Revealing the mechanism of indirect ammonia electrooxidation

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A B S T R A C T
The governing mechanism of indirect ammonia electrooxidation has been often described similarly to breakpoint chlorination. However, comparison of the chloramine concentrations which develop in batch indirect ammonia electrolysis and classical breakpoint chlorination experiments (performed under similar conditions) suggests that the governing reactions are different. Three experimental sets were carried out with excess-ammonia solutions, with the aim of elucidating the mechanism of indirect electrochemical ammonia oxidation: (1) chlorination with Cl2(aq) and NaOCl; (2) batch- and (3) single-pass electrolysis experiments.

Based on the results we propose a new mechanism for indirect ammonia electrooxidation, according to which trichloramine, rather than monochloramine, is the initial and primary product. NCl3 apparently forms from a reaction between NH3 and Cl2(aq), which occurs in the near anode area where pH is <2 and the bulk Cl− concentration is high. At such conditions Cl2(aq) is the dominant active chlorine species in the anode vicinity. Upon formation in the near anode area NCl3 decomposes to N2, NH4Cl and NHCl2 in the bulk solution or/and close to the cathode surface area, where pH >12. Under batch operation and/or single-pass electrolysis characterized by long contact times both NH4Cl and NHCl2 that form in the bulk electrolyte are oxidized to NCl3 by Cl2(aq) upon return to the near-anode zone.

1. Introduction
Electrochemical oxidation of ammonia using mixed metal–oxide anodes (Ti/TiO2–RuO2–M2O3, where M typically stands for Sn, Ir and Nb) has been shown effective for the removal of ammonia from various wastewater streams e.g. power plants [1]; tanneries [2]; landfill and bioreactor leachates [3,4]; aquaculture systems [5] and domestic wastewaters [6]. Both NH2(aq) and NH3(aq) can be oxidized electrochemically via either direct or indirect pathways. Within the direct oxidation pathway NH3 is converted mainly to N2(aq), following its adsorption to the anode surface (basic conditions) or by OH• radicals generated at the anode surface following oxygen evolution (acidic or neutral conditions) [7]. Indirect NH4+/NH3 oxidation, which is much faster, efficient and cost effective than the direct pathway, occurs in the presence of sufficiently high chloride ion (typically >300 mg l−1) concentrations [7].

The indirect ammonia oxidation process is invariably described in the literature by the ultimate stoichiometric reactions (Eqs. (1)–(6)) and its governing mechanism has been often described to be similar to the intensively studied “breakpoint chlorination” mechanism [8–10].

Dominant reaction on the anode:

2Cl− → Cl2 + 2e− (1)

Dominant reaction on the cathode:

2H+ + 2e− → H2 (2)

Main reactions in the aqueous phase:

Cl2 + H2O ↔ HOCl + H+ + Cl−. K2 = 3.94 × 10−4 (3)

HOCl + 2/3NH3 → 1/3N2 + H2O + H+ + Cl− (4)

HOCl + 2/3NH4+ → 1/3N2 + H2O + 5/3H3+ + Cl− (5)

HOCl + 1/4NH4+ → 1/4NO3− + 1/4H2O + 3/2H3+ + Cl− (6)

According to the classical breakpoint chlorination mechanism [11–13], the addition of active chlorine species (HOCl or OCl−) to ammonia containing solutions results in stepwise formation of chloramine species (monochloramine, dichloramine and trichloramine) according to Eqs. (7)–(9):

Monochloramine

NH4+ + HOCl → NH2Cl + H2O + H+ (7)

Dichloramine

NH3Cl + HOCl → NHCl2 + H2O (8)

Trichloramine

NHCl2 + HOCl → NCl3 + H2O (9)

The formation and speciation of chloramine species in a given solution depends mainly on the pH, temperature and active
chlorine to ammonia concentrations ratio [11–13]. Under operational parameters typical for conventional breakpoint chlorination (which is often used also to describe indirect ammonia electrooxidation), i.e. pH 7–8 and 20 °C, a gradual increase in the Cl2/N ratio should result in monochloramine formation during electrolysis, until a Cl2/N mole ratio of ~1 is attained. Considering this mechanism, translated into the conditions prevailing in electrolytic cells, further electrolytic production of Cl2 must then lead to decomposition of monochloramine, formation of dichloramine and its subsequent decomposition, and to N2(g) and NO3− release (trichloramine is reported to be the intermediate species of mono- and dichloramine decomposition). Finally, at a Cl2 to N mole ratio of 1.5 the breakpoint reaction is expected to be completed. However, during the time at which the Cl2 to N ratio is lower than ~1 the total dissolved nitrogen species concentration (i.e. the sum of NH3, NH4+, all chloramine species and other dissolved nitrogen compounds such as nitrate and nitrite) is expected to remain roughly constant, i.e. almost no N2(g) generation should occur.

In stark contrast with the above description, the results reported for batch electrochemical indirect ammonia electrooxidation experiments [1,3,7–10] indicate a gradual drop in the total ammonia nitrogen (TAN, defined as the sum of NH3 and NH4+ concentrations) concentration from the very beginning of the electrolysis experiment, indicating that N2 formation is attained immediately, i.e. long before a Cl2 to N ratio of 1.5 is attained. Furthermore, the accumulated concentration of chloramine species in the electrolyte solution during batch operation is typically lower than 7% of the initial ammonia concentration [1,3,7–10] i.e. far lower than the ~100% expected based on the classical breakpoint chlorination description.

Kapalka et al. [14], in an attempt to explain this discrepancy, ascribed these observations to a combination of excess concentration of HOCI and low local pH conditions prevailing close to the anode surface area during electrolysis, which (according to this hypothesis) promoted fast formation of chloramines through ammonia oxidation by HOCI, followed by fast decomposition of mono-, di- and trichloramine in the vicinity of the anode. These authors also suggested that ammonium ions are oxidized at the anode by HOCI mainly to N2(g) and that only a small fraction of combined chlorine makes its way to the bulk solution [14]. A fairly similar explanation (i.e. simple superchlorination) was suggested before by Vijayaraghavan et al. [5].

However, as shown later in this paper, under typical indirect electrooxidation operational conditions, the active chlorine species which form at the anode are dominated by the species Cl2(ano) rather than by HOCI. This fact alone suggests that the mechanism involved differs significantly from Kapalka et al.’s [14] description. Moreover, superchlorination alone, i.e. ammonia oxidation by excess HOCI or OCl− concentrations, cannot entirely explain the observed phenomena because based on a similar logic, high localized Cl2/N ratio should be expected also in the point of impact when conventional chloramination is carried out i.e. when active chlorine species are dosed to ammonia containing solutions in the form of concentrated NaOCl or Ca(OCl)2 solutions. However, such observations have never been reported.

The goal of the present study was to elucidate the mechanism that governs the oxidation of ammonia species in electrolytic cells. The first hypothesis laid out was that under operational conditions which do not promote significant Cl2(ano) hydrolysis in the vicinity of the anode (i.e. when Eq. (3) tends toward the reactants), i.e. low buffering capacity in the bulk solution and a high Cl− concentration, Cl2(ano) (and not HOCI) becomes the dominant ammonia oxidizing species. This fact induces a reaction sequence on the anode, cathode and bulk solution, which differs from the sequence encountered under the conditions prevailing in both classical breakpoint chlorination and superchlorination. To broaden and strengthen the conclusions regarding the effect of localized low pH and high Cl− concentration on the ammonia oxidation mechanism, Cl2(ano) dosage experiments were conducted under conditions resembling those prevailing in the vicinity of the anode during electrolysis operation. Finally, in order to differentiate between the reactions that occur near the anode/cathode and the reactions that occur in the bulk solution, low retention-time single-pass experiments were also conducted. Based on the results obtained in all the experiments a new reaction sequence was proposed for batch and single pass indirect ammonia electrooxidation.

2. Experimental

2.1. Reagents

Analytical grade NH4Cl, (NH4)2SO4 and NaCl were used as sources of NH4+ and Cl−. pH was determined using 827 pH lab pH meter and 718 STAT Titrino apparatus equipped with 6.0228.010 glass pH electrodes (Metrohm, Switzerland). Genesys UV/Vis scanning and Genesys 20 (Thermo Scientific) spectrophotometers were used for UV absorption spectra collection and colorimetric analysis. NaOCl stock solution was prepared by bubbling Cl2(g) (99.5%, Aldrich) through cold (~5 °C) 0.5 M NaOH solution until the pH of absorbing solution reached 11.0. Chloramine standard solutions were prepared in accordance to Kumar et al. [15]. See Appendix A for elaboration on this procedure.

2.2. Analyses

2.2.1. Available chlorine

Ammonium and mono-, di- and tri-chloramines were determined by the colorimetric DPD method [16], iodometrically [16], and by a UV-absorption technique, developed specifically for this work (see elaboration in Appendix B).

2.2.2. TAN and monochloramine

Concentrations of monochloramine and ammonia were determined by the modified salicylate method [17], details of which are given in Appendix C.

2.2.3. Nitrate

NO3− concentrations that developed during batch electrolysis experiments were determined using absorption at 220 nm and 275 nm [16]. To minimize interference from chloride ions, the UV spectra of the electrolyte solutions were collected before the electrolysis and used as the background for nitrate analyses.

2.3. Electrolytic cell construction

A flow-through electrolytic cell was used. Anode and cathode (6 cm × 8 cm × 0.3 cm) were made of Ti/RuO2/ITO–Ti/rutileO2 and Ti respectively. Electrodes were made from Ti sheets (6 cm × 8 cm × 0.33 cm). Ti rods (3 mm diameter) were connected perpendicularly to the center of one side of each plate for current collection and for mounting the electrodes into the electrolytic cell. Ti/RuO2/ITO–Ti/rutileO2 electrodes were prepared by the polymeric precursors method.

Prior to coating, titanium substrates were treated with sand paper (320 mesh); stored in isopropanol for 2 days; etched in hot (96 °C) HCl (18%, w/v) for 25 min; treated by boiling oxalic acid (10%, w/v) for 20 min and finally washed with distilled water. Polymeric precursor solutions (mole ratio 4:1:6:1, CA:EG:M) were made by dissolving citric acid (CA) in ethylene glycol (EG) at 60 °C, and subsequent dissolution of titanium isopropanoxide (97%, Aldrich) or ruthenium (III) chloride hydrate (ReagentPlus, Aldrich) at 90 °C for TiO2 and RuO2 precursors, respectively. Final polymeric precursor
solution ([Ru/Ti mole ratio of 30/70) was obtained by mixing individual RuO2 and TiO2 precursors. Coating was done by brushing the precursor mixture on preheated (60 °C) Ti substrates. After brushing, the electrodes were first dried at 110 °C for 30 min to promote polymerization; then at 250 °C for 20 min to improve oxide adhesion to the substrates and finally, the electrodes were subjected to calcination at 400 °C for 10 min. The procedure was repeated 10 times and was followed by calcination at 400 °C for 1 h, resulting in 2.2 mg cm−2 surface coating.

Electrodes were fixed on parallel PVC plates (14 cm × 28 cm × 0.8 cm) equipped with 6.2 cm × 8.5 cm × 0.33 cm notches at the center of the plates for electrode placement. An interelectrode gap of 0.6 cm was maintained by an elastic PVC spacer with a void for electrolyte flow, which also ensured that the cell did not leak. The PVC plates with the mounted electrodes and elastic PVC spacer were fixed together by screw bolts and nuts. To estimate the pH of the electrolyte solution close to the anode and cathode surface areas, 1.5 mm holes were drilled through each electrode and adjacent PVC wall. Through these holes two capillaries, with 1.13 and 0.3 mm external and internal diameters, respectively (1/2/35 μl glass micropipette, Marienfeld), were mounted in a way that one end was placed on the electrode surface (PVC cable insulation with external diameter of 1.5 mm was used to fix the capillaries onto the electrodes) and the other end outside the electrolytic cell, connected to a pH measuring station.

2.4. Breakpoint chlorination experiment

A commercial bleach solution (25.64 mg l−1 as Cl2, pH 13.1) was gradually added to 5 l of NH4Cl solution (200 mg l−1 as N) at a rate 22.063 mg Cl l−1 min−1 under intensive stirring until attaining a Cl2/NH4 ratio of 1.6. The pH value of the reacting mixture was maintained constant at pH 7.8 ± 0.15 during the experiment by automatic addition of NaOH (1 mol l−1) or H2SO4 (0.5 mol l−1). 5 ml samples of chlorinated solution were withdrawn periodically and analyzed for chloramines and ammonia.

2.5. Batch electrolysis experiments

A peristaltic pump (Masterflex®, 6–600 rpm with 24″ neoprene tubing) was used to recycle electrolyte (10 l) between the flow-through cell and the electrolyte holding vessel at an up-flow rate of 1.72 l min−1, resulting in single-pass hydraulic retention time of 1 s. A magnetically stirred PVC reactor (height 40.5 cm, internal diameter 19.5 cm) was used as the electrolyte holding vessel. 0–5 A DC power supply (Prova 8000, M.R.C. Ltd) was used to generate the required current. Temperature during the experiments was 19–23 °C.

A current of 1 A was applied in all the batch experiments, corresponding to a current density of 208.3 A/m2. Initial TAN concentration was 50 mg l−1 as N (NH4Cl as NH4+ source). pH was maintained constant (pH 8.0 ± 0.02 and pH 8.0 ± 0.15 for buffered and un-buffered solutions, respectively) during electrolysis by automatic addition of 2 mol l−1 NaOH solution, using a specifically programmed automatic titration apparatus (Titrino 718, Metrohm, Switzerland).

Two sets of batch electrolysis experiments were performed. The first set was aimed at investigating the effect of chloride ion concentration on the accumulation of chloramines in the electrolyzed solution. Applied Cl− concentrations were 10, 25 and 50 g l−1. The goal of the second set was to observe the rate of accumulation of chloramines in buffered and un-buffered electrolyte solutions (50 mg l−1 as N, 50 g l−1 as Cl): orthophosphate concentrations of 0, 0.1 and 0.25 mol l−1 were applied to provide buffering capacity (pH 5–7 of 2.3 × 10−2, 7.94 × 10−2 and 16.4 × 10−2 meq l−1, respectively) at the required pH range (~pH 2). In the batch electrolysis experiments electrolyte was collected from the near anode surface (~0.3 ml min−1) using a capillary and the pH value was continuously recorded.

5 ml samples were periodically withdrawn from the bulk electrolyte solutions during the experiments and the concentrations of TAN, free chlorine and mono-, di- and tri-chloramines were determined by the salicylate and DPD methods.

2.6. C5H6N dosage into TAN-containing solutions

Ammonium sulfate solutions ([TAN]0 = 50 mg l−1) were placed in a completely stirred PVC reactor (height 40.5 cm, internal diameter 19.5 cm) and C5H6N (Aldrich, 99.5%) was supplied through a glass diffuser placed at the bottom of the vessel. A constant C5H6N flowrate of 7 ml min−1 was applied in all experiments. Four chloramination experiments were performed, in which the composition of the initial chloraminated solution varied between the experiments as follows: (1) no chloride ions and no phosphate buffer; (2) [Cl−]0 = 50 g l−1 and no phosphate buffer; (3) [Cl−]0 = 50 g l−1 and phosphate buffer at 0.25 mol l−1; and (4) [Cl−]0 = 0 g l−1 and 0.25 mol l−1 phosphate buffer. The pH of the chloraminated solutions was adjusted prior to the start of the experiment to 7.8 and maintained constant during the experiments (pH 7.8 ± 0.2 and pH 7.8 ± 0.02 in the un-buffered and buffered experiments, respectively) by automatic addition of 2 mol l−1 NaOH solution using a specifically programmed 718 STAT Titrino apparatus (Metrohm, Switzerland). 5 ml samples were withdrawn periodically from the chloraminated solution and concentrations of TAN, free (Cl2 + HOCI) and combined (mono-, di-, and tri-chloramines) chlorine were determined by the salicylate and DPD methods.

2.7. Single-pass electrolysis experiments

Initial electrolyte composition in single-pass electrolysis experiments was [NH4+]0 = 50 mg l−1 As N (ammonium source: NH4Cl) and [Cl−]0 = 20 g l−1 (Cl− source: NaCl). Five up-flow-velocity experiments were carried out with flow rates corresponding to hydraulic retention times of 0.91, 1.15, 1.6, 2.64 and 6.36 s and constant 3 A current (current density = 625 A/m2). Thereafter, a second set (four experiments) was performed with applied electrical currents of 1, 2, 4 and 5 A (current densities of 203.8, 416.7, 833.3 and 1041.7 A/m2, respectively) and a constant retention time of 1.6 s. Electrolysis cell effluent was periodically sampled from a valve located 24 cm downstream the electrodes. In order to collect samples free of (mainly) H2O bubbles (produced in the electrolyzer) the effluent stream was split and a piece of glass wool was used to remove the bubbles just before the sampling point. UV spectra of at least three effluent samples were recorded in each experiment immediately after sample collection using full-to-the-rim sealed 1 or 5 cm quartz cuvettes. The pH value of the effluent was monitored using a pH electrode mounted inside the effluent pipe (~15 cm downstream of the electrodes cell). The pH value in the vicinity of the anode and cathode areas was approximated by measuring pH values of samples collected by capillaries mounted on the anode and cathode surfaces.

3. Results and discussion

3.1. Breakpoint chlorination versus indirect ammonia electrooxidation

Fig. 1 presents the difference between the accumulation of chloramines during a classic breakpoint chlorination experiment (batch test, NaOCl dosage) and the respective accumulation of chloramines in a batch indirect electrochemical ammonia oxidation experiment
may be higher than 22 mmol l\(^{-1}\), which is the Cl\(_2\)\(_{aq}\) saturation level attained when water is brought to equilibrium with Cl\(_2\)\(_{g}\) at partial pressure of 1 atm). At the neutral to acidic pH range the Cl\(_2\)\(_{aq}\) produced at the anode reacts with water in the bulk solution to form hypohalous acid according to Eq. (3) [19].

Observing Eq. (3)’s equilibrium constant it is clear that the extent of Cl\(_2\) hydrolysis is very low at the pH range 0–2.0, particularly when the Cl\(^-\) concentration is high; at the range pH 3–10.5 the rate of hydrolysis is high and almost constant and at pH > 10.5 the rate sharply increases with an increase in pH [19]. To complete the picture it is worthwhile noting that under acidic conditions the formation of the species Cl\(_3^-\) (Eq. (11)) has also been reported to occur, particularly in concentrated chloride ion solutions [20–22].

\[
\text{Cl}_2 + \text{Cl}^- \rightleftharpoons \text{Cl}_3^-
\]  

(11)

Acknowledging that Eqs. (3) and (10) are acidic, Cheng and Kellal [22] predicted that a pH value as low as 2.0 would develop in the vicinity of the anode during typical electrochemical batch chlorine production. In ammonia containing solutions, it can be expected that the pH in the vicinity of the anode would drop to below pH 2 due to the additional acidity that is released in the ammonia oxidation reactions (Eqs. (4)–(6)).

For estimating the distribution of active chlorine species in the electrolyte solution near the anode, the local pH value should be known, along with the bulk chloride ion concentration, the ionic strength and the temperature. Fig. 2 shows the results of such a calculation, performed using the PHREEQC software [23] using the ST database, as a function of pH, assuming that: (1) the three dominant aqueous active chlorine species are Cl\(_2\)\(_{aq}\), Cl\(_3^-\) and HOCl; (2) the chloride ion concentration in the near anode area is not significantly lower than the bulk concentration; and (3) the active chlorine species are in chemical equilibrium according to Eqs. (10) and (11), i.e. 

\[
K_1 = \frac{(\gamma H^+ H^+)(\gamma Cl^- Cl^-)(\gamma HOCl HOCl)(\gamma Cl_2 Cl_2)}{(\gamma Cl_3 Cl_3)(\gamma Cl_3 Cl_3)}
\]

and

\[
K_2 = \frac{(\gamma Cl^- Cl^-)(\gamma Cl_2 Cl_2)(\gamma Cl_3 Cl_3)}{(\gamma Cl_3 Cl_3)}
\]

Where \(\gamma\) stands for activity coefficient calculated by the Davies equation (\(b = 0.3\)), brackets represent active concentration in (mol l\(^{-1}\)) and the thermodynamic values of \(K_1\) and \(K_2\) are 3.944 \(\times\) 10\(^{-4}\) [24] and 0.215 [25], respectively. For calculating \(K_1\) and \(K_2\) it was assumed that in \(K_1\) \(\gamma Cl_2\)\(_{HOCl}\) approximates \(\gamma HOCl\) and in \(K_2\) \(\gamma Cl_3^-\) \(\gamma Cl^-\) and \(\gamma Cl_2 = 1\) [24,25]. Fig. 2a and b shows the computed fractions (\%) of each of the three species out of the overall total active chlorine concentration for 0.2 mol l\(^{-1}\) and 1.0 mol l\(^{-1}\) NaCl solutions respectively.

Fig. 2 reveals that under the typical conditions prevailing in indirect ammonia electrooxidation reactions (\(\gamma Cl^- > 0.2\) mol l\(^{-1}\) and pH value in vicinity of anode \(<\) 2.2) the majority of the active chlorine in the near anode area is in the form of Cl\(_2\)\(_{aq}\). i.e. the major ammonia oxidizing agent in the anode vicinity is in all likelihood Cl\(_2\)\(_{aq}\) rather than HOCl, as previously suggested. As the distance from the anode surface increases, the pH value goes up and Cl\(_2\)\(_{aq}\) (which had not reacted with ammonia species) may be hydrolyzed to hypohalous acid. Note that thermodynamic equilibrium on the anode–electrolyte interface is hardly possible, because of the high rate at which chlorine species are removed from the anode surface area due to both convection and rapid reaction with ammonia species. Thus, since the species that is generated at the anode is Cl\(_2\)\(_{aq}\), the values shown in Fig. 2 are in fact an underestimation of the actual Cl\(_2\)\(_{aq}\) portion out of the total chlorine species concentration. Therefore, it can be stated with reasonable certainty that the oxidizing agents that play a role in electrochemical ammonia oxidation are mostly Cl\(_2\)\(_{aq}\) and (to a much lesser extent) HOCl, rather than HOCl alone, as erroneously reported in many publications [1,3,7–10,14].

Another site where localized conditions develop, which also affects the reactions sequence in indirect ammonia electrooxidation, is the solution layer around the cathode. There, pH may be

![Fig. 1. Combined chlorine and total dissolved nitrogen concentrations during break- point chlorination (NH4Cl solution = 51, [TAN] = 200 mg l\(^{-1}\) as N; chlorine solution = 25.64 g l\(^{-1}\) as Cl\(_2\), pH\(_{initial} = 7.8 \pm 0.15\)); and indirect ammonia electrooxidation (101 of NH4Cl + NaCl solution, [TAN] = 200 mg l\(^{-1}\) as N; [Cl\(_2\) = 50 g l\(^{-1}\), pH\(_{initial} = 8.0 \pm 0.15\), current = 1 A).](Author's personal copy)
elevated to above pH 12 due to $H^+_{\text{aq}}$ depletion (Eq. (2)) [22]. The role of the cathode in the overall ammonia electrooxidation reaction sequence is discussed later.

To verify the hypothesis that the extent of $\text{Cl}_2[\text{aq}]$ hydrolysis in the vicinity of the anode is responsible for the different results observed in chemical breakpoint chlorination and electrooxidation operation, batch electrolysis experiments were carried out.

3.3. Batch electrolysis experiments

The aim of this experiment set was to show the difference in composition and overall concentration of chloramines which form during batch electrolysis tests, as a function of the localized conditions (pH, Cl\textsuperscript{−} concentration) which develop in the vicinity of the anode and are responsible for the composition of chlorine species, as shown previously (Fig. 2). Based on Fig. 2 we hypothesized that when the operational conditions promoted low pH (along with sufficiently high Cl\textsuperscript{−} concentration) in the near anode area, $\text{Cl}_2[\text{aq}]$ would be the main oxidizing agent and consequently, chloramine concentration accumulation would be low.

Fig. 3 presents the results obtained in the absence (3a) and presence (3b) of phosphate buffer. The bulk pH in the batch electrolysis experiments was maintained constant at pH 8.0, however the applied buffering capacity ($\beta$) was very low (pure ammonium chloride solution) in the 1st experiment (3a), allowing the pH to drop near the anode, while in the 2nd experiment $\beta$ was high due to the presence of 0.1 mol l\textsuperscript{−1} phosphate buffer (Fig. 3b). The orthophosphate weak acid system was chosen as the buffering agent because it has a thermodynamic $pK_a$ values at 7.2 and 2.16, where the former exerts buffering capacity at the pH range close to that of the bulk electrolyte and the latter exerts a high buffering capacity at the pH range that is expected to develop in the vicinity of the anode. Another experiment, conducted with 0.25 mol l\textsuperscript{−1} phosphate concentration, was stopped after 1 h due to very low ammonia removal efficiency (results not shown), ascribed to phosphate sorption on the anode which has been previously reported to hamper chloride ions oxidation and promote oxygen evolution instead [1,26].

During the operation of the un-buffered electrolysis test (Fig. 3a) the maximal chloramine concentration that developed was 4.42% out of the initial TAN concentration (comprising of 1.61 and 0.5 mg l\textsuperscript{−1} as N of NH\textsubscript{3}Cl and NHCl\textsubscript{2}, respectively). As expected, in the buffered test (Fig. 3b) a significant increase was recorded in chloramine accumulation, with the maximal accumulated concentration amounting to 24.5% of the initial TAN concentration (the highest monochloramine and dichloramine concentrations were 10.62 and 1.23 mg l\textsuperscript{−1} as N, respectively).

Current efficiencies for ammonia oxodation recorded in experiments 3a and 3b were 92.1% and 72.5%, respectively.

No trichloramine was observed (DPD analysis) in the bulk electrolyte in both experiments.

The pH values measured in the near anode area (anode-mounted capillary) during the electrolysis test were pH 1.75, pH 6.43 and pH 6.73 for the un-buffered-, 0.1 mol l\textsuperscript{−1} P-buffered- and 0.25 mol l\textsuperscript{−1} P buffered experiments respectively.

Although these pH values can only be considered a rough estimation, they allow concluding with a considerable certainty that during non-buffered indirect electrochemical ammonia oxidation of solutions rich in Cl\textsuperscript{−}, the pH value close to the anode surface area is lower than pH 2.0, corroborating the conclusion that $\text{Cl}_2[\text{aq}]$ is the main ammonia oxidizing species.

Decreasing the Cl\textsuperscript{−} concentration in un-buffered experiments did not alter significantly the accumulated chloramine concentration. The highest chloramine concentration which accumulated in the bulk solution in experiments operated with 50, 25 and 10 g l\textsuperscript{−1} as Cl\textsuperscript{−} (no P buffer) was 4.42%, 5.1% and 6.2%, respectively. In spite of the observed slight increase in the maximal accumulated chloramine concentration at the lower Cl\textsuperscript{−} concentrations, the Cl\textsuperscript{−} effect could not be deduced from the above results, mainly because further decrease in chloride ions concentration was shown to lead to oxygen formation on the anode. In order to show the Cl\textsuperscript{−} effect and to strengthen the hypothesis that the extent of $\text{Cl}_2[\text{aq}]$ hydrolysis is responsible for the reaction sequence observed in batch electrolysis, $\text{Cl}_2[\text{g}]$ dosage experiments were performed.

3.4. $\text{Cl}_2[\text{g}]$ dosage experiments

In indirect ammonia electrooxidation operation the anode can be considered as a $\text{Cl}_2[\text{g}]$ source. Therefore, experiments with $\text{Cl}_2[\text{g}]$ dosage to ammonia solutions may be effective in trying to corroborate the main hypothesis, i.e. that the extent of $\text{Cl}_2[\text{aq}]$ hydrolysis to HOCl (which is a direct function of the pH developing near the anode, or alternatively, the $\text{Cl}_2[\text{g}]$ bubble-aqueous phase interface, and of the Cl\textsuperscript{−} concentration in the bulk solution) has a direct effect on the accumulation of chloramines in the bulk solution. From an experimental standpoint, the main advantage of the $\text{Cl}_2[\text{g}]$ dosage approach is the ability to maintain high pH buffering capacity along with any desired concentration of chloride ions in solution without altering the rate of active chlorine addition.

Fig. 4a-d shows the changes in concentrations of total dissolved nitrogen, NH\textsubscript{3}Cl and NHCl\textsubscript{2} with time in the experiments in which $\text{Cl}_2[\text{g}]$ was dosed to ammonium sulfate solutions (ammonia in excess) at a constant rate. Results are divided into experiments conducted in the absence and presence of chloride ions (50 g l\textsuperscript{−1}) and in the absence and presence of phosphate buffer (0.25 mol l\textsuperscript{−1}). Based on the leading hypothesis it was expected that in the un-buffered solution with the high chloride ions concentration Eq. (3) would proceed the least to the right, i.e. that the $\text{Cl}_2[\text{aq}]$
concentration would be maximal, and consequently, chloramine formation minimal. In contrast, in the buffered solution in the absence of Cl\(^{-}\) it was expected that Eq. (3) would proceed toward the products and thus the solution would behave more like in the classical breakpoint chlorination, i.e. chloramine formation would be substantial.

The results, presented in Fig. 4, corroborated the hypothesis. Table 1 lists the maximal fraction (presented in % out of the initial TAN concentration) of chloramine concentration that was converted into chloramines and accumulated in the bulk solution during the experiments. Neither trichloramine nor free chlorine concentration was observed by the DPD method in the bulk solution during the experiments. The total maximal chloramine concentration (NH\(_2\)Cl and NHCl\(_2\)) that developed during Cl\(_2\)(g) dosage into buffered (0.25 mol l\(^{-1}\) orthophosphate solution) ammonium solution that contained no initial chloride ions (Fig. 4c) was high: 60.6% of the initial TAN concentration. As in the electrolysis experiments, this high result was ascribed to the buffer that the phosphate system exerted around pH 2.0, which minimized the decrease in pH in the Cl\(_2\)(g) bubble-electrolyte diffusion layer. Consequently, dissolved chlorine was (to a large extent) hydrolyzed into hypochlorous acid which, in turn, reacted with NH\(_4\)\(^+\) ions to yield monochloramine and dichloramine according to Eqs. (7) and (8).

It is noted that weak acid systems with pK values which are at a distance of more than one pH unit from pH 3 and the pH of bulk solution, pH\(_{\text{bulk}}\) = 7.8–8.0 in this study (for example the ammonia system with pK\(_A\) = 9.25), will have no practical buffering capacity and thus no practical effect on the pH value in the near anode area (or the Cl\(_2\)(g)-aqueous phase interface in the Cl\(_2\) dosage experiments). Considering the results presented in Fig. 4 and Table 1: when neither phosphate buffer nor initial Cl\(^{-}\) concentration were present in solution (Fig. 4d), the maximal chloramine concentration recorded was 28.4% of the initial TAN value. In this experiment, the absence of the reaction product (Cl\(^{-}\)) shifted Eq. (3) to the right i.e. a considerable percentage of dissolved chlorine

![Fig. 3. Change in NH\(_4\)\(^+\) and chloramines (mono- and di-) concentrations versus time in batch electrolysis experiments. • - total dissolved nitrogen, ▲ - monochloramine, ■ - dichloramine, ◆ - combined chlorine. 3a - [PO\(_4\)\(^{3-}\)] = 0 mol l\(^{-1}\), [Cl\(^{-}\)]\(_0\) = 50 g l\(^{-1}\); 3b - [PO\(_4\)\(^{3-}\)] = 0.1 mol l\(^{-1}\), [Cl\(^{-}\)]\(_0\) = 50 g l\(^{-1}\). Electrolyte volume = 10 l, pH\(_{\text{inlet}}\) = 8.0, current = 1 A.]

![Fig. 4. Change in NH\(_4\)\(^+\) and chloramine (mono- and di-) concentrations with time during constant Cl\(_2\)(g) dosage experiments. [TAN\(_0\)] = 50 mg l\(^{-1}\) as N, volume = 10 l, pH\(_{\text{inlet}}\) = 8.0, Cl\(_2\)(g) flow rate = 7 ml min\(^{-1}\). • - total dissolved nitrogen, ▲ - monochloramine, ■ - dichloramine, ◆ - combined chlorine. 4a - [PO\(_4\)\(^{3-}\)] = 0 mol l\(^{-1}\), [Cl\(^{-}\)]\(_0\) = 50 g l\(^{-1}\); 4b - [PO\(_4\)\(^{3-}\)] = 0.25 mol l\(^{-1}\), [Cl\(^{-}\)]\(_0\) = 50 g l\(^{-1}\); 4c - [PO\(_4\)\(^{3-}\)] = 0.25 mol l\(^{-1}\), [Cl\(^{-}\)]\(_0\) = 0.0 g l\(^{-1}\); 4d - [PO\(_4\)\(^{3-}\)] = 0.0 mol l\(^{-1}\), [Cl\(^{-}\)]\(_0\) = 0.0 g l\(^{-1}\).]
was hydrolyzed into hypochlorous acid which reacted with NH₄⁺ ions to yield monochloramine and dichloramine according to Eqs. (7) and (8).

When a high Cl⁻ concentration was added to an un-buffered ammonia solution and Cl₂(g) was dosed (Fig. 4a), only 1.66% of the initial TAN concentration accumulated in the bulk solution as chloramines. The high Cl⁻ concentration and the low pH that developed in the Cl₂(g) bubble-solution interface resulted in Eq. (3) shifting to the left hence only a little Cl₂(aq) fraction hydrolyzed to HOCl and consequently only a small amount of chloramines accumulated in solution. In the experiment in which a high Cl⁻ concentration was added along with a high phosphate concentration (Fig. 4b), the maximal chloramine concentration amounted to 47.6% of the initial TAN concentration. In this case two contradicting processes governed the HOCI concentration that developed in the Cl₂(g)-aqueous contact layer. On the one hand pH was buffered by the high phosphate concentration, which promoted Cl₂(aq) hydrolysis to HOCl, but on the other the high Cl⁻ concentration shifted Eq. (3) slightly toward less Cl₂(aq) hydrolysis and thus the maximal chloramine concentration was lower than that recorded in the absence of Cl⁻.

The results of both batch electrooxidation and Cl₂(g) dosage experiments indicate that the main mechanistic difference between indirect electrochemical ammonia oxidation and classical breakpoint chlorination (in which either HOCl or OCI⁻ is dosed) stems from the presence and participation of Cl₂(aq) alongside HOCl in the oxidation process. It can be seen that when the operational conditions applied resulted in high Cl₂(aq) concentrations (i.e. low pH, high [Cl⁻]) Cl₂(aq) dosage to ammonia containing solutions yielded almost similar results to indirect electrochemical oxidation. Conversely, when the conditions promoted Cl₂(aq) hydrolysis to HOCl (i.e. high pH and absence of chloride ions) the process closely resembled the results obtained in classical breakpoint chlorination experiments.

3.5. Single-pass electrolysis experiments

In the previous sections it was established that the extent of Cl₂(aq) hydrolysis in batch tests plays a major role in the formation and accumulation of chloramine species in both electrolysis and Cl₂(g) dosage experiments. However, in order to unravel the ammonia oxidation mechanism under conditions that result in minimal Cl₂(aq) hydrolysis near the anode, it is imperative to try and differentiate between the reactions occurring in three locations: the vicinity of the anode, the vicinity of the cathode and the bulk solution. Such differentiation cannot be done batch-wise since the measured results in stirred batch experiments represent the outcome of all the reactions occurring simultaneously in all three locations. In an attempt to (partly) differentiate between the different reaction types and zones, low retention time single-pass electrolysis experiments were conducted. At least three samples from each single pass electrolysis experiment were analyzed for chloramines distribution by the specially developed UV absorption technique. The standard deviation in the analysis of each chloramine species was lower than 3%. According to the results of the single pass electrolysis experiments shown in Table 2, at least 58% and up to 88% of the overall active chlorine concentration produced at the anode reaches the bulk electrolyte solution as chloramines, out of which NCl₃ constitutes 30–48% of the total available chlorine found in the electrolyzer’s effluent.

All three chloramine species were present simultaneously in the electrolyzer effluents collected from the single pass experiments. This finding contradicts the well-known assumption that no more than two chloramine species can be present in the aqueous solution at any given pH [27]. This assumption was published on the basis of chloramination experiments performed at different pH values where the pH of free active chlorine solution, the pH of the ammonia solutions and/or the pH of the reaction mixture were adjusted to a desired value before or during the reaction. Hence the pH in the reaction mixture in Corbett et al.’s experiments was uniform [27], i.e. completely different from the conditions that developed in the experiments reported here. Table 2 reveals that indirect ammonia electrolysis comprises of three separate reaction locations characterized by totally different pH values: (1) the near anode area with pH < 2; (2) the bulk solution with pH close to neutral (pH 8.0 in the present experiments) and (3) pH > 12 in the near cathode area. The simultaneous existence of three pH regimes is the major reason for the difference in the reaction sequence between conventional breakpoint chlorination and indirect ammonia electrooxidation.

3.6. The proposed mechanism

The species trichloramine (NCl₃), which was measured in the electrolyzer’s effluents in single pass electrolysis experiments, forms in the near anode area under conditions of high Cl⁻ concentration and low pH. As explained before, when these conditions are met Cl₂(aq) is the dominant oxidizing agent in the near anode zone. Two general pathways for NCl₃ formation in the near anode zone can be proposed from the results obtained in this work: the first pathway comprises a reaction between ammonium ions and Cl₂(aq) as described in Eq. (12). As discussed later, the exact mechanism of this stoichiometric reaction is unknown and Eq. (12) may comprise more than one elemental step.

\[
3\text{Cl}_2 + \text{NH}_4^+ \rightarrow \text{NCl}_3 + 3\text{Cl}^- + 4\text{H}^+ \tag{12}
\]

The second possible pathway for trichloramine formation is the oxidation of mono- and dichloramine by Cl₂(aq) in the near anode area. NH₂Cl and NCl₂ species encountered in the effluents of the single-pass electrolysis experiments are apparently formed in more distant electrolyte layers (i.e. farther away from the anode, where pH is higher, allowing for significant Cl₂(aq) hydrolysis to HOCl) by the reaction between NH₃ and HOCl (Eqs. (13)–(15)).

\[
\text{HOCl} + \text{NH}_3 \leftrightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \tag{13}
\]

\[
2\text{NH}_2\text{Cl} + \text{H}^+ \leftrightarrow \text{NHCl}_2 + \text{NH}_4^+ \tag{14}
\]

\[
\text{NH}_2\text{Cl} + \text{HOCl} \leftrightarrow \text{NHCl}_2 + \text{H}_2\text{O} \tag{15}
\]

Consequently, under long electrolysis contact times or in batch electrolysis operation monochloramine and dichloramine which form in bulk electrolyte solution have the opportunity to react with Cl₂(aq) in the near anode area, yielding NCl₃, as described in Eqs. (16) and (17). According to Saguinsin and Moris [28] dichloramine

<table>
<thead>
<tr>
<th>Exp#</th>
<th>Orthophosphate concentration (mol⁻¹)</th>
<th>Chloride ion concentration (g l⁻¹)</th>
<th>Maximal accumulated combined chlorine (% of initial [TAN])</th>
<th>Maximal monochloramine conc. (mg l⁻¹ as N)</th>
<th>Maximal dichloramine conc. (mg l⁻¹ as N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>0</td>
<td>50</td>
<td>1.66</td>
<td>1.03</td>
<td>0.68</td>
</tr>
<tr>
<td>3b</td>
<td>0.25</td>
<td>50</td>
<td>47.6</td>
<td>21.03</td>
<td>1.86</td>
</tr>
<tr>
<td>3c</td>
<td>0.25</td>
<td>0</td>
<td>60.58</td>
<td>26.9</td>
<td>2.79</td>
</tr>
<tr>
<td>3d</td>
<td>0</td>
<td>0</td>
<td>28.39</td>
<td>10.41</td>
<td>3.5</td>
</tr>
</tbody>
</table>
is oxidized by Cl₂(aq) to NCl₃ 10,000 times faster than its respective oxidation rate by HOCl.

\[
\text{Cl}_2 + \text{NHCl}_2 \rightarrow \text{NCl}_3 + \text{Cl}^- + \text{H}^+ \quad (16)
\]

Monochloramine is also expected to be oxidized rapidly by Cl₂(aq) to NCl₃ (Eq. (17)), in spite of the fact that the writers could not find data on the rate of this reaction.

According to the proposed mechanism, significant formation of trichloramine in the near anode area is the process that governs the overall reaction sequence of the indirect ammonia electrooxidation process. Once NCl₃ is formed in the near anode area it is transferred into the bulk electrolyte solution and (within batch electrolysis or single pass electrolysis process with a long enough contact time) into the near cathode area where it decomposes at high pH conditions.

NCl₃ decomposition under basic conditions (Eq. (20)) is a two-step process (Eqs. (18) and (19)), in which dichloramine serves as an intermediate which reacts rapidly with trichloramine at both neutral and basic conditions to produce N₂ and OCI⁻ [15].

\[
\text{NCl}_3 + \text{OH}^- \rightarrow \text{NHCl}_2 + \text{OCI}^- \quad \text{(rate-determining step)} \quad (18)
\]

\[
\text{NCl}_3 + \text{NHCl}_2 + 5\text{OH}^- \rightarrow \text{N}_2 + 2\text{OCI}^- + 3\text{Cl}^- + 3\text{H}_2\text{O} \quad (19)
\]

The overall reaction:

\[
2\text{NCI}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 3\text{OCI}^- + 3\text{Cl}^- + 3\text{H}_2\text{O} \quad (20)
\]

Another NCl₃ decomposition pathway may occur through its reaction with NH₃ (Eq. (23)). This two step process has been reported to be base- or acid-assisted (Eqs. (21) and (22)) [29]:

\[
\text{NCl}_3 + \text{NH}_3 \rightarrow \text{HNCl}_2 + \text{NHCl}_2 \quad (21)
\]

\[
\text{NCl}_3 + \text{NHCl}_2 + 3\text{OH}^- \rightarrow \text{N}_2 + 2\text{HOCl} + 3\text{Cl}^- + 3\text{H}_2\text{O} \quad (22)
\]

The overall reaction:

\[
2\text{NCI}_3 + 3\text{NH}^- + 3\text{OH}^- \rightarrow 3\text{NH}_2\text{Cl} + \text{N}_2 + 3\text{Cl}^- + 3\text{H}_2\text{O} \quad (23)
\]

From Eqs. (18)–(23) one can conclude that the NH₂Cl and NHCl₂ concentrations encountered in the electrolyzer effluents were the products of the decomposition of trichloramine in the bulk electrolyte and in the near cathode area, where high pH conditions prevail.

NCl₃ decomposition occurs very rapidly in the near cathode area, due to the very high pH (pH > 12) encountered there, however NCl₃ may diffuse to the cathode only when a sufficiently long contact time is applied in the electrolysis unit or, alternatively, when indirect ammonia electrooxidation is performed batch-wise and the electrolyte is recirculated back and forth from the bulk solution to the electrolyzing unit. Vanlangendonck et al. [1] found no effect of pH on the oxidation rate of ammonia at the range pH 5.5–10 and similar results were reported by Chiang et al. [3], who studied indirect electrochemical treatment of leachate in the range pH 4–10. Since the rate of trichloramine decomposition under acidic conditions is slow, the results of Chiang et al. [3] and of Vanlangendonck et al. [1] can be explained only by fast decomposition of NCl₃ in the near cathode area.

The major reactions that occur in the three main reaction zones (i.e. near anode, near cathode and the bulk electrolyte solution) are summarized in Table 3, according to the suggested mechanism.

### Table 2

<table>
<thead>
<tr>
<th>Exp#</th>
<th>Current (A)</th>
<th>Cell AV (V)</th>
<th>Electrolysis contact time (s)</th>
<th>% of produced chlorine that reached bulk electrolyte</th>
<th>Total available chlorine in effluent (mg l⁻¹ as Cl₂)</th>
<th>Chloramines conc. in the effluent (mg l⁻¹ as Cl₂)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>3.42</td>
<td>1.6</td>
<td>88.52</td>
<td>18.05</td>
<td>NCl₂</td>
<td>11.65</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>3.91</td>
<td>1.6</td>
<td>63.20</td>
<td>25.78</td>
<td>NCl₂, NHCl₂</td>
<td>11.97</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>4.36</td>
<td>1.6</td>
<td>59.89</td>
<td>36.64</td>
<td>NCl₂, NHCl₂</td>
<td>12.04</td>
</tr>
<tr>
<td>4</td>
<td>4.0</td>
<td>4.70</td>
<td>1.6</td>
<td>58.79</td>
<td>47.96</td>
<td>NCl₂, NHCl₂, NHCl₃</td>
<td>12.13</td>
</tr>
<tr>
<td>5</td>
<td>5.0</td>
<td>5.12</td>
<td>1.6</td>
<td>63.40</td>
<td>64.65</td>
<td>NCl₂, NHCl₂, NHCl₃</td>
<td>12.18</td>
</tr>
<tr>
<td>6</td>
<td>3.0</td>
<td>4.11</td>
<td>6.36</td>
<td>58.86</td>
<td>141.50</td>
<td>NCl₂, NHCl₂, NHCl₃</td>
<td>12.26</td>
</tr>
<tr>
<td>7</td>
<td>3.0</td>
<td>4.10</td>
<td>2.64</td>
<td>65.13</td>
<td>65.17</td>
<td>NCl₂, NHCl₂, NHCl₃</td>
<td>12.09</td>
</tr>
<tr>
<td>8</td>
<td>3.0</td>
<td>4.18</td>
<td>1.15</td>
<td>58.30</td>
<td>25.71</td>
<td>NCl₂, NHCl₂, NHCl₃, NH₃</td>
<td>12.16</td>
</tr>
<tr>
<td>9</td>
<td>3.0</td>
<td>4.43</td>
<td>0.91</td>
<td>62.38</td>
<td>21.72</td>
<td>NCl₂, NHCl₂, NHCl₃, NH₃</td>
<td>12.11</td>
</tr>
</tbody>
</table>

Under both scenarios NCl₃ reacts to form NCl₂. NCl₂, in turn, is a product of monochloramine disproportionation (Eq. (14)) [11,30,31] or a product of a reaction between NH₂Cl and HOCl (Eq. (15)) [32].

Eqs. (14) and (15) and Eqs. (24) and (25) suggest that under acidic conditions trichloramine is a product of a stepwise reaction of free chlorine and ammonia, which proceeds through the formation of mono- and di-chloramine. This conclusion agrees with Sagunin and Moris [28], who reported that combining NH₄⁺ and HOCl solutions under buffered low pH conditions resulted in formation of NH₂Cl as a rate limiting step, which was followed by generation of NHCl₂ and NCl₃.

The literature has not addressed thus far the mechanism of NCl₃ formation in the absence of NH₂Cl and NHCl₂ as intermediates. Qiang and Adams [33], who investigated the rate and mechanism of monochloramine formation, concluded that the reaction between the ionic form of ammonia (NH₄⁺) and the non-ionic form of hypochlorous acid (HOCl) is “mechanistically impossible” and that NH₂Cl is formed via reaction between the nonionic forms, i.e. HOCl and NH₃. This reaction has been reported very rapid at near neutral, slightly basic conditions, with a second order rate constant of k₂ ≈ 2.97 × 10⁶ M⁻¹ s⁻¹ [33]. Yet, under the acidic conditions (pH < 2) prevailing in the near anode area during indirect ammonia electrooxidation hardly any ammonia exists in the unionized form (NH₃). Moreover, HOCl concentration is also very low (see Table 2) because most active chlorine exists in the Cl₂(aq) form due to the low pH and high [Cl⁻] found in the near anode area. As a result, formation of monochloramine as a precursor for trichloramine in the
near anode area is bound to be very slow and thus cannot explain the rapid NCl3 production observed in the single-pass electrolysis experiments conducted in the present work (retention times in the order of seconds). Therefore, the results must lead to the conclusion that NH4+ ions are oxidized in the near anode area and most likely this is done by Cl2(aq), the most dominant active chlorine species. In contrast with this conjecture, Chapin [34] postulated that Cl2(aq) was inert toward NH4+. This postulation was based on NCl3 concentrations measured in chloramination experiments conducted at very low pH values, induced by addition of either H2SO4 or HCl. Chapin [34] observed that when H2SO4 was used NCl3 formed while when HCl was used to reduce pH, it did not. He deduced that since trichloramine was in equilibrium with hypochlorous acid (Eq. (26)), which in turn was in equilibrium with Cl2(aq) (Eq. (3)), that the high Cl− concentration resulting from the addition HCl drove Eq. (3) (i.e. Cl2 + H2O → HOCl + H+ + Cl−) to the left [27,31.34], resulting in negligible HOCl concentration. He also calculated that upon the addition of H2SO4 a certain HOCI concentration remained, which (under his logic) was responsible for NCl3 formation, according to Eq. (26).

\[
\text{NCl}_3 + \text{H}^+ + 3\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + 3\text{HOCl}
\]  

(26)

Since Qiang and Adams [33] and Chapin [34] contradict each other and also appear to contradict the results obtained in the current work, it seems that further work is required to attain an unequivocal explanation of the mechanism(s) involved in NCl3 formation in the near anode area during indirect ammonia electrooxidation.

4. Conclusions

- Trichloramine is a significant product of indirect ammonia electrooxidation. NCl3 forms mainly in the near anode area due to the presence of a high Cl2(aq) concentration and decomposes to N2 and monochloramine either near the cathode or in the bulk electrolyte. In contrast, in classic breakpoint chlorination (pH 7–8) NCl3 serves only as an intermediate for N2 formation, and forms only during the last stage of ammonia oxidation. This is the main reason for the different results observed in the operation of breakpoint chlorination and indirect ammonia electrooxidation experiments.

- The observation that indirect electrooxidation of ammonia proceeds under batch conditions without significant chloramine formation was explained mechanistically. In parallel, it was shown that single-pass ammonia electrooxidation may result in high chloramine concentrations in the effluents.

- In the classical breakpoint chlorination the observed results depend highly on the nature of the applied chlorine species. Dosage of Cl2(g) to a neutral or slightly basic excess ammonia solution, with low buffering capacity and high chloride ion concentration, will result in very low bulk chloramine concentrations. The introduction of Cl2(g) results in local low pH conditions in the bubble-aqueous phase interface, which promote NCl3 formation, which is thereafter oxidized to NCl2(g) upon arrival to layers in the bulk solution where neutral/basic pH prevails. Under similar conditions, but with hypochlorite as the oxidant, stepwise formation of chloramines will be observed, followed by decomposition of NCl3 and NHCl2 to N2, i.e. classical breakpoint chlorination.

- Further work is required to understand and define the precise reaction sequence leading to trichloramine formation in the near anode area (or Cl2(g)→aqueous solution interfaces).

Acknowledgement

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Appendix A. Preparation of chloramines' standard solutions

Monochloramine stock solution (5.74 × 10−4 mol l−1) was prepared by slow addition of 30 ml NaOCl solution (800 mg l−1 as Cl2, pH 10.0) to 950 ml ammonium sulfate solution (9.152 mg l−1 as N, pH 9.3) under intensive stirring. The pH of the active chlorine and ammonia solutions was adjusted prior to reacting to 10.0 and 9.3, respectively, by NaOH (0.5 mol l−1). Six monochloramine standards (1.15 × 10−5–2.87 × 10−4 mol l−1) were prepared from freshly prepared NH2Cl stock solution and by dilutions with pH 8.5 (adjusted by NaOH 0.5 mol l−1) distilled water, and used immediately. Dichloramine stock solution was prepared from NH2Cl stock solution by decreasing its pH with ∼1 M HClO4 to pH 3.7. Portions of HClO4 were added to adjust the pH to 3.7 until pH change was less than 0.02 units within 10 min. At this point the NCl3 solution was placed into a stoppered brown glass flask and left to react for six hours before use. Dichloramine standard solutions were prepared by diluting a stock solution with pH 4.0 (adjusted by −0.01 HClO4) distilled water.

Trichloramine stock solution was prepared by intensive mixing of 250 ml 40 mg l−1 as N ammonium sulfate and 750 ml of 202.6 mg l−1 as Cl2 sodium hypochlorite solutions. Prior to mixing, the pH of the (NH4)2SO4 and NaOCl solutions was decreased to 3.0 and 3.5, respectively. The mixture was placed in a brown-glass stoppered flask and allowed to complete the reactions for 4 days in the dark. Six NCl3 standard solutions (9.29 × 10−6–2.322 × 10−4 mol l−1) were prepared by dilutions of an NCl3 stock solution with pH 3.2 (adjusted by −0.01 HClO4) distilled water. Stock NCl3 solution was standardized at 336 nm where the molar absorptivity of trichloramine is 195 mol−1 cm−1 [29].

Molar absorbivities of NH2Cl, NHCl2 and NCl3 within 190–400 nm range (1 nm resolution) were obtained from UV spectra of chloramine standards using 1 cm and 5 cm quartz cuvettes.

Appendix B. UV-spectrophotometric technique for simultaneous determination of chloramine species

A futile attempt was first made to analyze the composition of chloramines in the effluents of the single-pass experiments by the DPD method. This technique was abandoned because it gave results which indicated, erroneously, that free chlorine existed in the tested samples (at pH > 7 and excess TAN free chlorine cannot be present). Furthermore, the color intensity of the “free chlorine”

---

**Table 3**

Proposed mechanism of indirect ammonia electrooxidation.

<table>
<thead>
<tr>
<th>Near anode area</th>
<th>Bulk electrolyte</th>
<th>Near cathode area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode: 2Cl2 → 2Cl+ 2e−</td>
<td>Cl2 + H2O → HOCl + Cl− + H+</td>
<td>Cathode: 2H2 + 2e− → H2</td>
</tr>
<tr>
<td>3Cl2 + NH4+ → NCl3 + 3Cl− + 4H2O</td>
<td>HOCl + H2O → Cl2 + H+ + O2</td>
<td>NCl3 + OH− → NHCl2 + OCl−</td>
</tr>
<tr>
<td>2Cl2 + NH4Cl → NCl3 + 2Cl− + 2H+</td>
<td>NCl3 + H2O → NHCl2 + Cl2</td>
<td>NCl3 + NCl2 + 5OCl− → N2 + 2OCl− + 3Cl− + H2O</td>
</tr>
<tr>
<td>NCl3 + HClO → NHCl2 + Cl2</td>
<td>NHCl2 + Cl− + 3OH− → N2 + 2H2O + 3Cl−</td>
<td></td>
</tr>
</tbody>
</table>
DPD determination increased rapidly with time i.e. the reading was highly dependent on sample preparation time and had a very poor reproducibility. Regardless of the inaccuracy associated with the free chlorine analysis, the DPD method, when applied to the single-pass effluent samples for combined chlorine analysis, showed high concentrations of mono- and tri-chloramine. Dichloramine was also measured, but at concentrations much lower than those of [NHCl₂] and [NCl₃]. The reason for the inaccurate results obtained by the DPD method in this respect was ascribed to NCl₃ decomposition during sample preparation. Due to the discussed limitations of the DPD method, a new UV-absorption-based method for simultaneous determination of chloramine species was developed in this study.

Fig. B.1 represents typical UV absorption spectra of fresh effluent samples collected from the single pass electrolysis experiments.

Fig. B.1 shows that a prominent absorption peak exists at 220 nm. As shown in Fig. B.2, which represents the UV absorption spectra obtained with standard solutions of the three chlorine species and of NaCl solution, all chlorine species absorb UV light at 220 nm, however only NCl₃ has a pronounced absorption peak at this wavelength. Another evidence for the presence of NCl₃ in the effluent samples comes from the relatively high absorbance of the samples above 330 nm and up to 400 nm (Fig. B.1). As evident from Fig. B.2, neither monochloramine nor dichloramine absorb UV significantly at wavelengths higher than 330 nm, whereas trichloramine has a clear second UV absorption peak at 336 nm.

The strong absorbance of the effluent samples at the 240–360 nm range indicates possible presence of NHCl₂ and/or NCl₃ despite the absence of pronounced peaks at 243 nm and 294 nm typically associated with NHCl₂ and NCl₃, respectively (Fig. B.2). Thus, on the basis of the UV absorption spectra, it appears that all three chlorine species were present simultaneously in the effluent of the single pass experiments or phrased differently, the probability that the three exist together cannot be ruled out. The pH of the effluent was higher than 7 (except for experiment #6 in which the pH was 4.65), hence no free available chlorine should be found in the samples because of the rapid reaction between HOCl and ammonia species.

In order to quantify the concentrations of mono-, di-, and trichloramine in the effluents, the molar absorptivities of the three species were first determined at the range 190–400 nm (resolution = 1 nm) from the absorption spectra of standard chlorine solutions (6 for each chlorine species) using linear regression at each wavelength. Linear correlations (R² > 0.99) between UV absorption intensity and the concentrations of NHCl₂, NCl₃ and NCl₃ were recorded at the UV ranges: 202–301 nm, 190–345 nm and 190–400 nm, respectively. Having done this, the determination of the concentrations of the three chlorine species in the single-pass effluents was carried out using two mathematical procedures: first, simultaneous determination of NHCl₂, NCl₃ and NCl₃ was performed by multiple linear regression with three independent variables (for each wavelength) i.e. the molar concentrations of chloramines, and one independent variable – the absorption of the sample at a particular wavelength, as shown explicitly in Eq. (27). Calculations were performed using the Matlab (2010 version) software.

\[
A_{Bi} = C_{(NHCl_2)} \cdot a_{(NHCl_2)}(i) + C_{(NCl_3)} \cdot a_{(NCl_3)}(i) + C_{(NCl_3)} \cdot a_{(NCl_3)}(i) + b
\]

where \(A_{Bi} \) – absorption of sample at \( i \) nm (AU); \( C_{(NHCl_2)} \cdot C_{(NCl_3)} \) and \( C_{(NCl_3)} \) - concentrations of chloramines (M); \( a_{(NHCl_2)}(i) \) and \( a_{(NCl_3)}(i) \) – molar absorptivities of chloramines at \( i \) nm (mol⁻¹ cm⁻¹); \( b \) – intercept (AU).

The second mathematical procedure involved (a) determination of NCl₃ concentration from UV absorption in the 360–380 nm range where the absorptivities of mono- and dichloramine can be neglected. [NCl₃] was calculated as the slope from the linear regression of Eq. (28).

\[
A_{Bi} = [NCl_3] \cdot a_{(NCl_3)}(i) + b
\]

and (b) determination of [NHCl₂] and [NCl₃] by multiple linear regression (Eq. (29)) with two independent and one dependent variables for each wavelength using Matlab.

\[
A_{Bi} = C_{(NHCl_2)} \cdot a_{(NHCl_2)}(i) + C_{(NCl_3)} \cdot a_{(NCl_3)}(i) + [NCl_3] \cdot a_{(NCl_3)}(i) + b
\]

The optimal UV range for the linearization applied in the first and second (2b) procedures was found using simulation calculations. Simulative UV spectra comprising one, two or three chlorine species were obtained by superposition of individual spectra of NHCl₂, NCl₃ and NCl₃ standard solutions with different concentrations. The simulative UV spectra were used as an input for both chloramines determination procedures. Calculated concentrations of chloramine species were compared to real concentrations that comprised the simulative spectra and the optimal UV range of 240–400 nm was obtained from the lowest error. Another justification for using the 240–400 nm range in the calculations was the possible presence of an “undefined intermediate” resulting from chloramines decomposition, which had been reported to absorb strongly at bellow 220 nm but also to have an insignificant absorbance above 240 nm [29]. Molar absorptivities calculated by linear regression in non linear (R² < 0.99) wavelength ranges (>301 nm for monochloramine and >345 for dichloramine) were relatively low (<5.5 and <15.6 mol⁻¹ cm⁻¹) for NHCl₂ and NCl₃, respectively). Consequently, poor accuracy of molar absorptivities determined by linearization in these wavelengths regions for
mono- and dichloramine should not have a significant influence on the results. The difference in NCl$_3$ concentrations calculated by two procedures was less than 10%. Table B.1 shows the results of several simultaneous determinations of three chloramine species (procedure I).

### Appendix C. Simultaneous determination of ammonia and monochloramine

Determination of ammonia by salicylate method [17] is based on transformation of NH$_3$ to NH$_2$Cl$_2$ by reaction with NaOCl which produces colored complex with salicylate under the presence of trisodium nitroprusside as catalyst. Monochloramine concentration can be determined by omitting the NaOCl addition step from the procedure of Willis et al. (1996) [35]. This analysis is not affected by the presence of ammonium ions and dichloramine [35]. The slope of color intensity versus NH$_2$Cl$_2$ concentration was higher by about 25% relative to the slope obtained with NH$_4^+$ at the same concentration (mg$^{-1}$ as N), however, the addition of NaOCl to monochloramine standards resulted in a slope increase of only 5%, possibly due to ~5% ammonia excess applied within the preparation of NH$_2$Cl$_2$ stock solution. Consequently, a modified Willis et al.'s [17] procedure was applied in the current study to determine the overall dissolved nitrogen concentration in samples which contained both NH$_3$ and NH$_2$Cl$_2$. To determine the TAN concentration, NH$_2$Cl$_2$ was determined by omitting the NaOCl addition step (a similar volume of distilled water was added instead to maintain the same mixture volume) and this concentration was subtracted from the total dissolved N concentration.

### References