amount of ammonia with dichloramine in order to form monochloramine according to:

$$2\mathrm{NHCl_2} + \mathrm{NH_3} \rightarrow \mathrm{NH_2Cl} + \mathrm{N_2} + 3\mathrm{H^+} + 3\mathrm{Cl^-} \tag{34}$$

In other case, a lack of ammonia leads to the formation of free chlorine according to the following reaction [44]:

$$2\mathrm{NHCl_2} + \mathrm{H_2O} \rightarrow \mathrm{HOCl} + \mathrm{N_2} + 3\mathrm{H^+} + 3\mathrm{Cl^-} \tag{35}$$

Due to the molar ratio Cl/N exceeds 1.5 at breakpoint chlorination, where there are sufficient proportions of the added chlorine and the present ammonia, then reactions (33) and (34) are not quantitative.

3.2.3. Trichloramine

Finally, the last generated chloramine is nitrogen chloride from the substitution reaction of hydrogen's dichloramine molecular by the chlorine atom of acid hypochlorous molecular as below [14]:

$$\mathrm{HOCl} + \mathrm{NHCl_2} \rightarrow \mathrm{HOCl} + \mathrm{NCl_3} + \mathrm{H_2O} \tag{36}$$

At the thermodynamics level, the formation reaction of nitrogen chloride is practically quantitative; its formation constant is in about 4.76×10^4 l/mol at 25˚C and its constant of hydrolysis is equal to 2.1×10^{-5} mol/l at 25˚C [36]. Concerning its kinetics, an evident disagreement appears in the published results on kinetics and on observed expressions shown on Table 2. Really, we find different significant rates constants and different proposed mechanisms [45]. In addition, if we calculate the constants going by the expressions of Table 2 at 20˚C and pH 7.5 (the average value of pH in the interval 6.5–8.5, pH of the water treatment), we will obtain the values of Table 3. For K_s and k_o values, to our knowledge, we have found a dispersal of the published results. For the $k_{\text{-c}}$ and $k_{\text{-o}}$ values, the given results by "Sanguinsin and Morris (1975)" and "Selleck and Saunier (1976)" seem agree and are very different from those published by "Wei and Morris (1972)". Concerning the stability, researches on trichloramine have found that the trichloramine tends easily to decompose in presence of ammonia excess or in the presence of dichloramine [46].

The rate expression of the trichloramine formation is [39]:

$$r_3[\mathrm{mol/l\ s}] = 2.00 \times 10^5 \exp(-3,420/T)\ [\mathrm{HOCl}][\mathrm{NHCl_2}] \tag{37}$$

It is suitable as well to express the formation rate of trichloramine according to the same expressive mode of two previous chloramines as a function of pH, the given expression by Kim and Stenstrom [47] appears the most appropriate.

$$r_3[\mathrm{mol/l\ s}] = k_{c3}\frac{\mathrm{C_0[H^+]}}{K_{a1} + [\mathrm{H^+}]}[\mathrm{NHCl_2}] \tag{38}$$

$$r_3[\mathrm{mol/l\ s}] = k_{c3}\alpha_{\mathrm{HOCl}}\mathrm{C_0}[\mathrm{NHCl_2}] \tag{39}$$

where

$$k_{o3} = k_{c3}\alpha_{\mathrm{HOCl}} \tag{40}$$

The hydrolysis reaction of trichloramine is independent of pH like the one reported in studies of Kim and Stenstrom [47]. And its hydrolysis reaction is elementary and follows kinetics law of first order [36,39]:

$$\mathrm{NCl_3} + \mathrm{H_2O} \rightarrow \mathrm{HOCl} + \mathrm{NHCl_2} \tag{41}$$

$$r_{-3}[S^{-1}] = 5.10 \times 10^3 \exp(-5,530/T)[\mathrm{NCl_3}] \tag{42}$$

Table 2
Expressions of kinetics constants and observed constants of trichloramine

Authors	Formation constants		Hydrolysis constants	
	Kinetic constant expression	Observed constant expression	Kinetic constant expression	Observed constant expression
Wei and Morris (1972)[a]	$k_c = 8.75 \times 10^{10} \exp(-1,912/T)$	$k_o = k_c \frac{H^+}{(1 + k_{a1}/[H^+])}$	$k_{-c} = 6.32 \times 10^{11} \exp(-6,542.53/T)$	$k_{-o} = k_{-c}[H^+]$
Saguinsin and Morris (1975)[b]	à pH = 4, $k = 1.61/\text{mol s}$		$k_{-o} = 3.2 \times 10^{-5}(1 + 5.88 \times 10^{-5}[OH^-])$	
Sellect and Saunier (1976)[a]	$k_c = 3.43 \times 10^5 \exp(-3,523/T)$	$k_o = k_c \frac{1 + 10^{-pK_{a1+1.4}}}{\left(1 + \frac{k_{a1}}{[H^+]}\right)}$	$k_{-c} = 8.56 \times 10^8 \exp(-9,059/T)$	$k_{-o} = k_{-c}\left(\frac{1 + 5.88 \times 10^5[OH^-]}{1 + k_{a1}/[H^+]}\right)$
Morris and Issac (1985)[c]	$k_c = 2.00 \times 10^5 \exp(-3,420/T)$		$k_{-c} = 5.10 \times 10^3 \exp(-5,530/T)$	

[a][50]. [b][19]. [c][39].

Fig. 4 shows the dependence of the observed constant of the trichloramine formation with pH, and therefore, its influence on its rate. More the pH value increases more the value of the observed constant decreases; this diminution is maximal at pH less than 4.5 [15]. To recap, if we refer to all preceding information, so in pH range of 7–8.5, monochloramine is the dominant species. Since the pH value decreases, dichloramine progressively dominates. At pH value 3, trichloramine constitutes the major species [48].

3.2.4. *Influence of the ratio of chlorine–ammonia*

The other important parameter that must be taken into account is the molar ratio or the weight ratio Cl/N. This parameter plays an important role in the determination of apparent quantities and the nature of generated products, as well as the chlorination byproducts [33]. Indeed, for an equimolar mixture of chlorine and ammonia; that is to say at an initial molar ratio Cl/N equal to 1/1 the main product is monochloramine and this case represents the chloramination process [32]. As soon as the molar ratio exceeds 1/1, we recorded the formation of dichloramine from the rupture of monochloramine until the molar ratio value 1.5/1, at this point the produced dichloramine amount is maximal [14,16,23] and we referred to the auto-decomposition of monochloramine [41]:

$$2NH_2Cl \rightleftharpoons NHCl_2 + NH_3 \qquad (43)$$

The rate expression of interconversion reaction mo-dichloramine is [39]:

$$r[\text{mol/l s}] = 80 \exp(-2,160/T)[NH_2Cl]^2 \qquad (44)$$

The empirical value of the reverse rate constant is 24 l/mol s at 25˚C. In addition, direct and reverse reactions are elementary and each one follows a kinetics law of second order [24,35,41]. Beyond the theoretical value of the molar ratio 1.5/1, the formation of trichloramine takes place [33].

3.3. *Destruction of free chlorine residual and chloramines*

3.3.1. *Formation of nitrogen hydroxide*

Researchers report that the formation of an instable entity in minimal quantity that reacts with free chlorine and chloramines to transform them into end-products [41,49]. This intermediate is suspected to be nitrogen hydroxide (NOH) [19,47,50,51]. Other authors have proposed the hydrazine ion (NCl_2^-), and other

Table 3
Calculated values of the formation and the hydrolysis constants of trichloramine at pH 7.5 and at 20˚C

Authors	Formation constant at 20˚C and at pH 7.5		Hydrolysis constant at 20˚C and at pH 7.5	
	k_c	k_o	k_{-c}	k_{-o}
Wei and Morris (1972)[a]	$1.28 \times 10^{+8}$	2.22	1.27×10^{2}	4.01×10^{-6}
Sanguinsin and Morris (1975)[b]	3.4		3.20×10^{-5}	
Selleck and Saunier (1976)[a]	2.06	1.13	3.2×10^{-5}	2.10×10^{-5}
Morris and Issac (1985)[c]	1.70		3.24×10^{-5}	

[a][50]. [b][45]. [c][39].

suggested the hydroxylamine as an intermediate species (NH_2OH) [24]. Indeed, Saunier and Sellect established a mechanism including the nitrogen hydroxide as an intermediate reactant [18]. Eilebeck [52] outlined the formation mechanism of NOH from the dichloramine decomposition according to the following reaction:

$$NHCl_2 + H_2O \rightarrow NOH + 2H^+ + 2Cl^- \tag{45}$$

The nitrogen hydroxide (NOH) intermediate is produced from the influence of the presence of two electronegative atoms of chlorine on the dichloramine molecule, which is given back more active for nucleophilic attack of the water's molecule leading to the formation of NOH. Really, this process is considered as complex including many reactions [17], and in other words, reaction (43) is not elementary then it follows kinetics of second order, namely first order for the water molecule as well for nitrogen hydroxide. In addition, the formation of the intermediate is linked with pH; it is favored at high values of pH [53]. The rate expressions (and so the observed expression constant) are written in function of the hydroxide ion concentration (Table 4); this one proves that is catalyzed by the presence of this ion, its rate formation is expressed as follows [44]:

$$r[\text{mol/l s}] = k_c[NHCl_2][OH^-] \tag{46}$$

It is important to precise that reaction (43) constitutes the limiting step of the entire mechanism of "Wei and Morris (1972)" and the mechanism of obtaining the breakpoint reaction (2) of "Saunier and Selleck (1976)". The nitrogen hydroxide constitutes the key element justifying the loss of monochloramine and dichloramine formed during the process of breakpoint chlorination, the hypothesis of destruction has been widely confirmed by the experiments of "Wei (1972)". Through the literature, we cannot find expression in agreement with the kinetics expression and the observed expression of formation of nitrogen hydroxide. According to our knowledge, the most important expressions are given in Table 4. Table 5 gives calculated values of k_c and k_o from Table 4 compared with the other published works.

3.3.2. Monochloramine disappearance

The intermediate reacts with chloramines in order to transform them to stable end-products like nitrogen molecule. Firstly, the nitrogen hydroxide reacts with monochloramine to produce harmless entities according to the following reaction [33]:

$$NOH + NH_2Cl \rightarrow N_2 + H^+ + H_2O + Cl^- \tag{47}$$

This latter is a second-order elementary reaction, and it is independent of pH [53]. The rate expression is written [50]:

$$r[\text{mol/l s}] = -5.53 \times 10^7 \exp(3,020/T)[NOH][NH_2Cl] \tag{48}$$

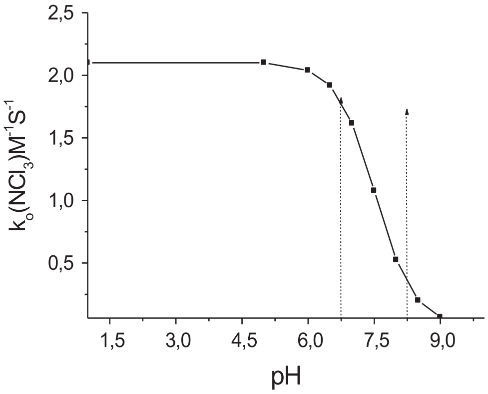


Fig. 4. Variation of the observed rate constant of the trichloramine formation with pH at 25˚C.

3.3.3. Dichloramine disappearance

Secondly, the nitrogen hydroxide reacts also with dichloramine for generating the hypochlorous acid through an elementary reaction of the second order, this reaction is independent of pH according to [50]:

$$\mathrm{NOH} + \mathrm{NHCl_2} \rightarrow \mathrm{N_2} + \mathrm{HOCl} + \mathrm{H^+} + \mathrm{Cl^-} \tag{49}$$

$$r[\mathrm{mol/l\ s}] = -6.02 \times 10^8 \exp(-3{,}020/T)[\mathrm{NOH}][\mathrm{NH_2Cl}] \tag{50}$$

3.3.4. Disappearance of free chlorine residual

Lastly, this intermediate destroys the residual chlorine to yield undesirable by-products, which are nitrate ions, by elementary process and follows kinetics of second order. However, Maston et al. [53] mentioned an argument very relevant that this reaction is unlikely because of its thermodynamics disfavored. Therefore, the reaction in question is [50]:

$$\mathrm{NOH} + 2\mathrm{HOCl} \rightarrow \mathrm{NO_3^-} + 3\mathrm{H^+} + 2\mathrm{Cl^-} \tag{51}$$

$$r[\mathrm{mol/l\ s}] = -7.18 \times 10^7 \exp(3{,}020/T)[\mathrm{NOH}][\mathrm{HOCl}]^2 \tag{52}$$

$$r[\mathrm{mol/l\ s}] = -k_c[\mathrm{HOCl}]^2[\mathrm{NOH}] \tag{53}$$

The fact that the hypochlorous acid is member of latter destruction reaction by the nitrogen hydroxide; we may express the influence of pH by the replacement of Eq. (11) in Eq. (51) rate to obtain:

$$r[\mathrm{mol/l\ s}] = -k_c\left(\frac{C_0 \times [\mathrm{H^+}]}{K_{a1} + [\mathrm{H^+}]}\right)^2[\mathrm{NOH}] \tag{54}$$

In this case, the observed constant expression becomes:

$$K_o = k_c\left(\frac{[\mathrm{H^+}]}{K_{a1} + [\mathrm{H^+}]}\right)^2 \tag{55}$$

4. Choice of the series of reactions at breakpoint

Operating conditions on which we have based our reasoning to obtain the appropriate series reactions at breakpoint are those applied in the production of drinking water. Treated water subject to chlorination process is the water that has been oxidized and filtrated in order to eliminate almost all reduced substances of chlorine (final chlorination step or post-chlorination). Preferably, this final water must not contain above 1 mg/l in ammonia concentration in order to provide the completion of the breakpoint chlorination [53]. Griffin [54] had put the breakpoint chlorination in its appropriate application to give better efficiency. He specified that the intervals of values related to influence parameters that can run better the chlorination process. So the optimum pH between 6.5 and 8.5, the weight ratio Cl/N including in 10/1–15/1 and the chlorination is relatively affected by the

Table 4
kinetics constant expressions and observed constant expressions of NOH formation

Authors[a]	Arrhenius expressions	Observables expressions
Wei and Morris (1972)	$k_c = 2.11 \times 10^{10} \exp(-3{,}623.55/T)$	$k_o = k_c[\mathrm{OH^-}]$
Selleck and Saunier (1976)	$k_c = 2.03 \times 10^{14} \exp(-3{,}623.55/T)$	$k_o = k_c\mathrm{N_0}[\mathrm{OH^-}]$

[a] [50].

Table 5
Calculated values of kinetic and observed constants of NOH at pH 7.5 and 25°C

Authors	Kinetic constants at 25°C	Observed constants at pH 7.5
Wei and Morris (1972)[a]	1.11×10^{-5}	3.50×10^{-2}
Selleck and Saunier (1976)[a]	1.06×10^{9}	2.40×10^{-2}
Leao and Selleck (1981)[b]	$2.77 \times 10^{+2}$	
Jafvert and Valentine (1987)[c]	$1.10 \times 10^{+2}$	

[a] [50]. [b] [56]. [c] [44].

Table 6
Proposed model of reactions at breakpoint chlorination

$HOCl \rightleftharpoons OCl^- + H^+$	(1′)	Acid/base equilibriums
$NH_4^+ \rightleftharpoons NH_3 + H^+$	(2′)	
$HOCl + NH_4^+ \rightarrow NH_2Cl + H_2O + H^+$	(1)	Model of reactions occurring at pH range 6.5–8.5 and initial weight ratio 10 /1 < Cl/N < 15 /1 at room temperature
$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	(2)	
$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$	(3)	
$NCl_3 + H_2O \rightarrow HOCl + NHCl_2$	(4)	
$NHCl_2 + H_2O \rightarrow NOH + 2H^+ + 2Cl^-$	(5)	
$NOH + NH_2Cl \rightarrow N_2 + H_2O + H^+ + Cl^-$	(6)	
$NOH + NHCl_2 \rightarrow N_2 + HOCl + H^+ + Cl^-$	(7)	

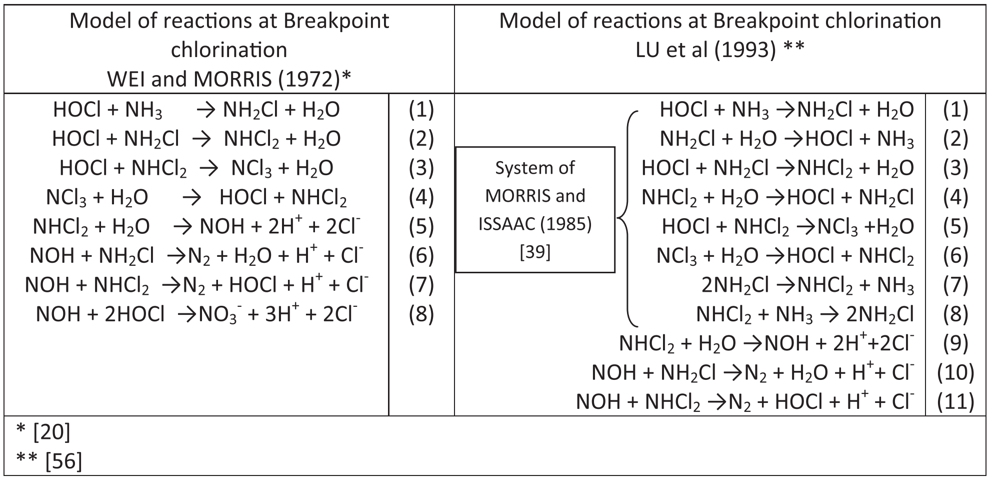
temperature. In light of these data, it is convenient to surround the required group reactions at room temperature. Moreover, it is necessary also to underline the following points:

- The formation reaction of monochloramine is spontaneous and quantitative compared with its hydrolysis reaction; the same fact is considered with dichloramine.
- The case of trichloramine is especially different, if we take into account these observations:

(1) Trichloramine is formed after the breakpoint; this explains clearly its stability in the presence of the free chlorine residual [55].
(2) The intermediate has not reacted with the trichloramine to destroy him such as monochloramine and dichloramine.
(3) The rest of the trichloramine amount is slightly compared with quantities of monochloramine and dichloramine produced during the chlorination process.

By the way, the important question, which can be posed, is: through any process the trichloramine quantity is decreased or disappeared if it is not destroyed by the intermediate species (NOH) and if it is stable toward the presence of the free chlorine? The logical answer provided after careful analysis of kinetics constants and observed constants of its formation reaction and its hydrolysis reaction is that the almost produced quantity of trichloramine is hydrolyzed by itself, so that it remains a little amount because the kinetics constants of formation and dissociation are near compared with those of monochloramine and dichloramine. Therefore, the hydrolysis reaction of

Table 7
The models of reactions



Model of reactions at Breakpoint chlorination WEI and MORRIS (1972)*		Model of reactions at Breakpoint chlorination LU et al (1993) **		
$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	(1)	System of MORRIS and ISSAAC (1985) [39]	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	(1)
$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	(2)		$NH_2Cl + H_2O \rightarrow HOCl + NH_3$	(2)
$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$	(3)		$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	(3)
$NCl_3 + H_2O \rightarrow HOCl + NHCl_2$	(4)		$NHCl_2 + H_2O \rightarrow HOCl + NH_2Cl$	(4)
$NHCl_2 + H_2O \rightarrow NOH + 2H^+ + 2Cl^-$	(5)		$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$	(5)
$NOH + NH_2Cl \rightarrow N_2 + H_2O + H^+ + Cl^-$	(6)		$NCl_3 + H_2O \rightarrow HOCl + NHCl_2$	(6)
$NOH + NHCl_2 \rightarrow N_2 + HOCl + H^+ + Cl^-$	(7)		$2NH_2Cl \rightarrow NHCl_2 + NH_3$	(7)
$NOH + 2HOCl \rightarrow NO_3^- + 3H^+ + 2Cl^-$	(8)		$NHCl_2 + NH_3 \rightarrow 2NH_2Cl$	(8)
			$NHCl_2 + H_2O \rightarrow NOH + 2H^+ + 2Cl^-$	(9)
			$NOH + NH_2Cl \rightarrow N_2 + H_2O + H^+ + Cl^-$	(10)
			$NOH + NHCl_2 \rightarrow N_2 + HOCl + H^+ + Cl^-$	(11)

* [20]
** [56]

trichloramine cannot be neglected like the hydrolysis reactions of monochloramine and dichloramine.

- The reaction of nitrogen hydroxide NOH with the free chlorine (reaction (23)) is not complete according to the thermodynamics data because it forms products less stables than the reactants; in addition, the principal aim of the chlorination is to keep free chlorine residual quantity in the process end.

Considering precedent data, our deduced series of reactions are constituted of the following reactions given in Table 6. Then, the model of Table 6 is composed of different reaction natures. Indeed, reactions (1)–(3) and (5) are reactions of substitution, reaction (4) is a hydrolysis or decomposition and reactions (7) and (9) are redox reactions.

Hereby, we present the famous model of reactions proposed by Wei and Morris taken of [19,47,50,51] and the other model appeared in research of Lu et al. [56] (Table 7). The model presented by Wei and Morris (1972) is constituted of two series of reactions, the first series of reactions shows the chloramines formation and the second series of reactions displays the destruction of monochloramine, dichloramine, and free chlorine. These two series are linked by a complex reaction of formation of the intermediate NOH; its role is to set off the destruction process for mono and dichloramine. On the other hand, the model of Lu et al. [56] is inspired by the aqueous chlorine/ammonia reactions proposed by Morris and Issac [39] on which Lu et al. [56] added the formation reaction of the intermediate and the destruction reactions of monochloramine and the dichloramine that are the same of theirs' Wei and Morris (1972). Concerning our model of group reactions, we take into account certainly, the formations' reactions of the chloramines with neglecting their hydrolysis reactions except the one of the trichloramine and the formation reaction of nitrogen hydroxide NOH and the destruction reactions of monochloramine and dichloramine induced by this intermediate.

5. Conclusion

On the basis of value constants of the thermodynamics and the kinetics related to pH and weight ratio Cl/N conditions, we can reach to establish a set of reactions which can take place at breakpoint chlorination. Our model of reactions has been compared with the most famous models and the most cited in the literature, which are: the model of Wei and Morris (1972), the model of and Isaac [39] and the model of Lu et al. [56], where we can reveal some differences that can produce an important consequence on determination the necessary chlorine dose for the disinfection by a chlorination process.

Indeed, the best choice of implicated reactions in the chlorination at the breakpoint helps on the one hand the resolution of several problems such as: the overdose of chlorine, the diminution of chloramine concentrations, and the decrease of chlorination disinfection by-products.

The understanding of the influence of these factors (Cl/N and pH) and them control will lead to find with accuracy the zone that characterized by the minimum of microbiological risk and chemical risk. On the other hand, it allows us to monitor and control more precisely the entities concentrations that can be generated, namely the free chlorine residual and chloramines especially at the levels of stock and in a distribution pipe which is the object of the nest part.

Acknowledgment

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Symbols

C_0 — initial molar concentration of free chlorine, mol/l, C_0 = [HOCl] + [OCl$^-$]
N_0 — initial molar concentration of ammonia, mol/l, N_0 = [NH$_4^+$] + [NH$_3$]
Cl/N — chlorine to ammonia nitrogen ratio
Cl_0/N_0 — initial ratio chlorine to ammonia nitrogen
K — thermodynamics constant, mol/l (M),or l/mol (M^{-1}), or (mol/l)^{2}or (M^{-2})
r — direct rate, mol/l s
r_{-1} — reverse rate, mol/l s
k_c — kinetic rate constant, s^{-1} (first order) or l/mol.s (second order)
k_{-c} — kinetic rate reverse constant, s^{-1} (first order) or l/mol s (second order)
k_o — observed rate constant, s^{-1} (first order) or l/mol s (second order)
k_{-o} — observed rate reverse constant, s^{-1} (first order) or l/mol s (second order)
α — species molar fraction
T — temperature, °K

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