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Short communication

Synthesis of enriched solutions of chloramine starting from hypochlorite at high chlorometric degree

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Abstract

The synthesis of high-grade chloramine was studied starting from sodium hypochlorite solutions containing 25% in NaOCl. The reagents at 100 chlorometric degrees are relatively stable and lose approximately 1.4° by 24 h at 17°C. They present a temperature of crystallization of 14.2°C (precipitation of $NaOCl\cdot5H_2O$) but it is possible to use them at −20°C in undercooling state. To obtain quantitative yields, it is necessary to neutralize the totality of hydroxide ions generated by the reaction and to operate below −10°C in order to limit oxidation of chloramine by the hypochlorite ions. The addition of an acceptor soluble salt is the most appropriate solution because it regenerates ammonia as soon as it is consumed and stabilizes chloramine by maintaining the pH around 10. The ammoniacal combinations NH_4NO_3–NH_4Cl–NH_3–H_2O and NH_4NO_3–NH_3–H_2O are compatible and allow to operate in monophasic medium until −30°C. The yields are close to 95% with a titre in NH_2Cl of 2.3 M (11.4%). Experiments carried out in continuous rating lead to a monochloramine solution of 2 M.

Keywords: Chloramine; Sodium hypochlorite; $NaOCl\cdot5H_2O$

1. Introduction

Chloramines are inorganic compounds, which have both research and industrial importance. The chemistry of chloramines is diversified not only because nitrogen and halogen act as reaction sites but also because of the different modes by which these functionalities react [1,2]. Thus, these haloamines can be considered as halogen release agents and many find use in bleaching, disinfecting and sanitizing applications.

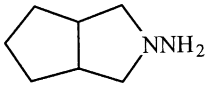
Only the monochloramine (NH_2Cl) presents a commercial interest. Aqueous solutions of chloramine are prepared by reaction of equimolar solutions of ammonia and sodium hypochlorite [3,4].

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$

Reaction of NH_2Cl with excess NH_3 in alkaline medium [5,6] is the basis of the industrial-scale production of hydrazines [7].

$$NH_2Cl + RR'NH + NaOH \rightarrow RR'NNH_2 + NaCl + H_2O$$

For example, reaction of monochloramine with 3-azabicyclo[3.3.0]octane yields *N*-amino-3-azabicyclo[3.3.0] octane, a pharmaceutical intermediate for hypoglycemic treatments [8,9].



This process, studied in the laboratory, arouses today a great interest taking into account its little polluting character compared to the former preparations involving *N*-nitrosamines [10,11]. However, it presents disadvantages related to the low hydrazine content in the reactional medium, which does not exceed 2–4%.

This limitation is due mainly to the great dilution of the reagents and in particular of hypochlorite, which leads to delicate and expensive operations of extraction. It results that, in the best of case, the instantaneous chloramine concentration in the reactor remains inferior to 1 M.

Taking into account the great instability of NH_2Cl in aqueous solutions, very few attempts have been carried out in more concentrated medium [12,13]. In all cases, they have not permitted to obtain high content chloramine solutions

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usable in laboratory scale or in industrial manufacturing. A higher chloramine titre requires the use of a new reagent at high chlorometric degree and the investigation of appropriated operating conditions. It is the object of this work.

2. Experimental details

2.1. Products

- The chloride and the nitrate of ammonia are pure products Aldrich for analyses.
- Sodium hypochlorite with 100 chlorometric degrees is a product of Elf-Atochem Society (Factory of Jarrie, Grenoble). It is titrated by iodometric [14] and directly by UV spectrophotometric method ($\lambda = 292\,\text{nm}$, $\varepsilon = 364\,\text{M}^{-1}\,\text{cm}^{-1}$) or after ammoniacal derivation with formation of NH_2Cl ($\lambda = 243\,\text{nm}$, $\varepsilon = 458\,\text{M}^{-1}\,\text{cm}^{-1}$).
- The aqueous ammonia solutions are reagents grade for analyses at 20% (Prolabo) and 32% (Aldrich).
- The water used was treated by passage through an ion exchange resin then twice distilled in a silica apparatus, deoxygenated, and stored under nitrogen.

2.2. Analytical methods

Chloramine shows an ultraviolet absorption in water at $\lambda = 243\,\text{nm}$ ($\varepsilon = 458\,\text{M}^{-1}\,\text{cm}^{-1}$). In reactional medium, it was analyzed by UV and HPLC at its maximum wavelength. The chromatograph used was a Beckman 421A equipped with an ultraviolet detector of variable wavelength. The column was a 250 mm × 4.6 mm ODS column ($d_\text{p} = 5\,\mu\text{m}$). The mobile phase was H_2O/MeOH (75/25 v/v) with a flow rate of $1\,\text{ml}\,\text{min}^{-1}$. UV spectra were measured with a Cary 1E double beam spectrophotometer. Thermodynamic data have been carried out using a Mettler TA8000 system equipped with a differential scanning calorimeter DSC 820.

2.3. Apparatus

- The discontinuous synthesis was effected in a cylindrical reactor with double wall in a borosilicated glass of 4 cm internal diameter. This reactor is maintained at low temperature by thermostatic fluid circulation. The ammoniacal solution is introduced into the vessel under agitation until the thermal equilibrium is reached. The hypochlorite solution is cooled and directly added with a regular flow so that the reactor temperature does not exceed −10°C.
- The continuous reactor (R_1) is dimensioned to produce 100 g of chloramine per hour. The two reagents and the reactor are thermostated by three independent fluids. The installation scheme is presented in Fig. 1.

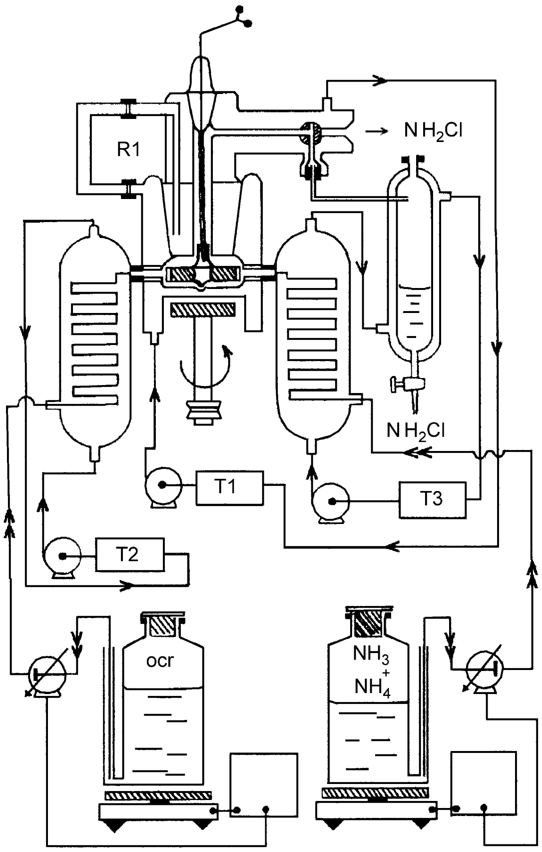

Fig. 1. Continuous preparation of high-grade chloramine from hypochlorite at 100 chlorometric degrees.

The inferior body of Pyrex glass with double wall is constituted of a mixing cylindrical chamber of $22\,\text{cm}^3$ in which a magnetic stirring rod is integrated. A coaxial thermal probe records the temperature in the reactional mixture. Two lateral adjutages of 2 mm diameter ensure the continuous introduction of the hypochlorite and the mixed ammoniacal solutions. The two thin tubes traversing the refrigerant vessel are thermally isolated by air matrix maintained in double concentric tubes. This precaution prevents the eventual crystallization of the hypochlorite solution before the reaction.

The reactor is surmounted by a second refrigerant vessel of L shape connected by a large prowled rod. A central ascending canal allows the absorption of the calories produced by the exothermicity of the reaction and maintains the reactional fluid at very low temperature. Three open valves included in the thermostatic envelope permits the bypass of the reactor flow R_1 to follow the running formation of the chloramine. The complete apparatus is maintained according to the experimental conditions between −20 and −30°C by the intermediate of Lauda cryostat.

The reactants are cooled by circulation in two helicoidal serpentines integrated in cylindrical thermostatic jackets (T_2 and T_3). On exit from R_1, the chloramine is collected in a cooled vessel at the same temperature of the ammoniacal solution, and then titrated by UV and HPLC. The alimentation of the reactor is ensured by two electromagnetic membrane pumps (Prominent® gamma/4b) ordered by microprocessor.

To register the weight lost as a function of time, we use two electronic balances Sartorius BP3100S equipped by an interface RS232. The pump flows are subdue to the mass variations by two numerical programmers Module-Lab NT9001 of Techindustries.

The head of the pump injecting the mixed ammoniacal solution is a polypropylene with Viton join and ceramic marbles. The pump injecting the high degree hypochlorite is equipped by a special Plexiglass titrating head "chlorine NS3" with an automatic purge. On starting, the solutions arrival must be simultaneous or with slight advance for the ammoniacal reagent. At the end of the cycle, the hypochlorite flow is stopped. This precaution avoids the interaction between the concentrated chloramine and the hypochlorite solution, which would cause a high production of heat with the liberating gas.

3. Results and discussion

The synthesis of high titre chloramine (HT) is studied starting from sodium hypochlorite solutions at 100 chlorometric degrees [15]. Table 1 gives an example of the composition of 4.54 M NaOCl solution.

Thus, the hypochlorite solutions at 100 chlorometric degrees corresponds to a molar concentration of 4.46 M. On contrary to the extract at 48 chlorometric degrees, the titres of NaCl and NaOCl are not in equimolar proportion. This deficiency is due to NaCl precipitation during the action of chlorine on sodium hydroxide solution. The yield of NaCl (1.7 M) is inferior to the solutions at 48 chlorometric degrees (2.14 M).

3.1. The investigation of the conditions of high-grade chloramine synthesis

The aqueous solutions of chloramine are unstable and evolve as a function of time. The nature of the formed products and the rate of degradation are narrowly influenced by the pH, the total concentration of ammonia ($[NH_3]_T = [NH_4^+] + [NH_3]$) and the temperature [16–25]. The degradation process leads to the acidification of the medium and to the simultaneous formation of chloride ions, dichloramine, trichloramine, ammonia ions and evolving of nitrogen [16].

Table 1
Composition of hypochlorite solution at high chlorometric degree

Chlorinated species	
%NaOCl	25.9
%$NaClO_3$	0.73
%NaCl	7.61
Alkalinity	
%NaOH free	0.71
%Na_2CO_3	0.092
%NaOH total	0.77
Chlorometric degree	101.9
Density	1.307
Temperature (°C)	17

In concentrated medium, the degradation reactions are exothermic; then the temperature rises and can carry the solution to boiling. These phenomena are summarized by the following reactions:

$$3NH_2Cl \rightarrow NH_4Cl + N_2 + 2HCl$$

$$2NH_2Cl + H^+ \rightarrow NHCl_2 + NH_4^+$$

$$3NH_2Cl + 2H^+ \rightarrow NCl_3 + 2NH_4^+$$

On fixed temperature and pH value, the stability domain of the chlorinated derivatives is a function of the $[NH_3]_T/[NH_2Cl]$ report [16,26–28]. In a strong alkaline medium ($pH > 12$), the chloramine solutions decompose spontaneously to form the nitrogen, N_2O, $N_2O_2^-$, and peroxynitrite ions $ONOO^-$ [29–32]. In addition, during the formation of chloramine, it is partially oxidized by the hypochlorite to give nitrogen and chloride ions [33].

$$2NH_2Cl + OCl^- + 2OH^- \rightarrow N_2 + 3H_2O + 3Cl^-$$

The quantification of these phenomena is difficult considering the number and the complexity of the mechanisms, which intervene simultaneously. The analysis of the reactional scheme enabled us to specify the conditions for the elaboration of HT chloramine:

- To obtain a quantitative yield, it is necessary to add in the reactional medium an acid species in order to neutralize instantaneously the total hydroxide ions generated by the reaction:

  $$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$

  An ammonium salt of the type $(NH_4^+)_\alpha H^+_\beta A^{(\alpha+\beta)-}$ is the most appropriate solution because it regenerates the ammonia as soon as it is consumed. This operation, which preserves the titre of NH_3 constant, promotes kinetically the formation of NH_2Cl on detriment of its in situ oxidation by the hypochlorite ions.
- The pH of the reaction controlled by the NH_3/NH_4^+ ratio must be maintained around 10 to stabilize the formed chloramine. We also prevent its conversion to $NHCl_2$, NCl_3, NH_2OH, N_2 and NH_3 according to reactions given previously.
- The temperature of crystallization of the reactive mixtures must be lowest possible because of the exothermicity of the reactions involved (formation, neutralization, and degradation). In particular, the in situ oxidation of the chloramine by hypochlorite is very exothermic ($\Delta H = -364.5\,kJ\,mol^{-1}$ [33]) and kinetically favoured compared with the formation by increasing the temperature; therefore it is necessary to realize the synthesis at low temperature.

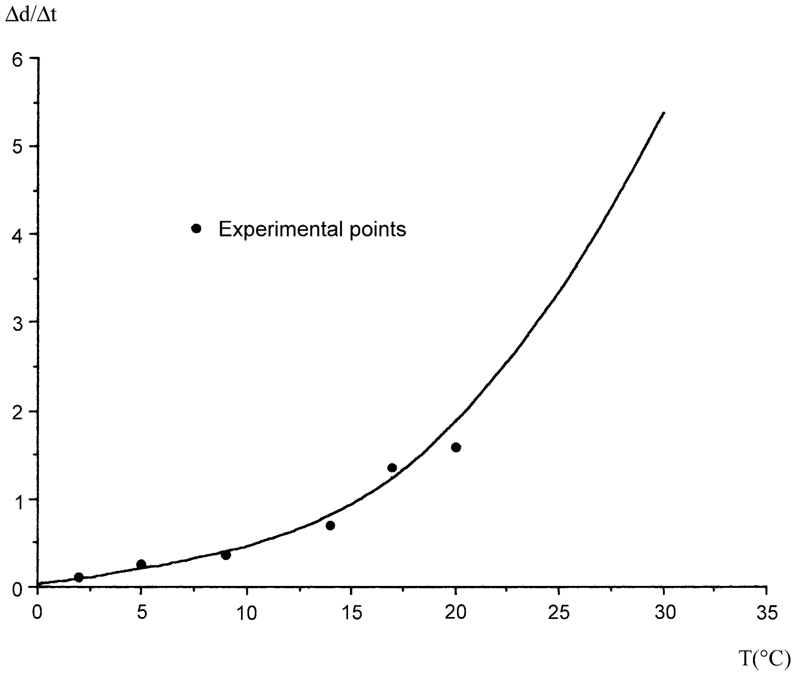

Fig. 2. Stability of sodium hypochlorite solutions at high chlorometric degree. Chlorometric degrees loosed (Δ*d*) by units of 24 h (Δ*t*) in terms of the temperature.

- At the end, in the plan of continuous preparation, it is necessary to operate strictly in a monophasic medium, which implies the preliminary knowledge of the physicochemical properties of the reactive mixtures.

3.2. *Physical-chemistry properties of reactional mixtures*

3.2.1. *Stability of the hypochlorite solutions*

The hypochlorite reactive at high chlorometric degree is unstable at room temperature. Many factors affect their stability [15,34–42]. The stability of hypochlorite solution was expressed as a loosed chlorometric degrees (Δ*d*) by units of 24 h (Δ*t*) as a function of temperature (Fig. 2).

The decomposition becomes relatively important as soon as the temperature increases above 30°C. In these conditions, it loses around 38% of its initial titre over one 20-day period (Table 2).

The degradation is considerably slowed down at lower temperature. Particularly, the $\Delta d/\Delta t$ report is below 1.35 at 17°C and 0.47 at 10°C. A lower temperature involves the partial precipitation of the hypochlorite pentahydrate $NaOCl{\cdot}5H_2O$. The crystallization is very difficult to take place because of the insufficient rate of crystals germination. It is therefore possible to maintain the solution at surfusion state during several hours at −20°C.

Table 2
Stability of sodium hypochlorite solutions at high chlorometric degree (variation of the NaOCl titre as a function of time at 30°C)

Time (days)	[NaOCl] (M)
2	3.70
4	3.35
6	2.80
9	2.25
14	1.90

Consequently, the solutions were stored during 2–3 days at 5°C, next reheated again towards 17°C if crystals are observed. In addition, the solutions were conserved in inactinic medium in polyethylene or glass tanks to prevent any catalysis by the metal ions. In spite of the little aptitude of high degree hypochlorite solutions to crystallize, it is necessary in industrial medium to use them around 15°C in order to avoid any mass collection in the canalization. To demonstrate at first time the synthesis feasibility, some trials were realized in undercooling state at −20°C.

3.2.2. *Polythermic systems* NH_4^+–NH_3–H_2O

The NaOCl concentration in hypochlorite solutions at 100 chlorometric degrees is 4.46 M, the titre of acceptor reagent must be higher in order to neutralize the formed hydroxide ions and to maintain the pH value around 10. In the case of continuous preparation, the crystallization point of ammonia mixture must be lower than −10°C to make up a loss frigories linked to the injection of chlorine reactive at +15°C. In that perspective, we sought the limit temperatures of ammoniacal reagent which allow a synthesis in monophasic medium according to the composition of nitrogen components.

With the goal to perform the continuous preparation in monophasic medium, we elaborated new ammoniacal combinations responding to pH and the temperature criteria. To prepare the chloramine, a great number of acids (HCl, H_2SO_4, etc.), neutral salts ($CaCl_2$, $MgCl_2$, etc.) and acid salts (NaH_2PO_4, NH_4HCO_3, etc.) can be used. A priori, some of these compounds are interesting since they present mainly acidity. On the other hand, very little are soluble and precipitate under 0°C. Then, the ammonium salts are most advantageous because their solubility increases with the quantity of ammonia in the medium. Otherwise, these salts maintain the titre of NH_3 constant by neutralization, which favour the formation step at the detriment of the degradation reactions.

In the synthesis conditions already defined, the exploitation of the polythermic diagrams involving NH_4^+ ions imply the use of ammonium nitrate systems: NH_4NO_3–NH_4Cl–NH_3–H_2O or NH_4NO_3–NH_3–H_2O [43–45]. These combinations allow to work in a homogeneous medium until a temperature of −30°C. In particular, the ternary combination NH_4NO_3–NH_3–H_2O ($[NH_3] = 7.2$ M, $[NH_4NO_3] = 4.76$ M) is compatible and crystallizes at −33.2°C. These conditions permit to realize the synthesis between −15 and −20°C with partial or total substitution of NH_4Cl by ammonium nitrate. In the absence of NH_4NO_3, the preparation of concentrated chloramine can be effected only in batch.

3.2.3. Preparation of high-grade chloramine

Experiment 1: NH_4Cl–NH_3–H_2O system — discontinuous synthesis — hypochlorite reactive at surfusion state — heterogeneous medium. The reaction is carried out in a cylindrical reactor with double wall maintained at −20°C by thermostatic fluid circulation. The ammoniacal solution contains 7.2 M of NH_3 and 4.76 M of NH_4Cl, which corresponds to the following composition: 12.1% NH_3, 25.2% NH_4Cl, 62.7% H_2O. Thirty millilitres of this mixture are introduced in the vessel under agitation until the thermal equilibrium is reached. The sodium hypochlorite solution (104.4 chlorometric degrees, 4.64 M) in undercooling state is added with regular flow (duration flow = 10 min) so that the temperature in the reactor does not exceed −10°C. The representative point of ammoniacal mixture being, at the initial instant, inside the diphasic domain liquid+NH_4Cl (isotherm −20°C of the ternary diagram NH_4Cl–NH_3–H_2O), 29.3% of the initial quantity of ammonium chloride are precipitated. During the addition of NaCl, the mixture becomes quickly homogeneous by dilution and elimination of the hydroxide ions. We obtain a chloramine solution titrating 2.18 M (11.2%), which corresponds to a yield of 98% with respect to hypochlorite. The NH_2Cl formed is relatively stable at −20°C and loses only 1.4% in concentration after 15 min.

Experiment 2: NH_4Cl–NH_3–H_2O system — discontinuous synthesis — hypochlorite reactive at 15°C — homogeneous medium. The realization of the synthesis in the same conditions but without initial precipitation of NH_4Cl (homogeneous medium) imposes a reduction of the ammonium chloride content and, correlatively, an increase of the ammonia titre. While operating with a commercial ammonia solution (32%), the dissolved maximum quantity of NH_4Cl permitted by the isotherm −20°C corresponds to the following total composition: 25.3% NH_3 (14.25 M), 20.9% NH_4Cl (3.74 M). One obtains a concentrated NH_2Cl solution containing 1.99 M (10.2%) that represents about 90% of NaOCl engaged. This slight diminution of yield is due to the fact that 16% of the reaction was conducted in unbuffered medium.

Experiment 3: NH_4Cl–NH_3–H_2O system — discontinuous synthesis — hypochlorite reactive at 15°C — heterogeneous medium. This trial is performed by using hypochlorite solution not in undercooling state but at a temperature superior to its crystallization point (15°C). Thirty millilitres of the mixed ammoniacal solution titrating 12.4 M of NH_3 (21.2%) and 5 M of NH_4Cl (26.8%) were introduced in a vessel maintained at −25°C. An equivalent volume of hypochlorite solution (103.8 chlorometric degrees, 4.63 M) is added drop by drop (duration flow = 15 min) in a manner that the temperature in the reactor is not higher than −15°C. As in experiment 1, the reactional medium is heterogeneous in the first moments (partial precipitation of NH_4Cl) and leads to NH_2Cl concentration above 2.19 M (11.3%), nearly 94% yield.

Experiment 4: NH_4NO_3–NH_4Cl–NH_3–H_2O system — discontinuous synthesis — hypochlorite reactive at 15°C — homogeneous medium. To carry out the preparation in a monophasic medium with hypochlorite solution at 15°C and to neutralize the total hydroxide ions liberated, a quaternary mixture NH_4Cl–NH_4NO_3–NH_3–H_2O has been employed. Its composition of NH_3, NH_4Cl, NH_4NO_3 and H_2O is, respectively, of 13.14 M (22.4%), 3.02 M (16.2%), 1.76 M (14.1%) and 26.2 M (47.3%). The experimental conditions are identical to experiment 3. With hypochlorite solution at 98.4 chlorometric degrees (4.39 M), one obtains a NH_2Cl solution reaching 2.01 M (yield 90%) with a tenor close to 10.3%.

Experiment 5: NH_4NO_3–NH_3–H_2O system — discontinuous synthesis — hypochlorite reactive at 15°C — homogeneous medium. This test is identical with experiment 4 but by replacing the totality of ammonium chloride by ammonium nitrate. By using a hypochlorite solution at 4.65 M (104.3 chlorometric degrees) and an ammoniacal mixture 7.55 M of NH_3 (12.9%) and 5 M of NH_4NO_3 (27%), the yield of the reaction is 95%, which corresponds to a solution of NH_2Cl 2.21 M (11.4%).

Experiment 6: NH_3–H_2O system — discontinuous synthesis — hypochlorite reactive at surfusion state — homogeneous medium. To confirm the predominant influence of an acid acceptor, hypochlorite solution was added to a commercial ammonia solution (32%) in the absence of ammonium salt (−20°C). The reaction time has been raised to 30 min in order to maintain the temperature below −10°C. In spite of these precautions, the final yield does not exceed 30%.

Experiment 7: NH_4NO_3–NH_4Cl–NH_3–H_2O system — continuous synthesis — hypochlorite reactive at 15°C — homogeneous medium. The synthesis of the chloramine is carried out in an agitated continuous reactor maintained at a temperature ranging between −20 and −30°C. The reactants have a composition identical to that defined in experiment 4. The flows are fixed at $4\,\mathrm{ml\,min^{-1}}$. The injection temperatures are maintained, respectively, at 15 and −30°C for NaOCl and the quaternary mixture NH_4NO_3–NH_4Cl–NH_3–H_2O. The temperature of the reactional mixture is regulated at −11°C. At the reactor exit, one obtains continuously a solution of NH_2Cl titrating 2.07 M (10.6%).

Experiment 8: NH_4NO_3–NH_3–H_2O system — homogeneous medium — hypochlorite reactive at 15°C — continuous synthesis. This experiment is identical to the preceding example but by replacing the totality of ammonium chloride by ammonium nitrate. The yield of the reaction is established to 93%, which corresponds to a solution of NH_2Cl of 2.05 M (10.5%).

4. Conclusions

This work indicates, for the first time, the possibility to obtain a chloramine higher than 11% from hypochlorite solutions at 100 chlorometric degrees. The conditions of the synthesis require the use of ammoniacal combinations with lower crystallization point. These results achieved in batch are transposable in continuous synthesis provided that they control the thermal transfers. This precaution is necessary on account of hypochlorite injection above its crystallization temperature. The feasibility of the synthesis was proven by the realization of a pilot plant with NH_2Cl titre around 2.1 M. Nevertheless, the high yields were obtained in batch with values close to 2.35 M. At a temperature of −20°C, the chloramine solutions are relatively stable and lose less than 0.1% in concentration per minute. They could be used for the preparation of hydrazine according to Raschig process. Thus, with the same unit volume of hypochlorite, it is possible to increase the productivity of hydrazine and to realize an economy in energy and matter during the operations of synthesis, recycling and distillation.

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