

CHLORAMINATION OF POLYAMIDE-BASED REVERSE OSMOSIS MEMBRANES IN THE PRESENCE OF HALIDES

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Dedication
To My Family

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LIST OF ABBREVIATIONS

Abbreviation	Name
mg/L	milligrams per liter
ppm	parts per million
nM	nano molar
μ M	micro molar
mM	milli molar
M	molar
nm	nano meter
HPLC	high performance liquid chromatography
	liquid chromatography with mass
LC/MS	spectrometry
DAD	diode array detector
GC/MS	gas chromatography with mass spectrometry

ABSTRACT

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Title: Chloramination of Polyamide-Based Reverse Osmosis Membranes in Halide-Containing Waters

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Polyamide based reverse osmosis (PA-RO) membranes are applied for the desalination of halide-containing waters such as seawater and brackish groundwater. They are the industry standard because of their high selectivity and ability to withstand a wide range of pH. However, one of their pitfalls is their propensity to undergo biofouling, which is deterioration due to biological growth. Biofouling is known to dramatically decrease membrane performance and increase energy consumption. In order to overcome biofouling, a disinfectant, typically free chlorine, is applied; however, free chlorine is known to react with the polyamide layer and result in further membrane deterioration and performance loss.

One topic that has garnered less attention is the application of chloramines and their interactions with the PA-RO membrane when applied as a biofouling control. Furthermore, the role of halides (e.g. chloride, bromide, and iodide) in the presence of chloramines must be further explored because they are known to react to form secondary species which are reactive toward PA-RO membranes. In Chapter 2, the PA based monomers benzanilide (BA) and *N*-Methyl-*N*-phenylbenzamide (*N*-CH₃-BA) were used to model the PA layer. Monomers were exposed to halide containing waters and chloraminated with pre-formed NH₂Cl over a wide range of pH. The decay and by-product formation after exposure were evaluated using HPLC-DAD, LC/MS, and/or GC/MS. Results indicated that pH of the system and bromide concentration controlled parent compound decay and brominated by-product formation, where low pH and high bromide concentrations led to the highest formation of brominated by-products.

In Chapter 3, commercially made PA-RO membranes (SWC4-LD) were chloraminated or chlorinated with and without halides over a wide pH range. Their performance was evaluated after exposure through flux experiments using a dead-end flow cell. Results indicated that exposure to free chlorine led to the greatest change in flux and monochloramine resulted in the smallest change in flux. During chloramination of the membranes, the reactors containing bromide led to further

change in flux than the chloramine only conditions. This was likely due to formation of secondary species that were reactive toward the PA membrane. Furthermore, Chapter 4 summarizes overall research contributions from this work and proposes future work pertaining to this topic.

1. INTRODUCTION

1.1 Problem with Diminishing Freshwater

Currently over 844 million people live without access to safe drinking water, and by the year 2025, half of the world's population will live in a water stressed area.¹ It is widely accepted that a lack of freshwater and overall water scarcity is one of the greatest issues of our time.² Various factors lead to the exacerbation of global water scarcity including population growth, climate change, and industrialization of developing countries.³ Water scarcity is especially dire since only ~ 0.8% of the world's freshwater is available for human consumption.⁴ Because of this lack in freshwater and the growing urgency to provide it, it is crucial to look towards unconventional yet sustainable technologies to harvest freshwater. Methods for water reuse and desalination include using seawater, brackish water, or recycled wastewater to meet global needs for freshwater consumption.

Finding ways to reuse and desalinate water has been of interest for thousands of years dating back to evidence of reusing wastewater for agricultural irrigation.⁵ The first application of desalination was through thermal desalination which occurred before the 17th century.⁶ Thermal desalination occurs when heat is applied to separate water from salt. The two types of thermal desalination, also known as thermal distillation, are multistage flash and multiple effect distillation.⁷ Thermal distillation paved the way for implementing more advanced membrane technology. The first place to implement thermal technology in a full-scale plant was in the Middle East, but it was highly inefficient.⁸ By the 1950s and 1960s, the use of membrane technology became of interest. Using membranes, a polymer film can separate salt from water. The first plants to use membrane technology were implemented in the Middle East, which has been a hub for water desalination technology since the 1930s.⁸

1.2 Principles of Membrane Separation

Membrane separation was created after thermal separation in order to remove dissolved constituents from water in a more effective way. The application of membranes is inherently more energy efficient than the use of thermal techniques.⁷ Membrane processes are either pressure driven or electrically driven. Pressure driven strategies include reverse osmosis (RO) or

nanofiltration (NF), and electrically driven separation is applied for electrodialysis (ED). ED membranes use electrically driven principles where the driving force of separation is an electrical potential. The ionized salts are either positively or negatively charged; therefore, when the direct current is applied, the positively charged salts will go to the anode and the negatively charged salts will go to the cathode. Salt is gradually removed from the solution, leaving a diluted solution behind.⁵

When using RO or NF to separate pure water from salt solutions, a pressure driven gradient opposes the direction, and is greater than, the osmotic pressure driven across the membrane leading to flow from the more concentrated stream to the less concentrated stream.⁵ Figure 1-1 below describes this phenomenon where Δp is the applied pressure and $\Delta \pi$ is the osmotic pressure.⁷

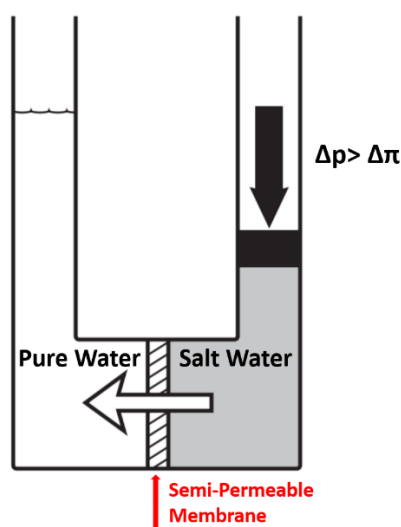


Figure 1-1. Reverse osmosis separation process (Figure modified from Baker 2004⁷)

In pressure driven processes, a feed stream is separated by the semi-permeable membrane into a concentrate stream and a permeate stream. Semi-permeable material is defined as a material that allows some components from the feed stream to pass through the membrane but does not allow others to pass through.⁹ In this process, the concentrate stream contains the rejected components and the permeate stream contains the components that were not rejected by the membrane. The concentrate is highly concentrated salts, microorganisms, or organics, and the feed leaves the system as the product with only the particles that the membrane allows to pass through.⁹ In Figure

1-2 below, Q, C, and P stand for flowrate, concentration, and pressure, respectively. The subscripts F, C, and P stand for feed, concentrate, and permeate, respectively.

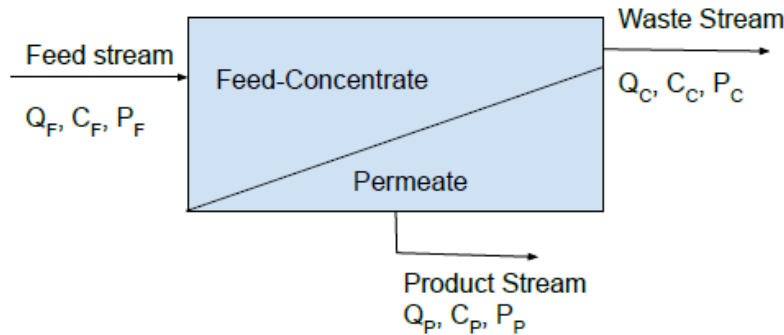


Figure 1-2. Simplified Diagram for RO and NF Membrane System

Although RO and NF are pressure driven processes that require the applied pressure to be greater than the osmotic pressure to achieve separation, the mechanisms by which they reject solutes vary due to their characteristics including permeability, charge, and pore size of the membranes.¹⁰ In nanofiltration (NF) membranes, transport through the membrane happens through a combination of mechanisms including advection and solution-diffusion.¹⁰ Transport through NF membranes can be described through a pore-flow model.¹¹ Using this model, rejection of particles can occur based physiochemical properties of the membrane through a combination of hindered diffusion, advection, and electromigration through membrane pores.^{11,12} Because of the conglomeration of mechanisms, NF transport is rigorous to model.¹⁰

In reverse osmosis (RO), the semi-permeable membrane is dense and does not contain defined pores. Therefore, the mechanism by which salt and water permeate through a reverse osmosis membrane can be described by the solution-diffusion model.^{7,10} The water and solute transport is guided by partitioning into and diffusion through the active layer.¹³ The water flux through the membrane can be associated with the pressure and concentration gradients across the membrane. The flux is described in equation 1 where J_w is the water flux, A is the water permeability coefficient, Δp is the applied hydraulic transmembrane pressure, and $\Delta\pi$ is the osmotic pressure difference across the active layer.^{3,7} When $\Delta p > \Delta\pi$, flow occurs across the membrane.

$$(1) J_w = A (\Delta p - \Delta\pi)$$

The salt flux across the membrane can be described by equation 2 where J_s is the salt flux, B is the salt permeability constant, and $c_{j,o}$ and $c_{j,l}$ are the concentration of the feed and permeate solutions, respectively.

$$(2) J_s = B (c_{j,o} - c_{j,l})$$

Because $c_{j,o}$ is much larger than $c_{j,l}$, equation 2 can be simplified to equation 3.

$$(3) J_s = B \times c_{j,o}$$

Based on these equations, it is evident that the water flux is dependent on applied pressure, whereas salt flux is independent of applied pressure. Therefore, membrane selectivity increases proportionally to pressure.⁷ One way selectivity can be measured is through salt rejection (R_{ej}).⁹ This is one way to determine the performance of the RO membrane. Rejection can be determined based on combining equations 1-3 to yield equation 4.

$$(4) R_{ej} = \left[1 - \frac{p_i B}{A(\Delta p - \Delta \pi)} \right] \times 100$$

The salt rejection (R_{ej}) of RO membranes can be experimentally determined by measuring the concentrations of $c_{j,o}$ and $c_{j,l}$ using a total dissolved solids (TDS) meter. Rejection can also be described by equation 5.

$$(5) R_{ej} = \left[1 - \frac{c_{j,l}}{c_{j,o}} \right] \times 100$$

1.3 Applications of RO and NF Membranes

Nanofiltration membranes have properties of both RO membranes and ultrafiltration membranes, where some separation occurs through diffusion but separation is also achieved through size exclusion mechanisms.¹³ Therefore, NF membranes are designed to reject different solutes at varying efficiencies and operate at a pressure of approximately 10 bar.⁷ For example, NF membranes reject NaCl only at a rate of 20 to 80%, but they can reject some divalent ions such as Mg^{2+} and Ca^{2+} at an efficiency of > 99%.⁷ Therefore, NF membranes are an excellent choice for water softening.⁹

Alternatively, RO membranes can reject monovalent ions such as NaCl at rates of over 99% and operate at different pressures depending on the concentration of NaCl and other ions in the feed.⁷ Because RO membranes have been designed with varying permeability and rejection characteristics, they can be used to: (i) desalinate ocean and brackish groundwater, (ii) for water reuse, and (iii) to create high purity process waters for industrial applications.^{7,9}

One of the major water quality parameters linked to membrane filtration and performance efficiency is the total dissolved solids (TDS) present in each type of water because it has implications on applied pressure and energy consumption of the process.⁷ For example, brackish groundwater has 1000 to 5000 mg/L TDS, and seawater contains 35,000 mg/L TDS.^{7,14} Therefore, the pressure applied for salt separation for brackish waters is approximately 30 bar compared to approximately 60 bar for desalination of seawater.⁷ This means the desalination of brackish water is much less energy intensive than seawater desalination. Because of the high quantity of TDS in seawater and brackish water streams, environmental issues arise when dealing with the discharge of brine and the high energy intensity, typically associated with seawater.³

For water reuse, RO is applied after the water has been treated by ultrafiltration (UF) and microfiltration (MF), and it is typically for recycling wastewater.⁵ Reused wastewater treated by RO can be applied for irrigation and industrial processes including cooling tower and evaporative cooler make up water.⁵ There is still some concern that remains with using RO due to the presence of pharmaceuticals and other endocrine disrupters present in the wastewater stream.⁹

1.4 Reverse Osmosis Polymer Materials

The search for the ideal membrane materials to implement for water desalination and reuse has always been a challenge because of membranes' high fouling susceptibility and the inherent tradeoffs between membrane selectivity and permeability.³ One major drawback to current RO membranes on the market is their predisposition to undergo fouling for several reasons, which causes the membrane performance to decline (e.g. change in flux and decrease in selectivity).⁷ In order to overcome the fouling attributed to biological growth (biofouling), a disinfectant, typically free chlorine, is added. Although free chlorine addition alleviates fouling, free chlorine reacts with the active layer to further deteriorate the membrane over time. This effect increases energy consumption and operating costs.^{2,15} Because of RO membranes' inability to withstand free chlorine, the ideal membrane for RO is chemically resistant and can effectively separate solutes (e.g. high selectivity) from water with a high flux (e.g. high permeability).³ The following sections will delve into characteristics and trade-offs of cellulose acetate (CA) and polyamide (PA) RO membranes.

1.4.1 Cellulose Acetate

The first generation of RO membranes were created in 1959, and they are known as cellulose acetate (CA) membranes.¹⁶ The degree of acetylation of CA membranes controls their performance where an increase in acetylation leads to a higher rejection but also a lower flux.¹⁷ Current CA membranes on the market that contain 40% acetate by weight, have a degree of acetylation of 2.7, and can reject salt at a rate of 98 to 99%.⁷ Although most CA membranes have been replaced today, some remain since CA membranes can continuously withstand free chlorine concentrations up to 1 mg/L.⁷ The ability to withstand even 1 mg/L of free chlorine is an excellent advantage because free chlorine mitigates biofouling. The major issues with these membranes lie within the structural properties. CA membranes undergo hydrolysis in acidic and alkaline pH.¹⁸ Hydrolysis leads to increased flux and decreased salt rejection. Therefore, they can merely operate in the pH range of 3 to 8. Additionally, they are unable to withstand a temperature greater than 35 °C.¹⁸ Due to the structural pitfalls of CA membranes, efforts have shifted towards thin film composite (TFC) membranes, which will be described in the following section.

1.4.2 Polyamide

In recent years, most RO membranes have a thin film composite (TFC) structure consisting of a thin film active layer, an intermediate polysulfone (PSf) layer, and a polyester base. The thin film active layer is 20 to 200 nm-thick and controls the membrane separation. The active layer resides on top of the polysulfone intermediate (~30 to 50 μm -thick) and a polyester base (~200 μm -thick), which provide structural integrity for the active layer.¹⁹ The top active layer contains polyamide-based (PA) polymers, which are currently the industry standard applied for forward osmosis (FO), NF, and RO.² The widespread use of PA based RO membranes is due to their ability to withstand a wide range of pH (3 to 11) without the result of hydrolysis, and because they allow for half the salt passage and twice the flux of the traditional CA membranes.⁷

Polyamide-based TFC RO membranes are made through interfacial polymerization. The interfacial polymerization process uses a diamine, typically m-phenylenediamine (MPD), in the aqueous phase and trimesoyl chloride (TMC) in the organic phase.^{20,21} The aqueous MPD is first in contact with the PSf support in order to allow the MPD to diffuse into the membrane before the excess MPD is removed. Next, the organic TMC is put into contact with the MPD on the PSf. The MPD and TMC crosslink forming the polyamide layer. Hydrolysis occurs on the non-crosslinked

acyl chloride groups leading to the formation of negatively charged carboxylic acid groups.³ Therefore, the membrane has a negative charge. A diagram for this process is shown below (Figure 1-3).

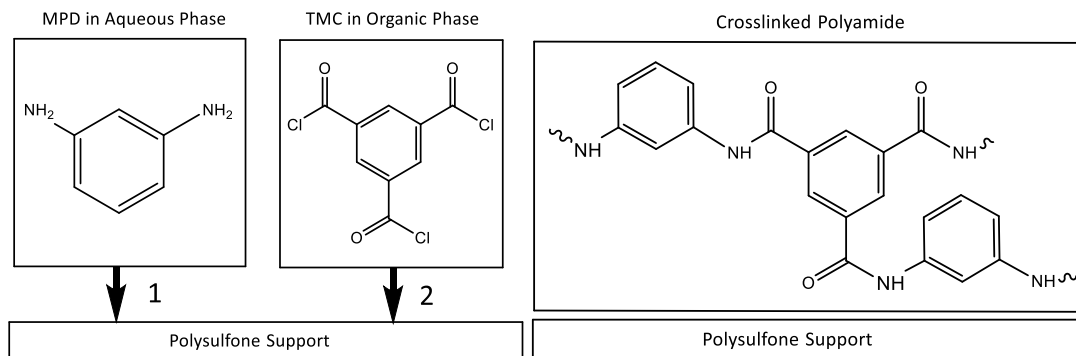


Figure 1-3. Interfacial Polymerization to Crosslinked Polyamide on a Polysulfone Support Layer

Despite the excellent qualities of TFC-PA-RO membranes, they are more susceptible to fouling by biological growth (biofouling) and less resistant to free chlorine than CA membranes. In fact, the effects of free chlorine on PA based RO membranes have long been a topic of interest. Studies using PA based monomers, PA powder, and commercial PA membranes have aimed to better understand the degradation mechanisms of PA-RO membranes when free chlorine is applied.^{22–27} Based on these studies it can be concluded that free chlorine does irreversible damage to the membrane, but some of the degradation mechanisms remain unclear. A full understanding of the degradation mechanisms of the PA layer informs future development of chlorine resistant membranes. Unfortunately, gaps pertaining to the degradation mechanisms remain when comparing behavior to PA based monomers and commercial membranes.^{26,27}

1.5 Novel Membrane Technology

There have been many strategies to make novel state of the art desalination membranes including using aquaporin channels, carbon nanotubes, synthetically designed nanochannels, graphene-based frameworks, and polymerizable surfactants.^{2,3} The objective of these membranes is to separate salt from water in a high flux and high rejection manner while resistant to damage by free chlorine. These novel materials have proved to only be marginally better than the widely used polyamide-based RO membranes.³ The development of next generation membranes will be

based on size exclusion separation mechanisms opposed to the current mechanism used in TFC membranes which is solution-diffusion.³

1.6 Industrial Use of Chloramines

Limitations of free chlorine and the only marginal improvements of novel membrane technology, lead to the need for further study on biofouling controls used for PA-RO membranes. One option to solve this problem is the use of chloramines opposed to free chlorine, which are commonly used as a residual disinfectant in water treatment.²⁸ Chloramines could serve as a promising alternative as a biofouling control because they are a weaker disinfectant than free chlorine.²⁹ In fact, chloramines have also proved to be an effective biofouling control for PA based RO membranes.^{30,31} However, previous studies have found that chloramines, particularly monochloramine (NH_2Cl), results in oxidative damage to the PA-RO membrane causing an increase in flux and decrease in salt rejection at pH 8 to 8.3 but to a substantially lesser degree than free chlorine.^{30,32,33}

Subsequently, issues arise when chloramines are applied to seawater or brackish waters due to the presence of halides (e.g. chloride, iodide, and bromide) in the water matrix. The seawater concentrations of these halides are 0.54 M, 0.84 mM, and 0.5 μM for chloride, bromide, and iodide, respectively.³⁴ For brackish waters, chloride and bromide are present at <0.37 and <0.007 mM, respectively.³⁵ Chloramines are known to react with bromide and iodide to form secondary agents that are reactive toward PA-RO membranes.^{15,24,36,37} One study investigating the effects of chloramination on bromide and iodide containing waters on PA membranes, found that irreversible ring halogenation and an increase in carboxylic groups occurs, where hydrolysis of the amide group results in amide bond cleavage at pH 8.³⁸ Although it is known that further damage occurs to the PA membrane when halides are present during chloramination, gaps regarding the halogenation and degradation pathways, role of halide concentrations, and role of pH remain unfilled when the PA membrane is chloraminated in the presence of halides.

Before further discussion on the reactivity of chloramines and halides towards the PA layer, focus will be directed to the history of chloramine use and fundamentals of chloramine chemistry in order to set the framework for the following chapters.

1.6.1 Background on Chloramines for Water Reuse

As a result of reactions between halides and chloramines forming stronger secondary agents, chloramines have typically been applied for water reuse where fewer halides are present compared to during water desalination. Chloramines have been applied as a disinfectant since the 1940s, but they became more popular once it was confirmed that they form less regulated disinfection by-products (DBPs) than when free chlorine (HOCl/OCl^-) is applied as a disinfectant.⁹ Other advantages in using chloramines as a disinfectant in distribution systems include their long-lasting residual and biocidal properties.^{28,30} As of 2004, approximately 1 in 4 water reuse utilities applied chloramines.⁹ Typically, when chloramines are used monochloramine (NH_2Cl) or free chlorine (HOCl/OCl^-) is the desired residual within the distribution system. NH_2Cl is a weaker disinfectant than free chlorine even though it has the same oxidizing capacity as free chlorine on a chlorine atom basis.²⁹

1.7 Fundamental Chloramine Chemistry

Chloramines offer capability in water disinfection and biofouling control but full understanding of their reactivity towards polyamide remains poorly understood. One factor that complicates this is the complexity of chloramine chemistry. First, when chloramines are applied as a disinfectant, either breakpoint chlorination or chloramination is the target method of disinfection, where free chlorine or monochloramine are the dominant desired residuals, respectively. When breakpoint chlorination is applied, the free chlorine (HOCl/OCl^-) to ammonia (N) ratio on a molar basis is approximately 1.6; whereas, in chloramination the Cl/N molar ratio is <1 . When converted to a mass basis, chloramination occurs when the Cl/N ratio is 3.5 to 5 and breakpoint chlorination occurs when the Cl/N ratio is around 8.5. Figure 1-4 is the breakpoint curve when applied at pH 8.

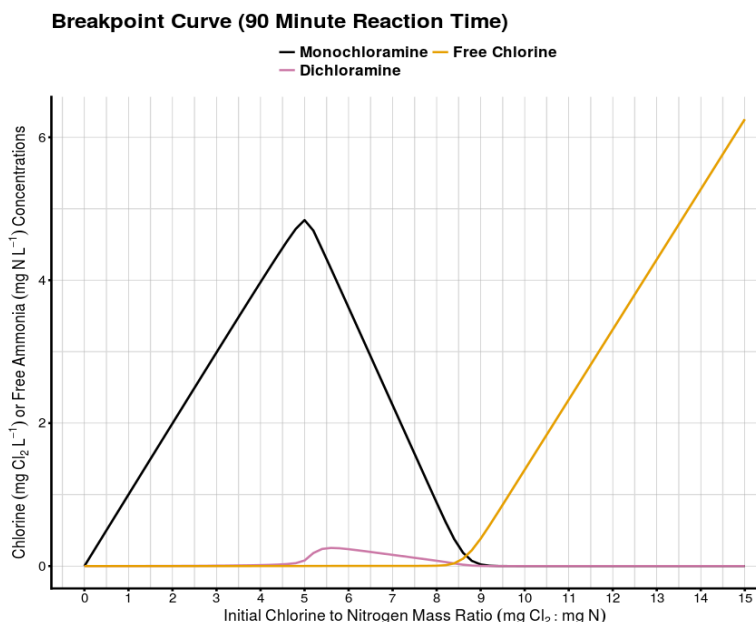
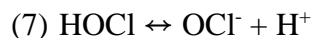
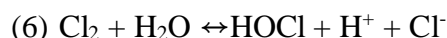


Figure 1-4. Breakpoint chlorination curve at pH 8, with 150 mg/L CaCO₃, t = 25° C, and 1.0 mg/L as free ammonia (<https://usepaord.shinyapps.io/Breakpoint-Curve/>)^{28,39}

When using chloramines, it is important to understand the chemistry behind how they form and decompose during breakpoint chlorination, chloramination, and the transition region ($1 > \text{Cl}/\text{N} > 1.6$). The speciation of formation and decomposition of chloramines occurs through a set of reactions including (i) substitution reactions between HOCl, ammonia, chlorinated derivatives of ammonia, and their corresponding hydrolysis reactions (eqs. 9-11), (ii) disproportionation reactions of chloramines and their back reactions (eq. 12) (iii) redox reactions that occur in the absence of free chlorine (eqs. 13-16), and (iv) the redox reactions that occur when free chlorine is present (eqs. 17-19).³⁹ All subsequent reactions are based on well-known equilibrium reactions between species and aqueous solutions (eqs. 6-8).⁴⁰⁻⁴²

Equilibrium Reactions:



Substitution Reactions:

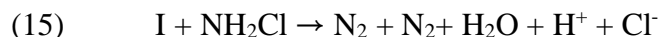
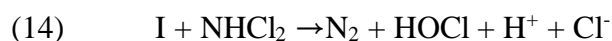
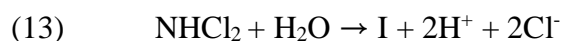


Disproportionation Reactions:



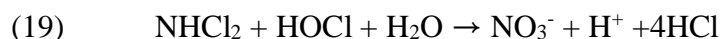
The disproportionation of NH_2Cl is general acid catalyzed; therefore, any species that can donate a proton will contribute to the catalysis of the disproportionation reaction. For example, as pH decreases, or the buffer concentration increases, the rate of the disproportionation reaction increases.³⁹ Before the disproportionation of NH_2Cl , there is no redox chemistry occurring in the system. The disproportionation of NH_2Cl leads to the formation of NHCl_2 , and all redox chemistry proceeds through NHCl_2 .³⁹

Under chloramination conditions, where $\text{Cl}/\text{N} < 1$, the redox by way of NHCl_2 occurs quite slowly. Therefore, at high pH and $\text{Cl}/\text{N} < 1$, NH_2Cl is the most stable residual. In this set of reactions “I” represents a reaction intermediate. The redox reactions that occur when NH_3 is in excess (e.g. chloramination) are shown below (eqs. 13-16):



In the transition region ($1 < \text{Cl}/\text{N} < 1.6$) or under breakpoint conditions, the redox reactions proceed extremely quickly compared to the redox reactions occurring when chloramination conditions prevail. These reactions control the location of the breakpoint, which is the Cl/N ratio where free chlorine becomes the dominant residual with trace NCl_3 present. As the pH increases, the location of the breakpoint will shift down (e.g. lower Cl/N ratio). The set of redox reaction that occur at high Cl/N ratios are as follows:





All subsequent models that assess how chloramines behave in the presence of other compounds or constituents in water are derived from this model. *The overall takeaways of this model are that pH and Cl/N ratio have the greatest impact on NH₂Cl stability.* The rate of NH₂Cl disproportionation increases when the pH decreases or when any additional species are present in the system that can donate a proton. Additionally, an increase in the Cl/N ratio results in higher NHCl₂ formation, and all redox reactions occur through NHCl₂ (eqs. 13 and 17).³⁹

1.7.1 Effect of Mixing Conditions on Chloramine Speciation

When chloramines are applied in industrial systems, precautions ensue so that the desired residuals persist. As previously stated, pH and Cl/N ratio have dominant effects on NH₂Cl stability,³⁹ but one less studied parameter is the order of addition of ammonia (typically in the form of ammonium (NH₄Cl), the conjugate acid) and free chlorine. There are many ways to apply chloramines. When free chlorine is applied for drinking water, it is either in the form of chlorine gas or hypochlorite solution. Ammonia must be also supplied to achieve a chloramine residual, which can be added in three forms including pure liquid ammonia, aqueous ammonia, and as an ammonium salt.⁹ The order of reagent addition is a topic of interest because adding chlorine to water that already has ammonia can lead to undesirable reactions when mixing occurs.⁴³ Another option is to make pre-formed NH₂Cl and add it to the system. The type of reagent and order of reagent addition has been found to alter how NHCl₂ is formed, which can subsequently affect how NHCl₂ generates disinfection by-products (DBPs), such as N-nitrosodimethylamine (NDMA).⁴³ It has been found that when OCl⁻ is added to the ammonia-containing solution to make NHCl₂, a high concentration of OCl⁻ is locally present prior to complete mixing and thus the Cl/N ratio is >1. This effect leads to the partial formation of NHCl₂.⁴³ Alternatively, when NH₄Cl is added to a solution of OCl⁻, the localized Cl/N ratio is <1, promoting the desired formation of NH₂Cl.⁴³

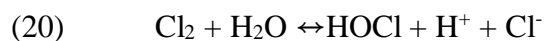
1.7.2 Chloramines and Halides

As stated previously, chloramines can be applied as a disinfectant in water reuse systems or as a biofouling control for PA-RO membranes.^{30,31} However, the presence of halides complicates

chloramine chemistry leading to formation for precursors for DPBs or secondary species that are reactive towards PA.^{24,36,37,44,45} Here, the focus will be on how chloramines behave in the presence of halides including chloride, bromide, and iodide. The primary objective will be on the reactions between chloride, bromide, and iodide with chloramines and how their secondary species react with the PA membrane.

1.7.2.1 Chloride and Chloramines

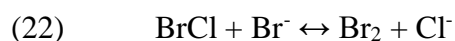
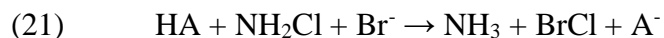
Less attention has been allocated to the role of chloride in the presence of chloramines and the subsequent effects on the PA-RO membrane. This is because chloride does not react directly with NH_2Cl to form other reactants (eqs. 6-13). However, the presence of chloride can impart an indirect role at low pH. As pH decreases, NH_2Cl is less stable and more products form.³⁹ One product that forms is HOCl , and when HOCl is in the presence of a high concentration of chloride and low pH, Cl_2 can form (equation 20).⁴¹

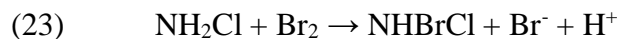


Cl_2 is known to react strongly with the PA layer based on experiments done with the PA model monomer benzanilide.²⁶ Most previous studies done with chloramines have focused on pH 7.8 to 8.3; therefore, the addition of chloride likely did not lead to the formation of Cl_2 .^{32,33,38}

1.7.2.2 Bromide and Chloramines

Furthermore, the presence of bromide in waters disinfected with chloramines, specifically NH_2Cl , has long been a topic of interest because bromide is oxidized in the presence of monochloramine.^{28,46,47} Bromide reacts with NH_2Cl , which leads to the formation of brominated halamines, other brominated species, and accelerated decay of NH_2Cl .⁴⁷ One secondary reactant of interest is bromochloramine (NHBrCl) and the mechanisms by which it forms and decays.⁴⁷⁻⁴⁹ Understanding the formation and decay of NHBrCl helps to inform the model for NH_2Cl decay in the presence of bromide.⁴⁹ When Trofe et al. 1980⁴⁷ first studied the formation of NHBrCl , general acid catalysis of the decomposition of NH_2Cl was not accounted for, but it was later found by Gazda and Margerum 1994⁴⁸ that the mechanism for bromochloramine formation was through general acid assisted Cl^+ transfer (eqs. 21-23).⁴⁸





When NH_2Cl and NHBrCl react with one another, they both decompose into N_2 , Cl^- , Br^- , and H^+ .^{28,49}



NHBrCl can be experimentally determined using UV-vis spectrophotometry at typical drinking water conditions using the Beer-Lambert law as a series of equations.^{49–51} Previous studies have found that the increase of bromide concentration, increase in initial monochloramine concentration, and decrease in pH have the largest effect on NH_2Cl stability and brominating species formation.^{39,49} When NH_2Cl is in the presence of bromide, many other secondary reactants are also present including NH_2Br , NHBr_2 , HOBr/OBr^- , Br_2/Br_3 , and BrCl/BrCl_2^- , which increase as the initial concentration of NH_2Cl or bromide increases.^{28,38,49}

1.7.2.3 Iodide and Chloramines

Although iodide is present in seawater at approximately 3 orders of magnitude lower than bromide, it still has implications on the formation of iodinated disinfection by products (I-DBPs) and further reactions with natural organic matter (NOM) while in the presence of chloramines.^{44,52,53} This is due to the high reactivity of iodide. Thus, when iodide is present, it reacts with NH_2Cl to form HOI ,⁵⁴ and NH_2Cl is unable to further oxidize HOI to form the non-toxic by-product, iodate (IO_3^-).⁵² This indicates that HOI is the final product in the reaction between NH_2Cl and I^- , and HOI is known to be reactive toward PA.^{38,52}

1.8 Objectives of Thesis

Although many types of membranes exist and there is a push for better water reuse and desalination technology, PA-RO membranes remain the best in the industry despite their limitations. Because the use of these membranes will not be obsolete in the near future, further research is needed on interactions between biofouling controls and the PA active layer. The use of chloramines as a biofouling control for PA based RO membranes has many factors that could result in further damage to the membrane. Factors to consider include the water matrix (e.g. halide concentration), pH changes throughout the water reuse or desalination plant, and mixing conditions used to form chloramines. Throughout this thesis, the focus will primarily be on how

chloramines in the presence of halides affect the PA membrane at varying pH. Each of the following chapters will focus on derivatives of the PA based RO membranes including a model monomer and the actual commercial made PA membrane. Chapters investigating the monomer and commercial membrane will focus on interaction with chloramines and halides and how they alter the monomer or the membrane properties over time. The chapter by chapter objectives are as follows:

Chapter 2: Understand the fundamental degradation kinetics of PA based monomers BA and *N*-CH₃-BA when chloramines are used as biofouling control in halide containing waters at pH 4 to 9.3 by evaluating monomer decay and by-product formation over time.

Chapter 3: Understand the change in performance of a commercially made PA-RO membrane when chloraminated in halide containing waters at pH 4 to 9 by measuring the change in membrane flux over time.

Chapter 4: Disseminate research contributions and environmental significance of work.

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2. CHLORAMINATION OF THE POLYAMIDE-BASED REVERSE-OSMOSIS MEMBRANE MONOMER IN THE PRESENCE OF HALIDES

2.1 Abstract

Benzanilide (BA) is a monomer that can be used to model the behavior of the polyamide (PA) layer of the PA reverse osmosis (RO) membrane. In this study, batch experiments were performed to evaluate how BA and *N*-CH₃-BA, a variation of BA, reacted with pre-formed NH₂Cl under varying pH and halide conditions. BA decay and by-product formation were evaluated by HPLC/DAD and LC/MS from pH 4 to 9.3. Results indicated that at pH 4, when BA was chloraminated in the presence of 840 μ M bromide, BA decay followed pseudo-first order loss, which yielded a k_{obs} of $6.7 \times 10^{-2} \text{ min}^{-1}$. This loss indicated that excess or steady-state concentrations of the unknown brominating agent were generated. Additionally, brominated by-products including ortho-brominated benzanilide (*o*-Br-BA) and para-brominated benzanilide (*p*-Br-BA) formed at concentrations of 0.7 μ M and 10.1 μ M, respectively. Results from *N*-CH₃-BA experiments under the same conditions suggested that direct ring bromination occurred, but *N*-CH₃-BA decay was much slower than BA. At neutral pH, BA decay and by-product formation remained unclear since the quenching agent used in this technique led one the major by-products formed, N-brominated-benzanilide (*N*-Br-BA), to reform BA. Chloramination experiments performed at pH 4 amended with bromide and chloride at 840 μ M and 540 mM, respectively suggested that the presence of the chloride in addition to the bromide led to faster BA decay and by-product formation. When bromide and chloride were both present, full BA decay occurred in 10 minutes opposed to 55 minutes when only bromide was present. When iodide was amended to solution at 0.5 μ M to 500 μ M at pH 4 to 9.3, no ring iodination occurred during chloramination over 24 hours, but *N*-iodination remained unclear. Overall, results from this study indicated that the combination of low pH and high bromide concentration during chloramination controlled irreversible ring bromination of BA.

2.2 Introduction

2.2.1 Degradation of BA During Chlorination

Understanding the degradation pathways of the polyamide (PA) based reverse osmosis (RO) membrane that occur during chlorination or chloramination is crucial for developing next generation desalination membranes. Originally, the most ubiquitously accepted mechanism for the chlorination of the PA membrane or PA model monomers was through two key pathways. The first pathway was through direct chlorination of the aromatic ring of the PA layer by way of Cl_2 or HOCl .¹⁻³ The second pathway was by chlorinating the amide nitrogen (N), which can later undergo intramolecular rearrangement where the chlorine proceeds to the ring.⁴⁻⁶ This pathway is widely known as Orton Rearrangement, and it has been accepted and used to describe degradation of the PA membrane or PA model monomers during chlorination. In all the following figures describing the PA membrane degradation mechanisms, benzanilide (BA) will be used to represent the PA layer because the BA monomer has proved to be a good model compound for analyzing the PA membrane.^{1,3,7} Direct chlorination and Orton Rearrangement of BA is displayed in Figure 2-1.

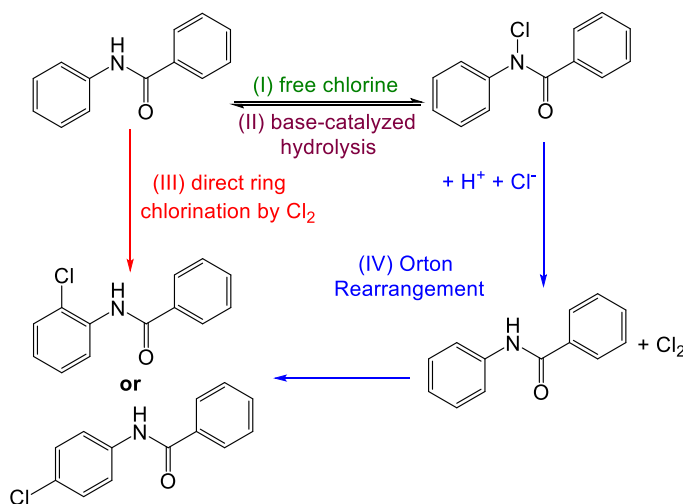
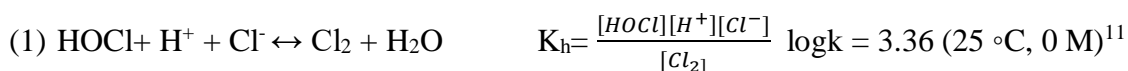


Figure 2-1. Direct Ring Chlorination and Orton Rearrangement of BA

Throughout this mechanism, there are many inconsistencies from a chemistry perspective, which have led recent studies to further investigate these pathways. The first discrepancy in the Orton Rearrangement mechanism occurs when chloride is present in solution, where the chloride ion, Cl^- , should be more reactive with HOCl (equation 1), than with the N-Cl moiety to form Cl_2

when H^+ is not limiting the reaction. This is because equation 1 is markedly faster than the reaction between $N-Cl$, Cl^- , and H^+ to form Cl_2 . The reaction between Cl^- , H^+ , and $N-Cl$ to form Cl_2 is known as the rate limiting step of Orton Rearrangement.^{5,8} Additionally, the $N-Cl$ moiety must form in order for Orton Rearrangement to occur, but free chlorine reacts slowly with amide groups ($k_{app} = 10^{-3}-10^{-1} \text{ M}^{-1}\text{s}^{-1}$) at pH 7.2 to 7.4, which is due to the electron withdrawing effect of the carbonyl group.^{9,10} Due to these discrepancies, one recent study questioning Orton Rearrangement was performed and aimed to better understand PA degradation mechanisms, which exposed BA to free chlorine under different water quality parameters.⁷



Specifically, this section will focus on Huang et al.⁷ which investigated degradation pathways using the BA monomer when chlorinated under different water quality parameters. When evaluating effects of free chlorine on the BA monomer, there are some key properties of free chlorine that must be considered. First, the pKa of free chlorine is 7.5¹²; therefore, when the pH is above 7.5, OCI^- dominates and below 7.5 $HOCl$ dominates (equation 2). Also, the addition of chloride into the system promotes the formation of chlorinating agents including (i) Cl_2 (equation 1¹²) and (ii) Cl_2O (equation 3¹³), which have found to be stronger chlorinating agents than $HOCl$.^{11,14}



In Huang et al.⁷, specific chlorinating species were isolated based on adjusting the pH and Cl^- concentration in the system. The BA monomer was exposed to the specifically targeted chlorinating species, and the decay of BA and by-product formation were evaluated by LC/MS/MS, HPLC/DAD, and/or GC/MS. Based on the experiments with BA and other PA model monomers, a new chlorination mechanism was proposed where ring chlorination of BA only occurred through one pathway by way of Cl_2 or $HOCl$, and N -chlorination of the amide N was promoted when OCI^- was dominant in the system, e.g. neutral or high pH.⁷ The mechanism by Huang et al.⁷ is displayed below in Figure 2-2.

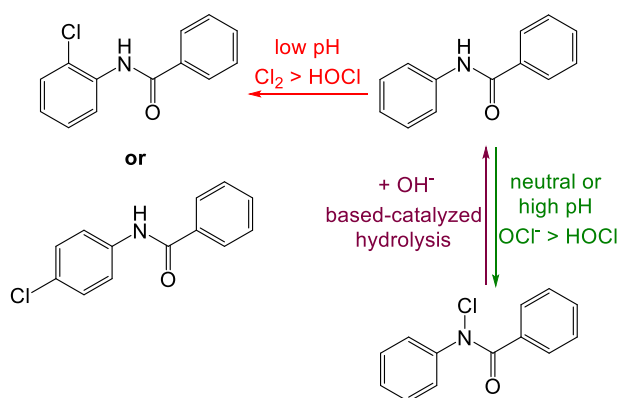
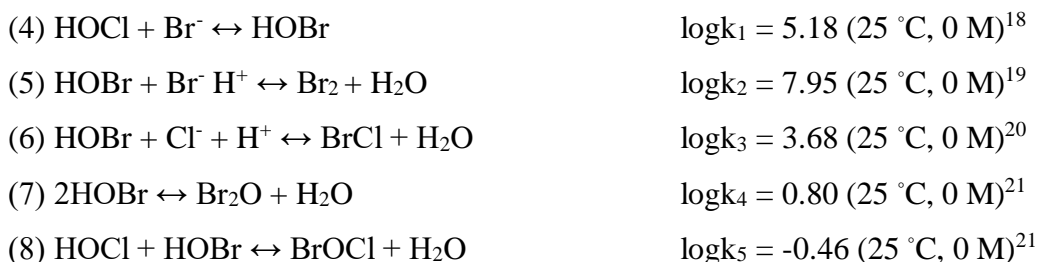


Figure 2-2. Direct Chlorination and Ring Chlorination as Two Separate Pathways

Overall, this study supports the findings that Orton Rearrangement cannot be fully attributed to explaining the mechanisms of PA degradation during chlorination.¹⁵ Results from this study suggested that ring chlorination and *N*-chlorination are independent pathways that are influenced strongly by the water quality parameters including pH and the Cl^- concentration. The reactivity of BA with the chlorinating agents decreased as $\text{Cl}_2 > \text{OCl}^- > \text{HOCl}$.⁷

2.2.2 Degradation of BA During Chlorination with Bromide

Bromide is present in seawater and brackish groundwater at 0.84 mM and 0.007 mM, respectively.^{16,17} The presence of halides, especially bromide and chloride, play an important role during chlorination of PA-RO membranes in seawater or brackish groundwater due to the reactivity between free chlorine, bromide, and chloride (equations 1-3 and 4-8, below).



Huang et al.²² performed experiments using BA, the PA model monomer, to investigate the role of bromide, chloride, and free chlorine on the decay and by-product formation of BA. Experiments were conducted to (i) identify how BA reacts with pre-formed HOBr amended with bromide, chloride, and/or HOCl to form a host of reactive species (e.g. HOBr, Br_2 , Br_2O , BrCl, and BrOCl) (ii) evaluate BA degradation kinetics and by-product formation, and (iii) derive series

specific rate constants for targeted brominated species. Results from this study indicated that regardless of the brominating species present, only ring halogenation occurred (Figure 2-3). However, when BrOCl was the targeted species, ring chlorination occurred, which may have been due to HOCl residual; whereas, the rest of the targeted species led only to ring bromination. Results indicated that the ability for the brominating agents to undergo substitution decreased as $\text{BrCl} > \text{BrOCl} > \text{Br}_2 > \text{Br}_2\text{O} > \text{HOBr}$. Experiments conducted verified that there was no formation of the *N*-brominated product. Because results indicated irreversible ring bromination even with low bromide concentration over a wide range of pH, this study suggested the presence of the bromide ion during chlorination permanently damages to the PA membrane.²²

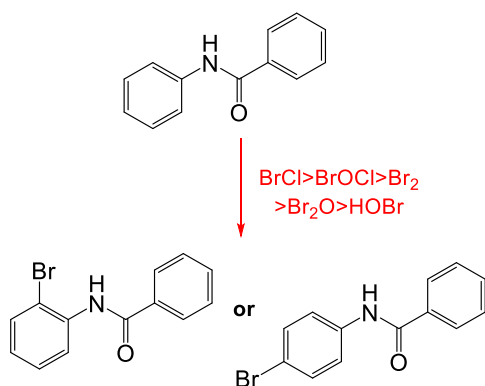


Figure 2-3. Direct Ring Bromination of BA

2.2.3 General Reactivity of Organic Compounds with Free Chlorine and Iodine

Although iodide is present in seawater, little attention has been dedicated to the presence of iodide when the PA-RO membrane or model monomers undergo chlorination. One reason for this is likely due to the fast reaction between I^- and HOCl to form hypiodous acid (HOI) ($k=4.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$).²³ When HOI is in the presence of free chlorine (HOCl/OCl^-), HOI is further oxidized to form non-toxic iodate (IO_3^-), and this occurs in a matter of minutes through a series of second and third order reactions.²⁴ Interestingly, when chloramination is applied to waters containing iodide, a pre-chlorination step is typically applied to convert I^- to IO_3^- in order to limit the formation of iodinated-DBPs (I-DBPs).²⁴⁻²⁷ The chlorination step must occur for an allowable time for full conversion of iodide to non-toxic IO_3^- .²⁵ Therefore, little focus has been attributed to the effects of HOCl/OCl^- and I^- on PA-RO membranes likely due to the ability for these reactants to form IO_3^- .

2.2.4 Chloramination of PA-RO Membranes

As stated in the previous chapter, chloramines have biocidal properties and can be applied to mitigate biofouling for PA-RO membranes.^{28,29} In this chapter, the focus will be on how chloramines behave in the presence of chloride, bromide, and iodide, and how the secondary species formed react with PA based model monomers, BA and *N*-CH₃-BA. One previous study used a commercially made PA-RO (SW30HR) membrane and investigated the effects of chloramination of halide impaired waters on the membrane.³⁰ This study found that the addition of halides, specifically bromide and iodide, led to membrane bromination and iodination. Furthermore, this study found that the bromination kinetics were first order with respect to Br₂ under the conditions tested (pH 7.8 or 8.0, 2 mg/L NH₂Cl as Cl₂).³⁰

2.2.5 Objectives

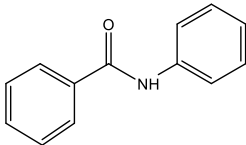
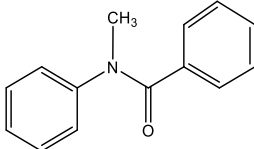
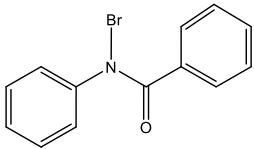
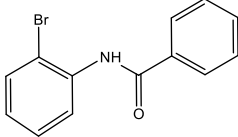
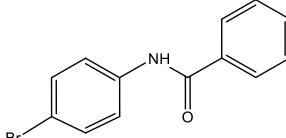
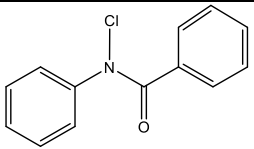
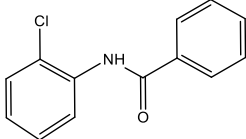
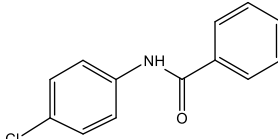
Although the study just mentioned above provided valuable insights to the degradation of PA-RO membranes during the chloramination of halide-impaired waters, research gaps remain. For example, this study did not specifically evaluate the role of individual halides in the presence of chloramines, the concentrations of the halides, or the role of pH on PA-RO membrane degradation.

Thus, the objectives of this study aimed to form a better understanding PA degradation mechanism during exposure to chloramines in halide-containing waters. Throughout this chapter, research gaps were explored which investigated BA degradation and by-product formation in the presence of chloramines and halides. The first objective evaluated how chloramine exposure affected BA decay at low and neutral pH conditions. The second objective assessed the role of different halides on these processes. The final objective evaluated the effect of chloramines in the presence of both bromide and chloride simultaneously on BA degradation and by-product formation at varying pH. Through exploring different halide and chloramine conditions, the overall aim was to gain insight on what specific pathways and chloramine-based halogenating agents contributed to BA degradation.

This chapter addressed these research gaps through experiments using BA and *N*-CH₃-BA. The structures for these compounds and their potential by-products are in Table 2-1 below. First, the BA monomer was exposed to chloramines at varying pH conditions. Second, BA and *N*-CH₃-BA were exposed to varying halide concentrations, pre-formed NH₂Cl concentrations, buffer concentrations, and pH conditions. For all scenarios, parent compound decay and by-product

formation were monitored. Lastly, the speciation of NH_2Cl and NHBrCl were experimentally determined at pH 6.2 to 9.3 under varying $[\text{NH}_2\text{Cl}]_0$, bromide, and buffer concentrations.

Table 2-1. Monomers used or evaluated in this study.

Compound Name	Structure	Acronyms
Benzanilide		BA
<i>N</i> -Methyl- <i>N</i> -phenylbenzamide		<i>N</i> -CH ₃ -BA
<i>N</i> -Bromo- <i>N</i> -phenylbenzamide		<i>N</i> -Br-BA
<i>N</i> -(2-Bromophenyl)benzamide		<i>o</i> -Br-BA
<i>N</i> -(4-Bromophenyl)benzamide		<i>p</i> -Br-BA
<i>N</i> -Chloro- <i>N</i> -phenylbenzamide		<i>N</i> -Cl-BA
<i>N</i> -(2-Chlorophenyl)benzamide		<i>o</i> -Cl-BA
<i>N</i> -(4-Chlorophenyl)benzamide		<i>p</i> -Cl-BA

2.3 Materials and Methods

2.3.1 Standards and Reagents

The standards and reagents for the experiments were (i) sodium hypochlorite 5%, glacial acetic acid, formic acid, $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, $\text{NaH}_2\text{O}_5\text{C}_2$, Na_2SO_3 , and KI from Acros Organics; (ii) sodium tetraborate decahydrate, NaCl, $(\text{NH}_4)_2\text{SO}_4$, NaBr, BA, naphthalene, dichloromethane (DCM) from Sigma-Aldrich, and (iii) LC/MS Optima grade methanol (MeOH) from Fisher Scientific. All standards and reagents were purchased at reagent grade or better and did not undergo further purification. Reagent water was (18.2 M Ω -cm) was from a Thermo Scientific Barnstead NANOpure water system.

Some compounds used in this study were synthesized by Dr. Keith Reber at Towson University. These compounds include *o*-Br-BA, *p*-Br-BA, *o*-Cl-BA, *p*-Cl-BA, and *N*-CH₃-BA. The structures for these compounds are in Table 2-1. These compounds were stored at -18 °C.

2.3.2 Preparation of Stock Solutions

Model compounds were prepared as a primary stock in 5 g/L in MeOH and diluted to a 500 μM secondary stock and stored in in -18 °C. Primary stocks were re-made on a monthly basis and secondary stocks were made as needed. Monochloramine (NH_2Cl) was prepared daily through the following method. First, the free chlorine stock was standardized monthly by quantifying OCl^- at 292 nm ($\epsilon = 362 \text{ M}^{-1}\text{cm}^{-1}$).³¹ The concentration was determined by equation 9.

$$(9) A_{292} = \epsilon_{\text{OCl}^-, 292} C_{\text{OCl}^-}$$

Each day, an 80 mM free chlorine (HOCl/OCl^-) solution was made in a 20 mL glass vial. In a 40 mL glass vial, a 20 mL 48 mM solution of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ was prepared. The pH of the $(\text{NH}_4)_2\text{SO}_4$ solution was adjusted with 45 μL of 2 M NaOH in order to reach a pH of 8.3. Then, in a dropwise manner, the 80 mM free chlorine solution was added to a rapidly mixing $(\text{NH}_4)_2\text{SO}_4$ solution. After free chlorine was added to the ammonium sulfate solution, the 40 mL vial was covered with aluminum foil to ensure that it did not photodegrade. In order to determine the actual concentration of the NH_2Cl stock, a 250 μL aliquot of NH_2Cl was added to 10 mL of water to generate a 40-fold dilution of the original stock. The actual concentration of the monochloramine stock solution was determined spectrophotometrically at wavelengths 295 nm and 245 nm where $\epsilon_{\text{NH}_2\text{Cl}, 245} = 445 \text{ M}^{-1}\text{cm}^{-1}$, $\epsilon_{\text{NHCl}_2, 245} = 208 \text{ M}^{-1}\text{cm}^{-1}$, $\epsilon_{\text{NH}_2\text{Cl}, 295} = 14 \text{ M}^{-1}\text{cm}^{-1}$, and $\epsilon_{\text{NHCl}_2, 295} = 267 \text{ M}^{-1}\text{cm}^{-1}$.³² The concentrations of NH_2Cl and NHCl_2 were found through the

following equations (10 to 11) where A equaled the absorbance at each wavelength, ϵ equaled the molar absorptivity ($M^{-1}cm^{-1}$) at each wavelength, C equaled the concentration (M), and b equaled the pathlength of 1 cm.

$$(10) A_{245} = \epsilon_{NH_2Cl,245}C_{NH_2Cl} + \epsilon_{NHCl_2,245}C_{NHCl_2}$$

$$(11) A_{295} = \epsilon_{NH_2Cl,295}C_{NH_2Cl} + \epsilon_{NHCl_2,295}C_{NHCl_2}$$

The quenching agent Na_2SO_3 was prepared fresh daily at 10 g/L in a 2 mL amber glass HPLC vial.

2.3.3 Set up of Kinetic Experiments

2.3.3.1 Experiments Analyzed using Liquid Chromatography (LC)

Experiments monitoring BA or *N*-CH₃-BA decay and by-product formation were all conducted in 20 mL synthetic solution for up to 24 hours at room temperature (24 ± 1 °C). These solutions contained the parent compound (BA or *N*-CH₃-BA) at 10 μ M, and they were buffered from pH 4 to 9.3 at 10 to 50 mM using acetate buffer (pH 4), phosphate buffer (pH 6 - 7.3), or borate buffer (pH 9.3). The solutions were amended with halides including chloride, bromide, or iodide at concentrations of 20 to 540 mM, 54 to 840 μ M, or 0.5 to 500 μ M, respectively. Reactions were initiated by adding pre-formed NH_2Cl at concentrations ranging from 200 μ M to 500 μ M. Samples measured by HPLC/DAD or LC/MS, were first quenched with a 10 μ L aliquot of Na_2SO_3 , where the Na_2SO_3 was in at least 10-fold molar excess to $[NH_2Cl]_0$.

It should be noted that using Na_2SO_3 as the quenching agent led to constraints for the analysis of *N*-halogenated by-products. Na_2SO_3 is in the category of quenching agents that reduce chlorine from Cl(+1) to Cl(-1).³³ If an *N*-halogenated product of BA forms, the addition of the quenching agent will transform the halogenated product back to the parent compound.⁷ Figure 2-4 demonstrates the reaction of *N*-halogenated-BA when Na_2SO_3 is applied as a quenching agent.

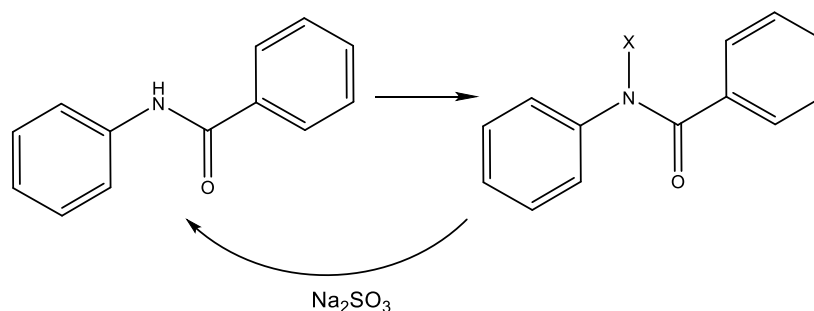


Figure 2-4. Reaction of the *N*-halogenated-BA with the quenching agent

Unquenched samples were not injected into the HPLC/DAD or MS, since the decay of BA will likely be affected due to the low pH of 2.7 in the mobile phase. It is also possible that the chloramines could react with the stationary phase of the column resulting in a damaged column. Therefore, since samples were always quenched with Na_2SO_3 , the *N*-halogenated product was measured as BA, which was denoted as BA+N-X-BA, where X could be Cl, Br, or I.

BA+N-X-BA or *N*-CH₃-BA decay and by-product formation were analyzed by HPLC with UV/vis diode-array detection (DAD) (Agilent 6420) or through LC/MS (Agilent 6420 Triple Quadrupole MS). Compound separation was carried out through Eclipse C18 column (2.5 mm x 150 mm, 3.5 μm). Eluent flow was preformed through isocratic mode at 0.3 mL/min. Solvent A contained reagent grade water with 0.1% formic acid, and solvent B contained LC/MS grade or HPLC grade MeOH, depending on analysis type, with 0.1% formic acid. Solvent A and B were held in isocratic mode at 30 and 70%, respectively. For HPLC/DAD, only the absorbance at the wavelength 260 nm was monitored.

All quantification of BA, *N*-CH₃-BA, *o*-Br-BA, and *p*-Br-BA was preformed through standards analyzed by HPLC/DAD. The method detection limits (MDLs) were found by Huang et al.⁷ and Huang et al.²² for BA, *N*-CH₃-BA, *o*-Br-BA, and *p*-Br-BA and were 22, 51, 30, and 27 nM, respectively.^{7,22} For LC/MS, all of the LC parameters were the same, but the MS was on and operating using electrospray ionization in the positive mode (ESI+). The single quad was operated in scan mode from *m/z* 50 to 350. The MS was not used for quantitative data but only to obtain qualitative data. For BA, the monitored *m/z* ratios were 77, 105, and 198, and the brominated by-products were monitored at 275.9 and 277.9 *m/z*. For *N*-CH₃-BA the monitored *m/z* ratio was 212.9, and the brominated by-products were monitored at 290 and 292 *m/z*.

2.3.3.2 GC/MS Analysis

When GC/MS was used for compound analysis, reactions were maintained in 100 mL synthetic solutions for up to 24 hours at room temperature (24 ± 1 °C). Similar to the set up for HPLC/DAD and LC/MS experiments, these solutions contained BA at 10 μ M, and they were buffered from pH 4 to 6.2 with 25 mM acetate buffer (pH 4) or phosphate buffer (pH 6.2). Solutions were amended with 840 μ M bromide. This method used an alternative quenching mechanism due to the limitations of Na_2SO_3 , as noted above. In this case the aim was to transfer all the organic compounds from the aqueous phase to the organic phase using a liquid-liquid extraction mechanism in order to preserve any *N*-halogenated compound. It is known that charged chlorinating agents remain in the aqueous phase³⁴, but it was not confirmed if this transfer method was fully quenching the chloramines and other halamines present in solution. The liquid-liquid extraction mechanism was as follows. A 9 mL aqueous sample was transferred into a 20 mL capped glass vial. After this, 1.5 mL of DCM containing 2 mg/L of naphthalene, where naphthalene served as the internal standard (IS), was added to the 20 mL vial with the sample. The glass vial was shaken for ~ 1 min. Then, ~ 0.2 mL of sample was removed from the DCM phase and transferred to an HPLC vial containing 0.8 mL of DCM not containing naphthalene. This step led to a 5-fold dilution of the sample. After this, the sample was analyzed by GC/MS. Calibration curves were made using the same extraction method for BA at 0, 2.5, 5, 10, and 15 μ M.

Compounds were analyzed by GC/MS (Agilent 7000C) using liquid injection, following a method adapted from Huang et al. 2019.⁷ Samples (1 μ L) were injected at 180 °C using a 1:25 split ratio onto a HP-5MS (30 m x 0.25 mm x 0.25 μ m) column. The temperature gradient was as follows, the oven was held at 80 °C for one min, then the temperature increased to 240 °C at a rate of 25 °C/min, and then held at 240 °C for 4 min. The MS analysis was operated using electron ionization (70 eV) in the positive mode. The MS was run in selected ion monitoring mode (SIM), where *m/z* ratios for naphthalene, BA, *o*-Br-BA, *p*-Br-BA, *o*-Cl-BA, and *p*-Cl-BA were monitored. These *m/z* ratios were 136, 77, 105, 198, 276, 278, and 232.

However, there were certain limitations when using this method. First, when trying to differentiate the *N*-halogenated peak from BA, unstable results were obtained from sample to sample, which was likely due to the thermal decomposition of *N*-Br-BA in the injector port. During BA experiments at pH 6.2 BA signal fluctuated over time followed by an extremely high value for *p*-Br-BA ($>>10$ μ M), and then followed by a much lower concentration of *p*-Br-BA. It was

hypothesized that *N*-Br-BA would transform into *p*-Br-BA in the injector, and this would build up overtime and eventually come out of the system all at once. Figure 2-5 below supports this hypothesis. Therefore, this was also not a viable option for analyzing BA decay at neutral pH.

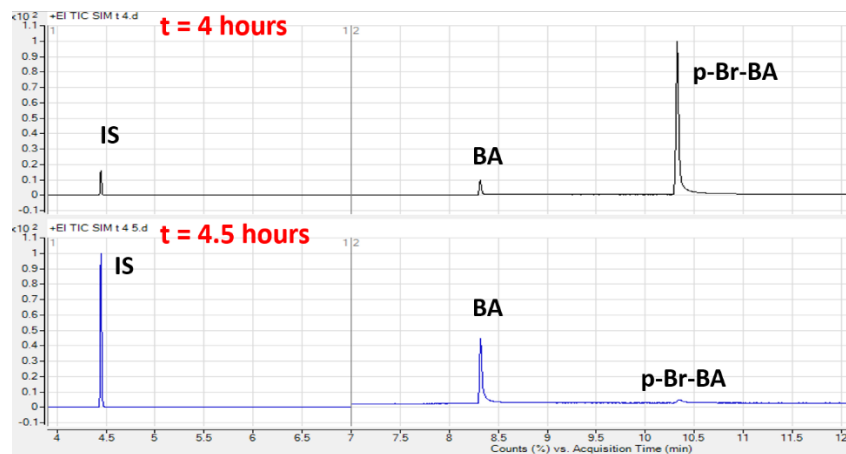


Figure 2-5. Top chromatogram showing the overwhelming *p*-Br-BA peak at $t = 4$ hours, and the bottom chromatogram showing no *p*-Br-BA peak at 4.5 hours ($[BA]_0$ 10 μM , pH 6.2, $[C_{PO4}]_T$ 25 mM, $[NH_2Cl]_0$ 200 μM)

2.3.3.3 Quantitation of NH_2Cl , $NHCl_2$, and $NHBrCl$

Experiments were conducted to monitor the residual NH_2Cl concentration and the $NHBrCl$ concentration that formed using a spectrophotometric method developed by Luh and Mariñas, 2014.³⁵ In these experiments, BA was not present in the water matrix. The absence of BA was due to the fact that BA absorbs light in this range and would interfere with the absorbances of NH_2Cl and $NHBrCl$.⁷ This absence was not expected to influence the results since bromide (840 μM) and NH_2Cl (200 to 500 μM) were in considerable excess to BA (10 μM). The pH of the solutions ranged from 6.2 to 9.3 using phosphate buffer (pH 6.2 to 7.3) and borate buffer (pH 9.3) from 10 to 50 mM. Bromide was amended to the solutions followed by the addition of pre-formed NH_2Cl to start the reaction. Samples were analyzed immediately after NH_2Cl was added.

Concentrations of NH_2Cl , $NHCl_2$, and $NHBrCl$ were found using Beer's Law, as a set of three simultaneous equations (12-14). Parameters for this set of equations are found in Table 2-2. However, $NHCl_2$ concentrations were not reported because their concentration was considered negligible.³⁶

$$(12) A_{243} = \epsilon_{243, NH_2Cl} C_{NH_2Cl} l + \epsilon_{243, NHCl_2} C_{NH_2Cl} l + \epsilon_{243, NHBrCl} C_{NHBrCl} l$$

$$(13) A_{294} = \epsilon_{294, NH_2Cl} C_{NH_2Cl} l + \epsilon_{294, NHCl_2} C_{NH_2Cl} l + \epsilon_{294, NHBrCl} C_{NHBrCl} l$$

$$(14) A_{320} = \epsilon_{320, \text{NH}_2\text{Cl}} C_{\text{NH}_2\text{Cl}} + \epsilon_{320, \text{NHCl}_2} C_{\text{NH}_2\text{Cl}} + \epsilon_{320, \text{NHBrCl}} C_{\text{NHBrCl}}$$

Table 2-2. Molar absorptivity values for species of interest

Species	Wavelength, λ (nm)	Molar Absorptivity, ϵ ($\text{M}^{-1}\text{cm}^{-1}$)
NH_2Cl	243	457 ³⁶
	294	15 ³⁶
	320	7 ³⁶
NHCl_2	243	235 ³⁶
	294	282 ³⁶
	320	125 ³⁶
NHBrCl	243	500 ³⁷
	294	145 ³⁷
	320	195 ³⁷

This method comes with limitations including the inability to assess NH_2Cl or NHBrCl at pH conditions lower than pH 6. This limitation likely occurs because there are many competing species occurring at higher concentrations at low pH. Therefore, in this study, the only pH where speciation of NH_2Cl and NHBrCl were determined were at pH 6.2 to 9.3.

2.4 Results and Discussion

2.4.1 Chloramination

First, the decay and by-product formation of BA was monitored at low and neutral pH conditions. When pre-formed NH_2Cl was added to the reaction solutions containing BA there was no formation of ring-chlorinated products regardless of the pH. Figure 2-6 describes BA+ *N*-Cl-BA decay at pH 4.1 and 7.2 during chloramination.

The lack of BA conversion to ring chlorinated products is likely because the dominant species in the system were NH_2Cl and NHCl_2 depending on pH, which are known to react with organic compounds more slowly than free chlorine.^{33,38} However, it is possible that *N*-Cl-BA formed, but *N*-Cl-BA cannot be determined due to analytical constraints of the HPLC-DAD method discussed

in the materials and methods section (2.3.3.1). In all subsequent sections that use HPLC/DAD and/or LC/MS as the detection mechanism, the quenching agent converted any *N*-halogenated compound back to the parent compound.

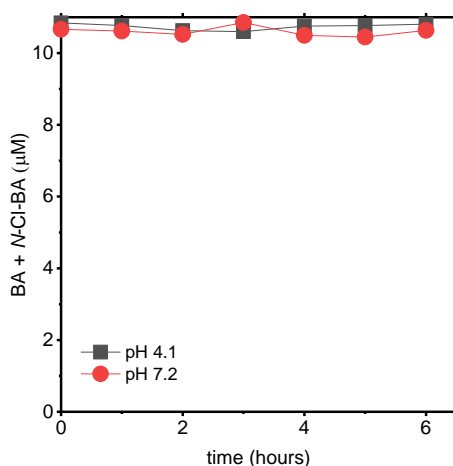


Figure 2-6. Decay of BA+N-Cl-BA when $[BA]_0$ 10 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{C}_{\text{Buffer}}]_T$ 25 mM buffer (acetate buffer ($[\text{C}_{\text{Ace}}]_T$) at pH 4.1 and phosphate buffer ($[\text{C}_{\text{PO}_4}]_T$) at pH 7.1)

2.4.2 Chloramination with Iodide

Iodide is present in seawater at 0.5 μM .¹⁶ The presence of iodide has severe implications on I-DBP formation in chloraminated water compared to I-DBP formation in chlorinated water.²⁴ This is because during the chloramination of iodide, HOI is the final product which can react with natural organic matter (NOM) to form I-DPBs, the most toxic of the halogenated-DBPs.^{39,40} However, when BA in the presence of iodide was chloraminated, BA+ *N*-I-BA concentration remained constant over time regardless of pH or iodide conditions present in the system. Figure 2-7a. shows a series of different pH and iodide conditions from pH 4.1 to 7.2, and Figure 2-7b. uses the same pH, NH_2Cl , and iodide conditions as a study that finds iodine uptake by the PA membrane.³⁰ The only conclusion drawn was no ring-iodinated products formed above detection limits over 24 hours.

Previous studies have investigated the effects of chloramination on iodide containing waters on polyamide-based materials or tyrosyl dipeptides.^{30,41,42} In the study investigating the PA-RO membrane, results indicated iodine uptake in the PA layer was present, confirmed by Rutherford

Backscattering Spectrometry (RBS).³⁰ The relative uptake of iodine was greater than bromine due to the uptake of bromine being only 1 order of magnitude greater than iodine, but concentration of iodide in the system was three orders of magnitude lower than bromide.³⁰ The other study on the chloramination of aromatic tyrosyl dipeptides in iodide containing waters, found that ring iodination occurred after 24 hours using an HPLC-MS/MS method.^{41,42} Studies conducted by Huang et al. never observed amide *N*-iodination, only ring iodination.^{41,42} It is unknown if the quenching mechanism in Huang et al.⁴² reversed the *N*-iodinated compounds back to the parent compound or if *N*-iodinated compounds never formed. More work needs to be done to find a quenching mechanism that differentiates between *N*-I-BA and BA. Furthermore, additional work should be conducted to understand the role of low pH on chloraminated iodide containing waters' interactions with PA membranes. Previous studies have only used pH 7.8 to 8.2 when studying the PA membrane in chloraminated iodide-containing waters.³⁰

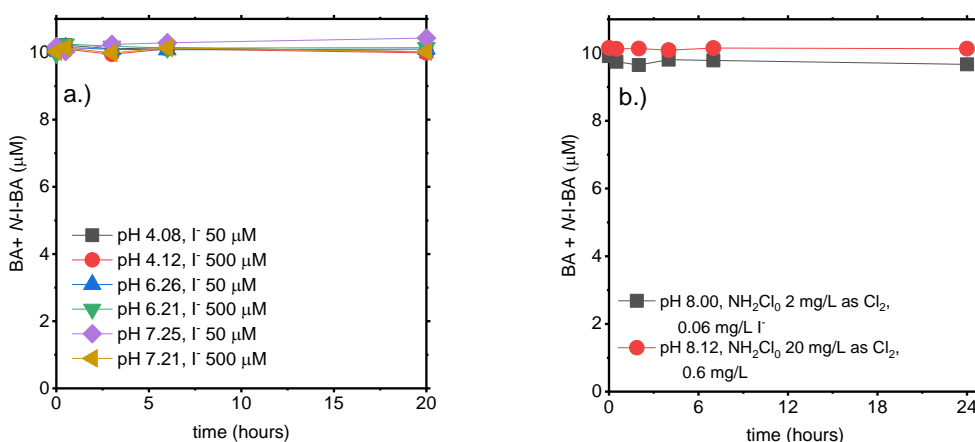


Figure 2-7. BA+N-I-BA when [BA]₀ 10 μM and [C_{Buffer}]_T 25 mM, (a.) [NH₂Cl]₀ 200 μM, (b.) Valentino et al. pH, [NH₂Cl]₀, and [I⁻] conditions.

2.4.3 Chloramination of Bromide

As stated previously, the presence of bromide occurs in both brackish groundwater and seawater at concentrations of 7 and 840 μM, respectively.¹⁶ Therefore, 840 μM was used as the highest bromide concentration of interest. When BA was chloraminated in the presence of bromide, there were two factors that predominantly controlled ring-brominated by-product formation which were (i) bromide concentration and (ii) pH of the system. First the role of bromide concentration

at pH 4 on BA decay and by-product formation will be discussed followed by the role of pH at constant bromide concentration.

At pH 4, the bromide concentration in the system had stark implications on BA decay where complete degradation of BA occurred in less than 90 minutes when 840 μM bromide was present. Figure 2-8 shows the decay and pseudo-first order decay of BA in the presence of bromide during chloramination using two methods of analysis to determine BA decay. The true decay of BA at pH 4 was determined because the experiment was analyzed using two methods, HPLC-DAD and GC/MS. For both cases, the k_{obs} values corresponding to pseudo-first order BA decay were obtained. The BA decay and $\ln(\text{BA}/\text{BA}_0)$ plots for both methods are displayed in Figure 2-8. Results supported that the true BA decay was observed because the k_{obs} value for both methods are only marginally varied.

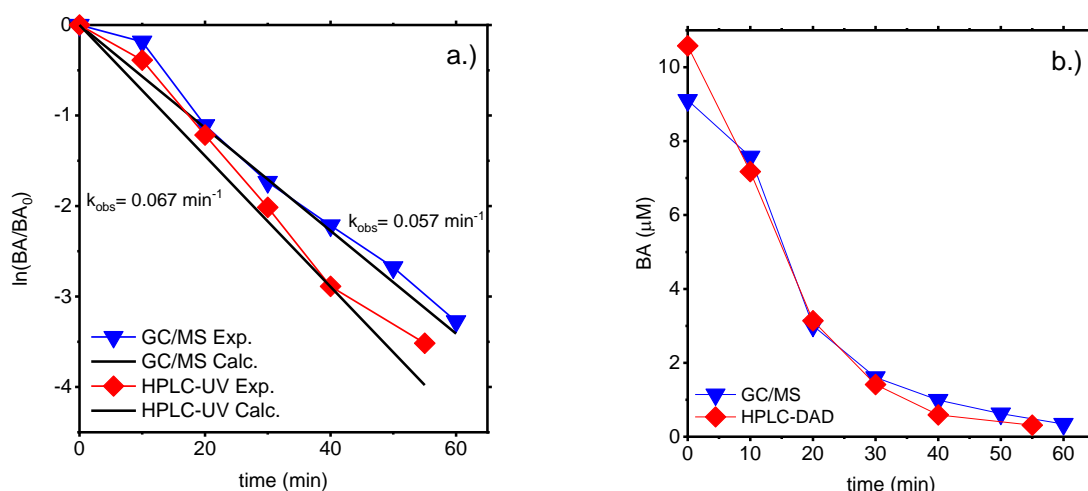


Figure 2-8. $[\text{BA}]_0$ 10 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{Br}^-]$ 840 μM , $[\text{C}_{\text{Ace}}]_{\text{T}}$ 25 mM analyzed by GC/MS and HPLC-DAD where (a.) $\ln(\text{BA}/\text{BA}_0)$ over time and (b.) BA decay over time

When BA was chloraminated in the presence of bromide, the brominating agent(s) that promoted BA decay and by-product formation was unknown. BA followed pseudo-first order decay when the unknown brominating agent(s) was in excess (equations 12-15). Pseudo-first order became less true as less bromide was amended to the system (e.g. 84 μM compared to 840 μM). This is because when bromide was present at a low concentration, the unknown brominating agent(s) likely formed to a lower extent, and therefore was no longer in molar excess to BA.

$$(12) \frac{d[BA]}{dt} = k[BA][Brominating Agent]$$

$$(13) k_{obs} = k[Brominating Agent]$$

$$(14) \frac{d[BA]}{dt} = -k_{obs}[BA]$$

$$(15) \ln \frac{[BA]}{[BA]_0} = -k_{obs}t$$

Valentino et al.³⁰ modified the model developed by Luh and Mariñas³⁵ and found the specific brominating agent that promoted ring bromination of the PA-RO membrane during the chloramination of seawater.³⁰ This study found that the bromination of the PA-RO membrane was first order with respect to the brominating agent Br₂ at pH 7.8 to 8.2 with 65 mg/L Br⁻ and 2 mg/L NH₂Cl as Cl₂.³⁰ The finding that Br₂ is a stronger ring brominating agent than HOBr is consistent to what Huang et al.²² observed in a study that investigated the role of brominating species formed during the chlorination of bromide and chloride containing waters on the degradation of BA. This study found the species-species specific rate constants for HOBr and Br₂ with BA were 5.3±1.2x10⁻² and 3.7±0.2x10², respectively.²²

Due to the dominant role that pH played on the decay of NH₂Cl and the speciation of the brominated species, the brominating agent found at pH 8 cannot be directly compared to the brominating at pH 4. At pH 4, the bromide concentration controlled the BA decay and ring brominated by-product formation, but the species and mechanism remained unclear. Figure 2-9 displays the decay of BA over 2 hours during the chloramination of bromide containing waters and the pseudo-first order decay of BA at pH 4.

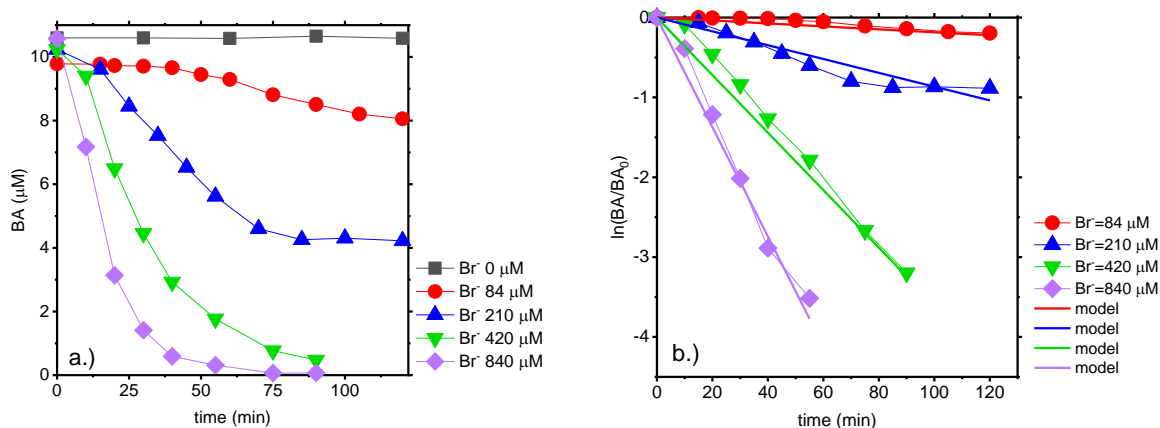


Figure 2-9. BA decay when $[\text{BA}]_0$ 10 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{C}_{\text{Ace}}]_{\text{T}}$ 25 mM, pH 4 on (a.) BA decay (b.) $\ln(\text{BA}/\text{BA}_0)$

In Figure 2-9 $\ln(\text{BA}/\text{BA}_0)$ is plotted as a function of time, and each of the decay curves appear to be linear. However, when each curve is plotted on its own graph, it shows that pseudo first order decay was less true when less bromide was amended to the system. Figures 2-10(a-d), display $\ln(\text{BA}/\text{BA}_0)$ decay for each bromide concentration. The k_{obs} values are in the Table 2-3.

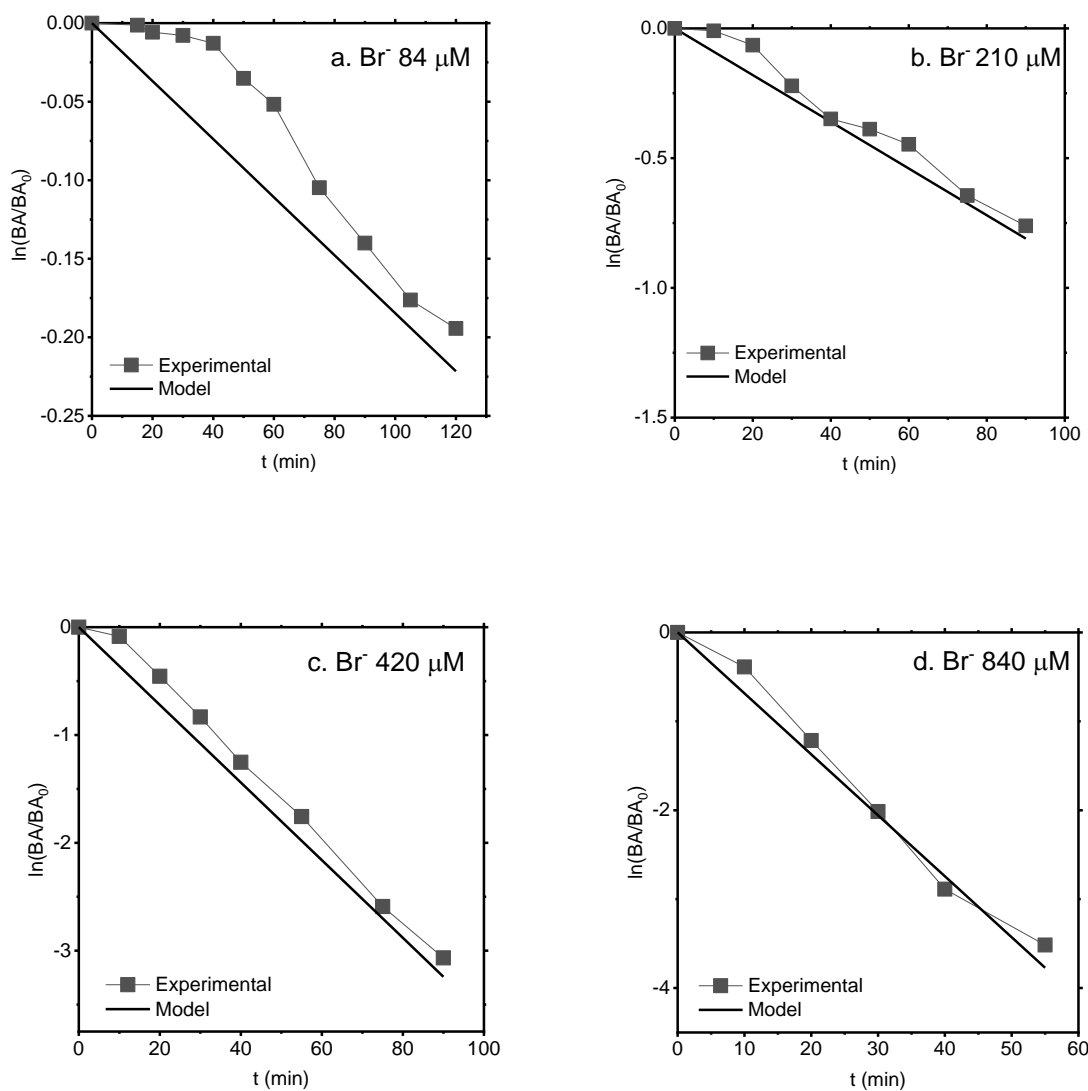


Figure 2-10. $\ln(BA/BA_0)$ pseudo first order decay when pH 4.1, $[BA]_0$ 10 μM , $[NH_2Cl]_0$ 200 μM , $[C_{Ace}]_T$ 25 mM (a.) $[Br^-]_0$ 84 μM (b.) $[Br^-]_0$ 210 μM (c.) $[Br^-]_0$ 420 μM (d.) $[Br^-]_0$ 840 μM

Table 2-3. k_{obs} and R^2 values for all bromide conditions when pH 4.1, $[\text{BA}]_0$ 10 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{C}_{\text{Ace}}]_{\text{T}}$ 25 mM

	$[\text{NH}_2\text{Cl}]_0$ 200 μM	
$[\text{Br}^-]_0$	k_{obs}	R^2
μM	min^{-1}	
84	-1.85E-03	0.966
210	-1.15E-02	0.991
420	-3.60E-02	0.997
840	-6.86E-02	0.997

Another component of the chloramination of bromide containing waters at low pH is the formation of ring brominated by-products such as *o*-Br-BA and *p*-Br-BA. As the concentration of amended bromide increased, the concentration of *p*-Br-BA increased. For example, after 90 minutes, when 840 μM compared to 210 μM bromide was amended to the system the total % of BA products as *p*-Br-BA were 95.3% and 50.3%, respectively. However, regardless of amended bromide concentration, *o*-Br-BA never reached greater than 5.5% of total BA products. Furthermore, the total mass balance with respect to BA was closed for all bromide additions (84 μM to 840 μM). It is important to note that even when bromide was only added at 84 μM , formation of *p*-Br-BA occurred within an hour. This indicated that at low pH during chloramination, even a low presence of bromide could lead to irreversible damage to the PA layer of the RO membrane over a short period of time. Figure 2-11 shows formation of *p*-Br-BA and *o*-Br-BA.

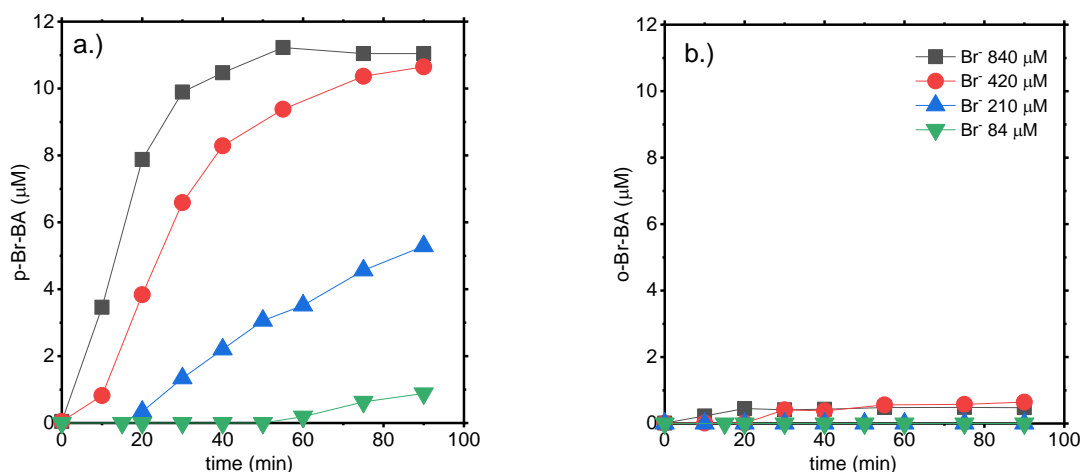


Figure 2-11. BA by-product formation when pH 4.1, $[\text{BA}]_0$ 10 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{C}_{\text{Ace}}]_{\text{T}}$ 25 mM a.) *p*-Br-BA b.) *o*-Br-BA

This by-product distribution followed a similar trend as results of pre-formed HOBr (200 μM) in the presence of BA and bromide (840 μM) at neutral pH (6.2), where *p*-Br-BA was the dominant by-product and *o*-Br-BA formed at < 20% of the total BA products.²² This is likely because of the size of the bromide ion. Because it is larger than the chloride ion, it is less likely to reside in the ortho position; thus, the formation of *p*-Br-BA dominates. The degradation pathways at pH 4 during the chloramination of bromide containing water remain unclear. It is not known if the brominating agent only brominates BA through direct ring bromination or if it goes through Orton Rearrangement where the amide N is brominated, followed by intramolecular rearrangement and ring bromination. In order to address this, experiments with *N*-CH₃-BA were conducted at pH 4 to investigate whether brominated ring products formed.

First, decay of the parent compound was determined during the chloramination of *N*-CH₃-BA in the presence of bromide at pH 4. Figure 2-12 displays *N*-CH₃-BA decay during chloramination. Results indicated decay of *N*-CH₃-BA, but at a much slower rate than BA. The experiment for *N*-CH₃-BA was conducted over a period of 24 hours, opposed to only one to two hours for BA. Additionally, *N*-CH₃-BA still followed the same trend as BA, where an increased bromide concentration resulted in a faster decay of the parent compound. This is again likely because the brominating agent(s) was present at a higher concentration when more bromide was present.

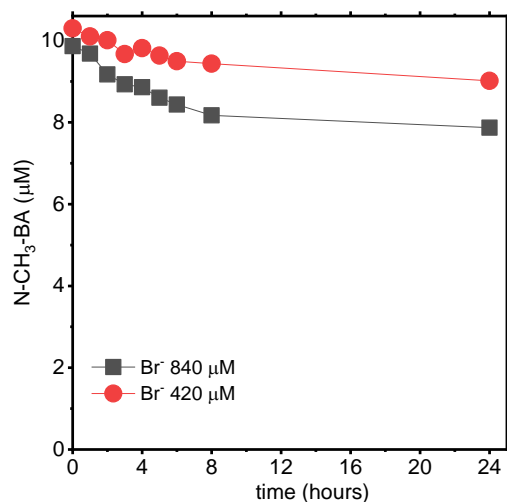


Figure 2-12. *N*-CH₃-BA decay at pH 4.1, [*N*-CH₃-BA]₀ 10 μM, [NH₂Cl]₀ 200 μM, [C_{Ace}]_T 25 mM

Furthermore, ring brominated by-products likely formed during the chloramination of *N*-CH₃-BA in the presence of bromide. The existence of these ring products was hypothesized based on the extracted ion chromatograms (EICs) from the mass spectrum after ~ 4 hours of the reaction. The extracted *m/z* ratios were 290 and 292, which accounts for the 212.9 *m/z* for *N*-CH₃-BA plus 78 *m/z* or 80 *m/z* for the bromide isotopes. Figure 2-13 shows the EIC *m/z* ratios 212.9, 290, and 292.

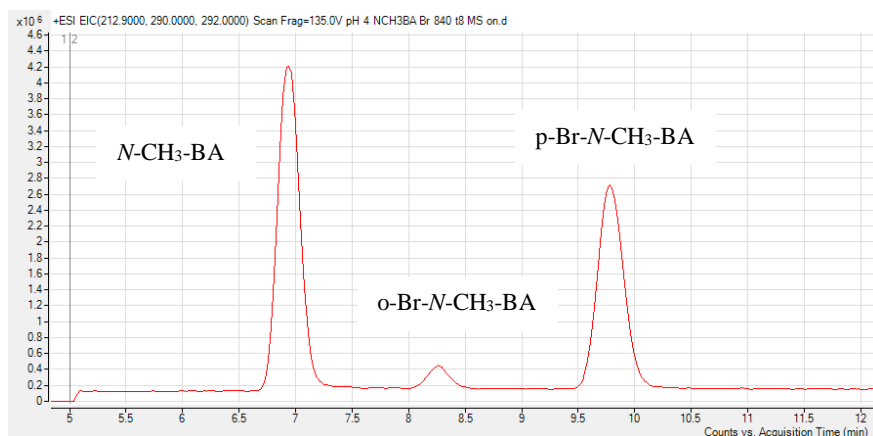


Figure 2-13. EIC 212.9, 290, 292 m/z after 8 hours for [*N*-CH₃-BA]₀ 10 μ M, [NH₂Cl]₀ 200 μ M, [Br⁻]₀ 840 μ M, pH 4.1, [C_{Acce}]_T 25 mM

The first peak with the retention time of 6.9 minutes was *N*-CH₃-BA. This was known because there was a standard for this compound. It was hypothesized that the second peak was the ortho brominated by-product of *N*-CH₃-BA and the third peak was the para brominated by-product. This was hypothesized because for *o*-Br-BA and *p*-Br-BA, the ortho brominated by-product eluted from the column before the para-brominated by-product. Additionally, for the BA experiment under the same conditions, *p*-Br-BA formed at a much higher quantity than *o*-Br-BA, which further supported this hypothesis.

Based on the assumption 290 and 292 m/z corresponded to *p*-Br-*N*-CH₃-BA and *o*-Br-*N*-CH₃-BA, the formation of brominated by-products followed the same trend as BA where the para substituted ring product (*p*-Br-*N*-CH₃-BA) was the dominant product. A higher signal for *p*-Br-*N*-CH₃-BA was observed when more bromide was amended to the system. Figure 2-14 below displays the DAD signal that is hypothesized to correspond to *p*-Br-*N*-CH₃-BA when 840 μ M or 420 μ M Br⁻ was present.

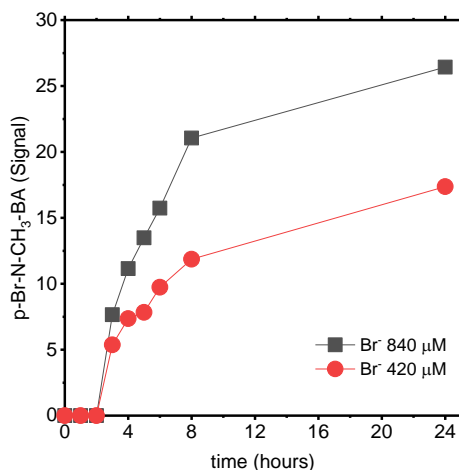


Figure 2-14. DAD signal for *p*-Br-*N*-CH₃-BA at pH 4.1 [*N*-CH₃-BA]₀ 10 μM, [NH₂Cl] 200 μM, [C_{Acce}]_T 25 mM

The ortho products are not shown in the plots above because they were only detected through the MS and not the DAD likely because the ortho by-products formed at a comparatively low quantity to the para products. However, the percent of product formed was not determined due to not having *p*-Br-*N*-CH₃-BA or *o*-Br-*N*-CH₃-BA standards to quantify the data. Since it was highly likely brominated by products formed and the amide N is blocked by a methyl group, there was only one possible degradation pathway for *N*-CH₃-BA (Figure 2-15). Although this suggested that *N*-CH₃-BA underwent direct ring bromination, it is still not clear whether the ring products formed during the chloramination of BA in the presence of bromide was a result of direct ring bromination, *N*-bromination followed by Orton Rearrangement, or both.

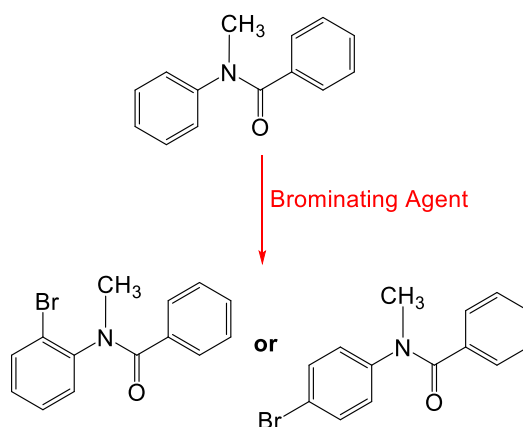


Figure 2-15. Hypothesized Direct Ring Bromination of *N*-CH₃-BA

Furthermore, the pH of the system presented an important role in BA+*N*-Br-BA decay and formation of ring brominated by-products when BA is chloraminated in the presence of bromide. Due to the inability to quantify BA decay at pH 6.2 to 9.3, the kinetics of BA decay under these conditions were not evaluated. However, the decay of BA+*N*-Br-BA from low to high pH varied dramatically as portrayed by Figure 2-16 below.

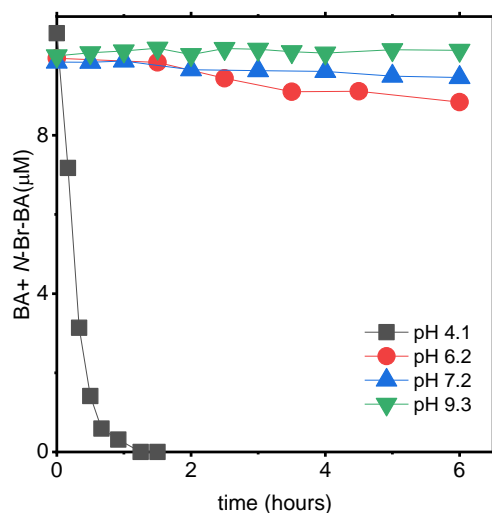


Figure 2-16. BA+N-Br-BA decay at pH 4.1 to 9.3 when $[BA]_0$ 10 μM , $[\text{Br}^-]$ 840 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{C}_{\text{Buffer}}]_{\text{T}}$ 25 mM

Regarding brominated by-products, *p*-Br-BA and *o*-Br-BA by-products only formed at a quantifiable level when the system was at pH 4. At neutral pH, additional experiments were conducted where the injection volume was increased from 10 μL to 50 μL in order to detect low quantities of brominated by-products. After the injection volume increased, brominated by-products were detected at pH 6 based on the m/z signals which corresponded to *o*-Br-BA and *p*-Br-BA. Figure 2-17 shows the EIC for 275.9 and 277.9 after 8 hours. The peaks with the retention times of approximately 8.8 and 9.9 minutes corresponded to *o*-Br-BA and *p*-Br-BA, respectively.

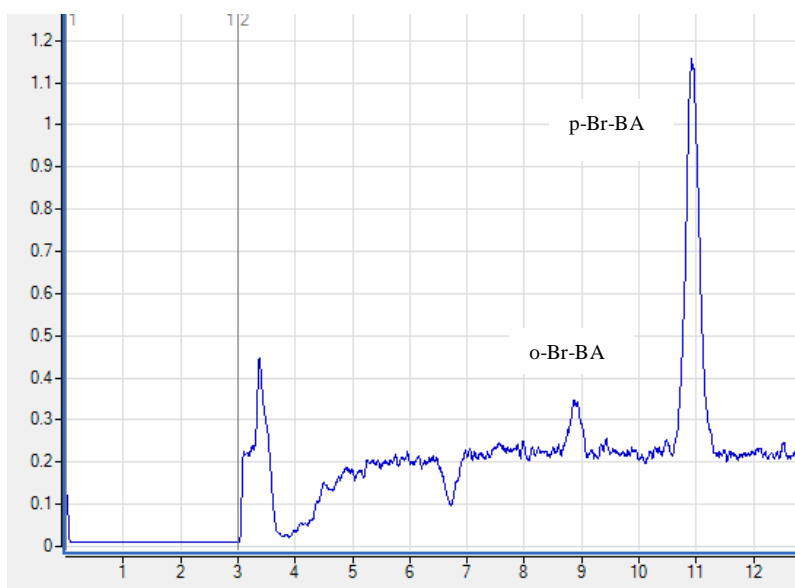


Figure 2-17. EIC for 275.9 and 277.9 after 8 hours for pH 6.2, $[BA]_0$ 10 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{Br}^-]$ 840 μM , $[\text{CPO}_4]_{\text{T}}$ 25 mM

At pH 6.2, the signal for *p*-Br-BA increased over time, but even after 8 hours, it was below detection limits. At pH 7.3, no peak for *p*-Br-BA was observed even with the increased injection volume. Additionally, no ring brominated by-products formed at pH 9.3. Previous literature has found when a PA-RO membrane is exposed to HOCl/OCl^- with bromide or NH_2Cl with bromide at neutral pH, there were more carboxylic acid groups present on the membrane surface meaning hydrolysis of the amide bond occurred which led to deterioration of the membrane.^{3,30,43} Therefore, when experiments were done at neutral pH the MS was also used for detection. The purpose of this was to try to extract m/z ratios for potential BA products that would result from amide scission of BA. Using this strategy, still no BA by-products were observed.

The role of pH was also evaluated in experiments conducted with *N*-CH₃-BA during the chloramination of bromide containing waters. Moreover, *N*-CH₃-BA followed a similar trend to BA, where pH impacted decay and ring brominated by-product formation. The true decay at neutral pH was known because the N moiety is blocked with a methyl group so it cannot undergo *N*-halogenation. Figure 2-18 displays *N*-CH₃-BA decay at different pH where at low pH *N*-CH₃-BA decreased over time, but negligible change occurred at neutral pH.

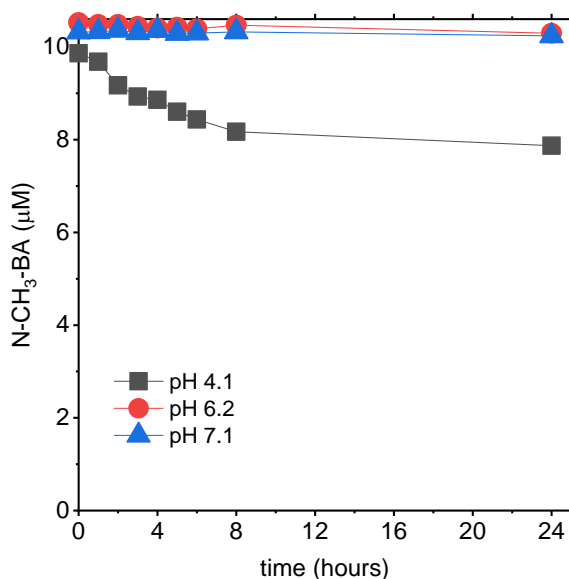


Figure 2-18. *N*-CH₃-BA decay at pH 4.1- 7.1 when [*N*-CH₃-BA]₀ 10 μM, [Br⁻] 840 μM, [NH₂Cl]₀ 200 μM, [C_{Buffer}]_T 25 mM

Another aspect of interest during the chloramination of bromide containing waters was the decay of NH₂Cl and the formation of brominated halamine species in the water matrix. However, the only brominated species that could be determined experimentally was NHBrCl.³⁵ At pH 6 to 9.3 speciation of NH₂Cl and NHBrCl were experimentally determined along with decay of BA+*N*-Br-BA. At pH 9.3, no NHBrCl was observed over a 6-hour period. The decay of NH₂Cl varied dramatically over pH 6.2 to 9.3, where the decay was fastest at lower pH. This was because the reaction between NH₂Cl and bromide is general acid catalyzed, and at pH 6.2 the concentration of H⁺ is higher than at pH 7.2 or 9.3.⁴⁴

Furthermore, the maximum formation of NHBrCl was much higher at pH 6.2 compared to 7.2. This was consistent to what was observed in previous literature where pH and bromide concentration control rate of NH₂Cl decay and maximum NHBrCl formation.³⁵ Despite dramatic changes in speciation at varying pH, little change was observed for BA+*N*-Br-BA over the pH range of interest. This led to the hypothesis that NHBrCl was not the brominating agent that promoted ring bromination because at pH 6.2, NHBrCl almost completely decayed after 2 hours.

Figure 2-19 below describes BA+N-Br-BA decay, NH_2Cl decay, and NHBrCl formation and decay at pH 6.2 to 9.3.

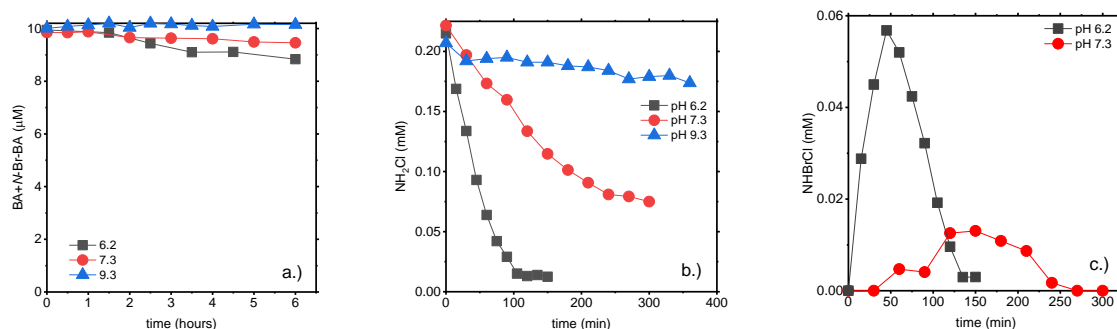


Figure 2-19. BA+N-Br-BA, NH_2Cl , or NHBrCl decay when $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{Br}^-]_0$ 840 μM , $[\text{C}_{\text{Buffer}}]_{\text{T}}$ 25 mM a.) $[\text{BA}]_0$ 10 μM b.) NH_2Cl decay c.) NHBrCl formation and decay

Additionally, the role of initial concentration of NH_2Cl on BA during the chloramination of bromide containing waters was explored. Experiments were first conducted at pH 4 because decay kinetics could be compared with k_{obs} values. The $\ln(\text{BA}/\text{BA}_0)$ was assessed when 500 μM or 200 μM NH_2Cl was amended to chloraminated the system in the presence of a range of bromide concentrations. Results based on k_{obs} values indicated that NH_2Cl had little effect on BA decay regardless of bromide concentration in the system. All k_{obs} values are in Table 2-4. A lack of change in BA decay when the initial NH_2Cl concentration changed was consistent with the conclusion that the bromide addition and pH of the system had the largest effect on BA decay. Figure 2-20 displays comparisons between 200 and 500 μM $[\text{NH}_2\text{Cl}]_0$ on $\ln(\text{BA}/\text{BA}_0)$ over time in chloraminated bromide containing waters.

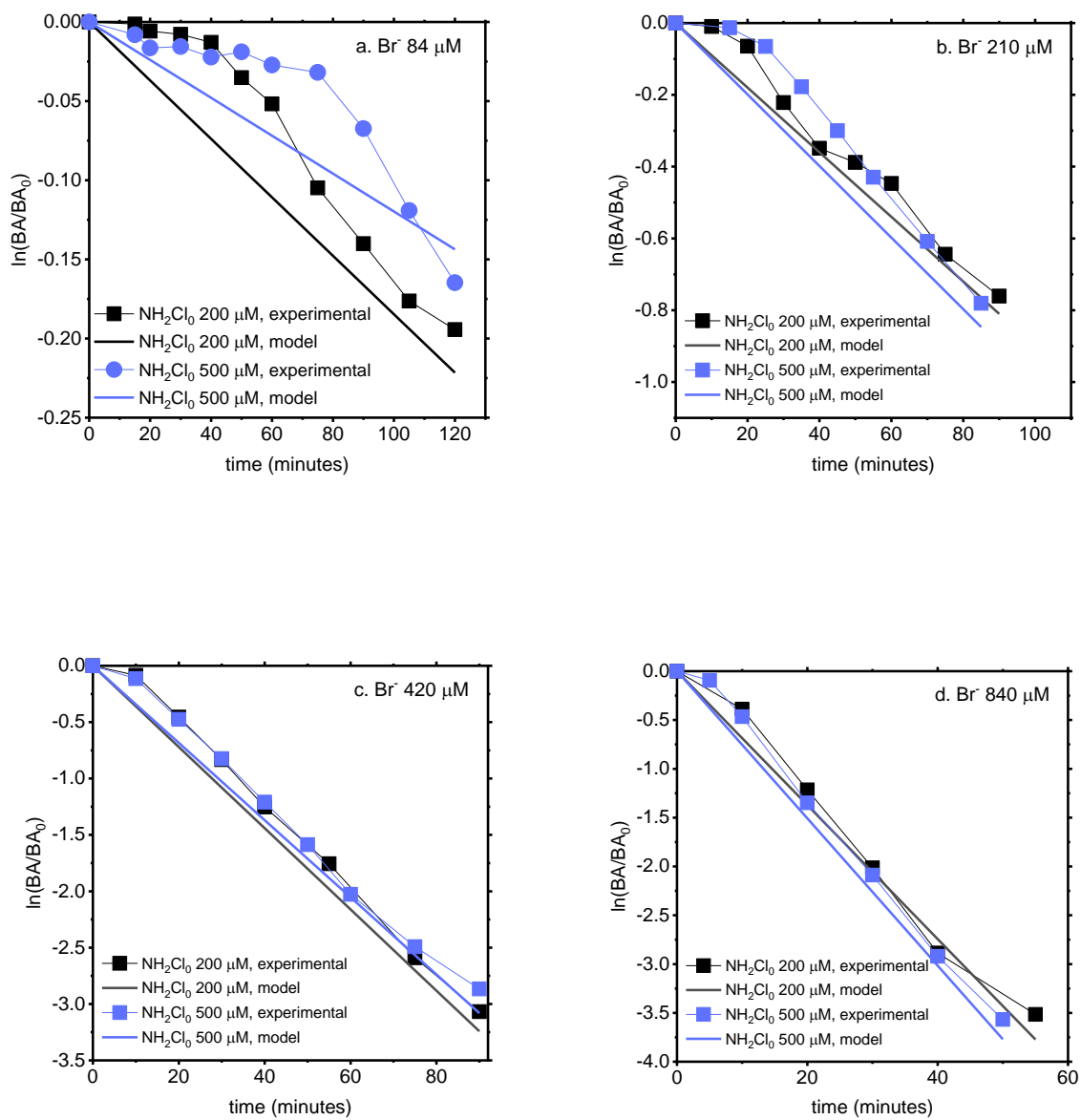


Figure 2-20. $\ln(BA/BA_0)$ when $[BA]_0 = 10 \mu M$, pH 4.1, $[C_{Ace}]_T = 25 \text{ mM}$, with varying $[NH_2Cl]_0$ and $[Br^-]_0$

Table 2-4. k_{obs} and R^2 values for each condition

	[NH ₂ Cl] ₀ 200 μM		[NH ₂ Cl] ₀ 500 μM	
Br ⁻	k_{obs}	R^2	k_{obs}	R^2
μM	min^{-1}		min^{-1}	
84	-1.85E-03	0.966	-1.20E-03	0.894
210	-1.15E-02	0.991	-9.96E-03	0.978
420	-3.60E-02	0.997	-3.42E-02	0.995
840	-6.86E-02	0.997	-7.54E-02	0.997

At pH 6.2 to 9.3, the effect of initial NH₂Cl was evaluated on BA+N-Br-BA decay and NH₂Cl and NHBrCl speciation. Again, the change in [NH₂Cl]₀ had negligible effect on BA+N-Br-BA decay. It is unknown if this result would be consistent if the decay of BA were isolated from N-Br-BA. At pH 6.2, regardless of initial NH₂Cl concentration, most of the monochloramine decayed from the system after 100 minutes. At both pH 6.2 and 7.3, a higher concentration of NHBrCl formed when more NH₂Cl was in the system. This further supported the hypothesis that NHBrCl was not the brominating agent that led to ring bromination. The concentration of NHBrCl dramatically changed based on pH, [NH₂Cl]₀, and Br⁻ concentration, but it still did not lead to ring bromination of BA above detection limits. At pH 9.3 little to no change occurred for BA+N-Br-BA over the course of 6 hours. Additionally, very little decay of NH₂Cl occurred while in the presence of bromide regardless of [NH₂Cl]₀. Figures 2-21 to 2-23 describing BA+ N-Br-BA, NH₂Cl decay, and NHBrCl formation and decay at pH 6.2 to 9.3 with varying [NH₂Cl]₀ are displayed below.

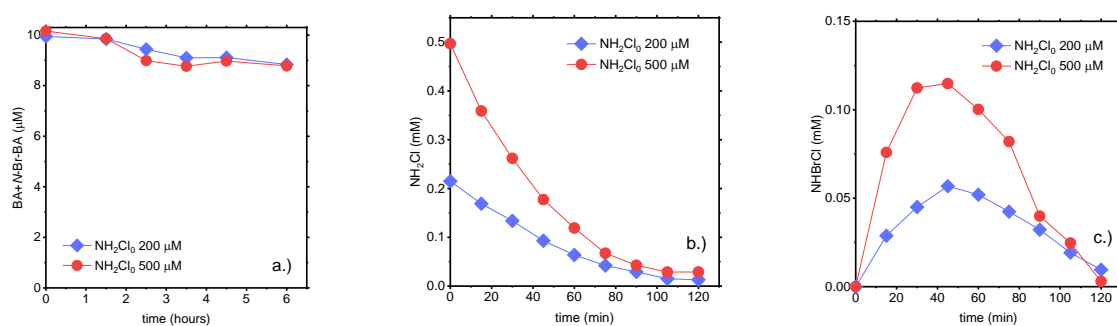


Figure 2-21. pH 6.2, $[\text{Br}^-] = 840 \mu\text{M}$, $[\text{CPO}_4]_T = 25 \text{ mM}$ a.) $[\text{BA}]_0 = 10 \mu\text{M}$ b.) NH_2Cl decay c.) NHBrCl formation and decay

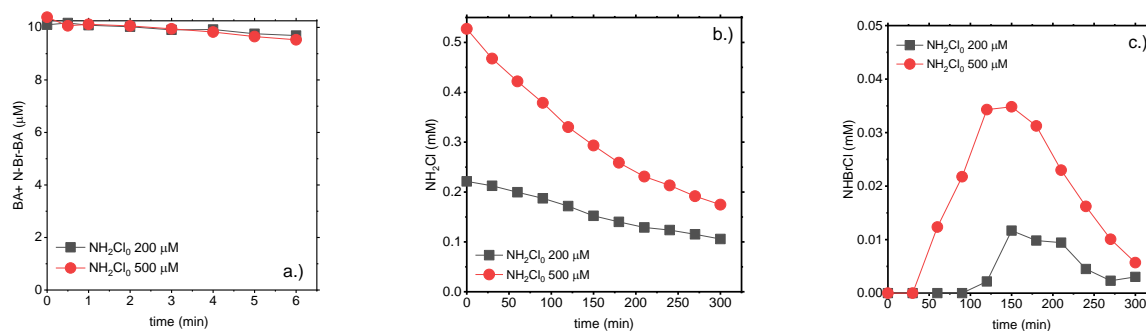


Figure 2-22. pH 7.3, $[\text{Br}^-] = 840 \mu\text{M}$, $[\text{CPO}_4]_T = 25 \text{ mM}$ a.) $[\text{BA}]_0 = 10 \mu\text{M}$ b.) NH_2Cl decay c.) NHBrCl formation and decay

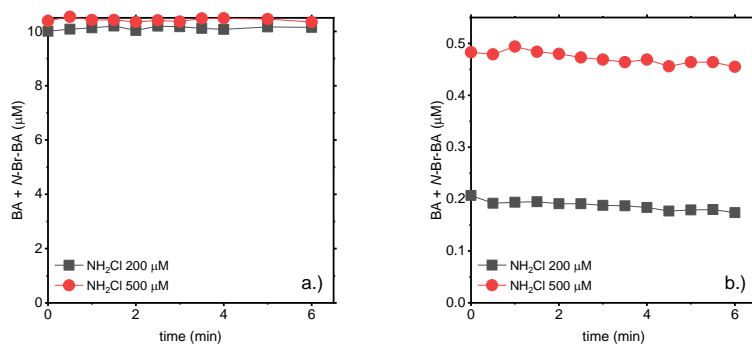


Figure 2-23. pH 9.3, $[\text{Br}^-] = 840 \mu\text{M}$, $[\text{CBO}_3]_T = 25 \text{ mM}$ a.) $[\text{BA}]_0 = 10 \mu\text{M}$ b.) NH_2Cl decay

Furthermore, the role of phosphate buffer concentration on BA+N-Br-BA decay, NH_2Cl decay and NHBrCl formation and decay during was examined. Phosphate buffer concentration was of interest because, as stated previously, the decay of NH_2Cl is general acid catalyzed.⁴⁴ An increase in phosphate buffer leads to more H^+ in the system, thus, affecting the disproportionation of NH_2Cl .⁴⁵ However, at pH 6.2 to 7.3, the concentration of phosphate buffer had no effect on NH_2Cl or BA+N-Br-BA decay or NHBrCl formation. Alternatively, phosphate buffer concentration had a slight effect on the decay of NHBrCl , where lower phosphate buffer concentration resulted in slower NHBrCl decay. These experiments were not carried out at pH 9.3 because experimentally there was no formation of NHBrCl and the decay of NH_2Cl was much slower than NH_2Cl decay at neutral pH. Additionally, these experiments were not conducted at pH 4 because speciation of NH_2Cl and NHBrCl cannot be spectrophotometrically determined at low pH. Figures 2-24 and 2-25 below show the effect of phosphate buffer on BA+N-Br-BA, NH_2Cl , and NHBrCl .

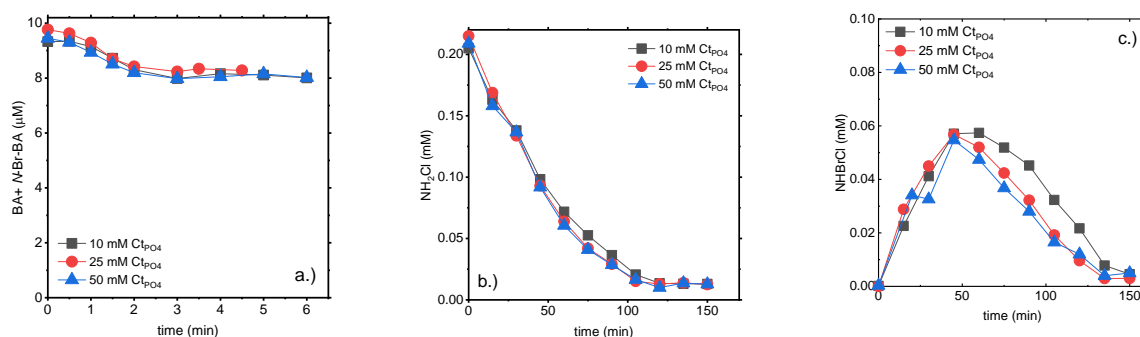


Figure 2-24. pH 6.2, NH_2Cl_0 200 μM , Br^- 840 μM , a.) BA_0 10 μM b.) NH_2Cl decay c.) NHBBrCl formation and decay

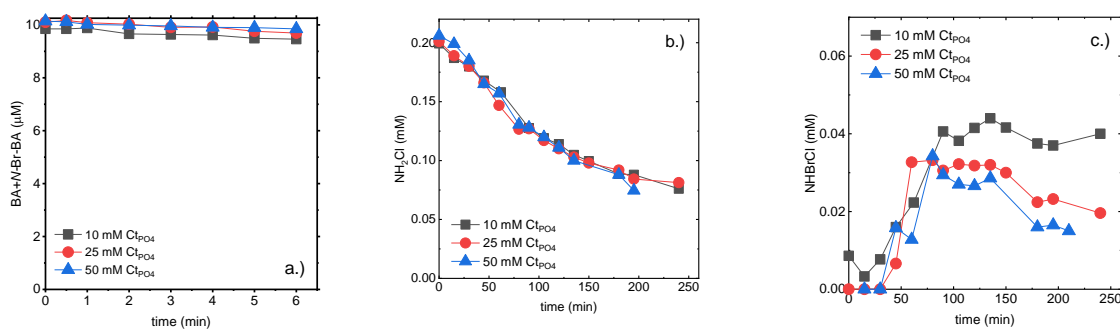


Figure 2-25. pH 7.3, NH_2Cl_0 200 μM , Br^- 840 μM , a.) BA_0 10 μM b.) NH_2Cl decay c.) NHBBrCl formation and decay

2.4.4 Chloramination with Chloride

The role of chloride was explored during the chloramination of BA. For these experiments, the target pH were 4 and 7, but they are reported as 3.97 and 6.64 because the pH meter measures activity, and the high addition of chloride led to a higher activity. In all experiments conducted with chloride, the chloride used was high purity; however, trace amounts of bromide were present at <0.01% (99.5% high purity NaCl from Sigma Aldrich). When 540 mM of chloride was amended to the system containing BA, the upper limit of bromide concentration was 54 μM . The trace amount of bromide was the cause of brominated ring products for the chloramination experiments with chloride. There was not a simple method to isolate chloride from bromide for the chloramination experiments with amended chloride.

When the solution containing BA was amended with chloride at 540 mM (seawater concentration) during chloramination, vastly different BA+N-X-BA decay occurred between pH 3.97 and 6.64. X is representative of chlorine (Cl) or bromine (Br) because it is unknown if *N*-halogenation occurred and whether it was due to the presence of chloride or bromide. At low pH, < 15% of BA+N-X-BA remained after ~ 4 hours; however, at neutral pH > 90% BA+N-X-BA remained after 8 hours. Figure 2-26 displays the decay of BA+N-X-BA at pH 3.97 and 6.64, where at pH 3.97 decay occurred much faster.

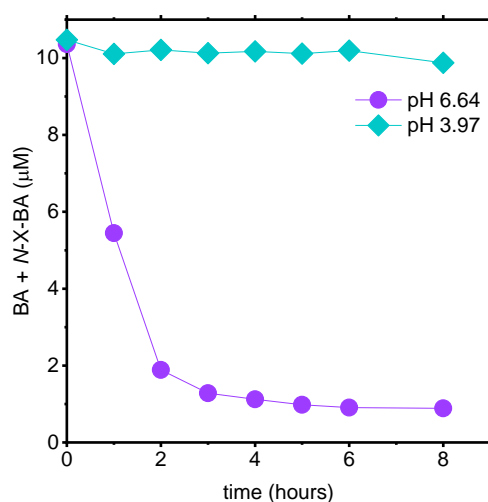


Figure 2-26. BA+ *N*-X-BA decay when $[BA]_0$ 10 μ M, $[Cl^-]$ 540 mM, $[Br^-] < 54 \mu$ M, $[NH_2Cl]_0$ 200 μ M, $[C_{Ace}]_T$ 25 mM

Under conditions tested with chloride, ring halogenation occurred. However, it was ring bromination not chlorination. This happened because of the trace concentration of bromide present in the purchased NaCl. This supported the finding that bromide led to more reactive secondary species during chloramination compared to the chloride ion during chloramination. At neutral pH (6.64), ring bromination only occurred at the para position (*p*-Br-BA) at a quantity lower than detection limits. The formation of *p*-Br-BA was verified based on the extracted ion chromatogram where a signal with 275.9 and 277.9 *m/z* occurred, which corresponded to *p*-Br-BA.

During the chloramination of chloride and trace bromide containing waters at low pH (3.97), the mass balance with respect to BA was > 80% closed, where both *o*-Br-BA and *p*-Br-BA formed. The approximate 20 % discrepancy of the mass balance may be attributed to the formation of other

products that were not accounted for or experimental error. Figure 2-27 displays BA decay and ring brominated by-product formation is shown below.

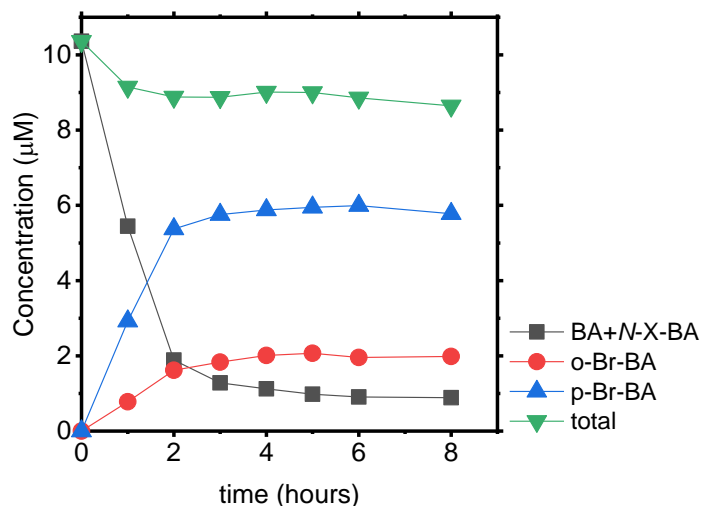


Figure 2-27. BA+N-X-BA decay and by-product formation at pH 3.97, $[BA]_0$ 10 μM , $[Cl^-]$ 540 mM, $[Br^-] < 54 \mu\text{M}$, $[NH_2Cl]_0$ 200 μM , $[C_{Ace}]_T$ 25 mM

Furthermore, the effect of ionic strength during chloramination was tested using perchlorate (ClO_4^-) at low pH. For the first 6 hours negligible change occurred for BA+N-X-BA, but after 8 hours small quantities of *o*-Br-BA and *p*-Br-BA formed based on the MS, but at levels too low for quantification. This was likely due to trace concentrations of bromide present in the purchased $NaClO_4$, although the trace bromide was not specified like it was for the $NaCl$. However, when the same concentration of chloride was present, brominated by-products were formed at 23% and 67% for *o*-Br-BA and *p*-Br-BA, respectively. This may be because there was less trace bromide in $NaClO_4$ than in $NaCl$ or because reactions between bromide, chloride, and chloramines formed more reactive species. Figure 2-28 shows change in BA+N-X-BA during the chloramination of solutions containing chloride or perchlorate.

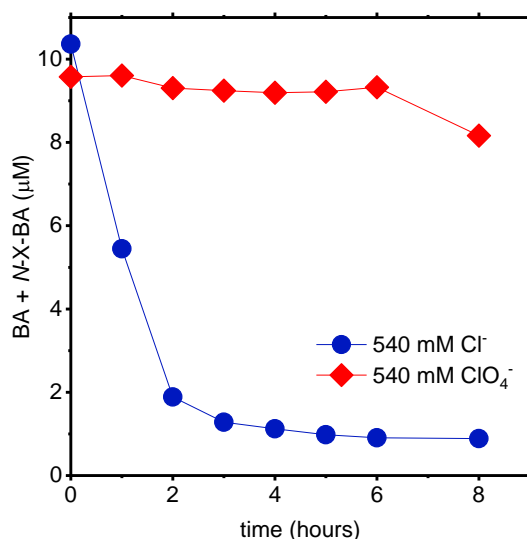


Figure 2-28. BA+N-X-BA decay pH 3.97, [BA]₀ 10 μM, [NH₂Cl]₀ 200 μM, [C_{Acc}]_T 25 mM

Chloride concentration also contributed to the decay of BA under chloraminated conditions. At neutral pH when low concentration of chloride was amended to the system (20 mM), no change occurred to BA+ N-X-BA. Additionally, after 8 hours there was no sign of ring halogenation under these conditions. This was only slightly different than when high chloride (540 mM) was amended at neutral pH where ring brominated products formed below detection limits.

At low pH, dramatically different BA+ N-X-BA decay occurred over 8 hours between the addition of high and low chloride concentrations. At high chloride concentration the decay occurred quite rapidly. Figure 2-29 displays BA+N-X-BA decay at pH 4 for varied amended chloride concentrations. However, these results were likely driven by the trace amount of bromide present. When only 20 mM of chloride was present, the upper limit of bromide was 2 μM compared to when 540 mM of chloride is added, the upper limit for bromide was 54 μM.

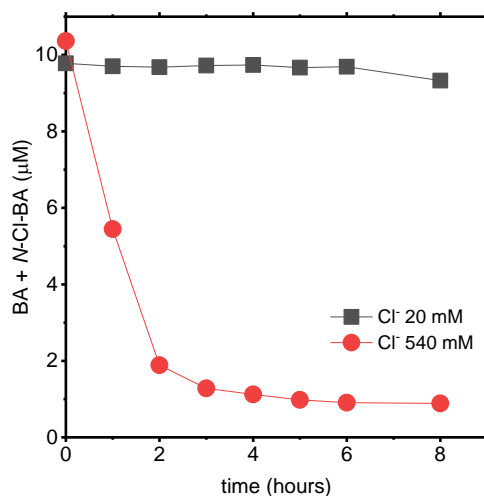


Figure 2-29. BA+N-X-BA decay pH 3.97, [BA]₀ 10 μM, [NH₂Cl]₀ 200 μM, [C_{Acc}]_T 25 mM

2.4.5 Chloramination with Bromide and Chloride

In seawater and brackish water, halides are present together in the water system. Therefore, it is important to understand how the presence of multiple halides (e.g. chloride and bromide) in solution affect BA during chloramination. Valentino et al.³⁰, the study investigating the effects of chloramination of seawater on PA-RO membranes, modified the model for NH₂Cl decay in the presence of bromide developed by Luh and Mariñas and applied it to understand speciation of brominating species. Because Valentino et al.³⁰ investigated seawater, the model was amended to reflect the contribution of chloride to the system by adding equation 16.^{20,30}



Because the addition of chloride leads to further halamine and oxidant speciation within the chloramine, chloride, and bromide system, additional experiments were conducted to further explore how the addition of both chloride and bromide affect the degradation of BA and subsequent by-product formation. As stated in the previous section, the NaCl used for the addition of chloride contained bromide up to 54 μM when chloride was present at 540 mM.

In order to assess the extent that the presence of chloride intensified the brominated by-product formation, an experiment was conducted comparing the effects of (i) 54 μM bromide and (ii) 540 mM chloride with < 54 μM bromide during the chloramination of BA at low pH. Results indicated that the solution with chloride and trace bromide led to faster BA+N-X-BA decay and higher *p*-

Br-BA formation even though the total bromide concentration was likely less than the bromide concentration in the bromide only reactor. This suggested that not only did bromide lead to ring bromination, but the addition of chloride exacerbated the formation of ring brominated by-products. Figure 2-30 below demonstrates BA+*N*-X-BA decay and *p*-Br-BA formation when 54 μM bromide or 540 mM chloride plus trace bromide were present.

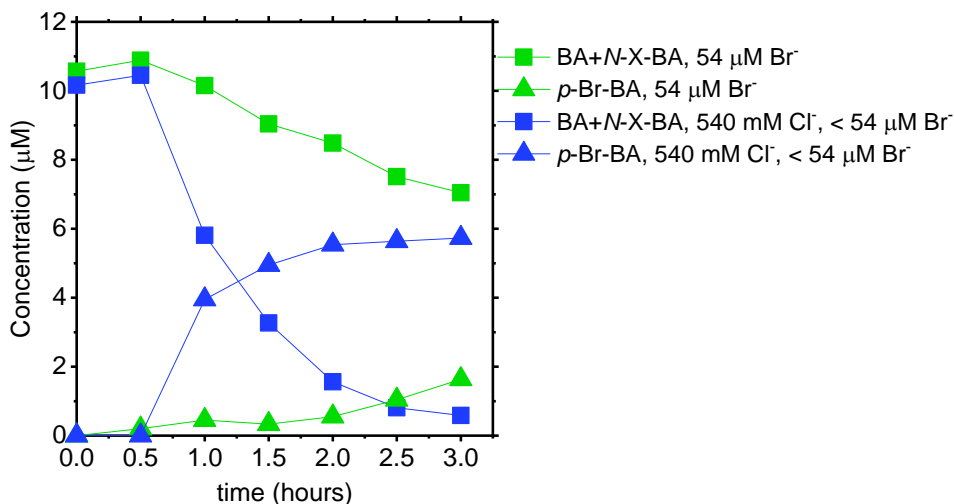


Figure 2-30. BA+*N*-X-BA decay and *p*-Br-BA at pH 3.97, $[\text{BA}]_0$ 10 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{C}_{\text{Ace}}]_{\text{T}}$ 25 mM

Furthermore, an experiment containing BA in the presence of bromide and chloride at concentrations present in seawater during chloramination was conducted at low pH. Amended bromide concentration is reported as 840 – 894 μM to account for trace bromide in the amended NaCl. Results indicated again only brominated by-product formation. Full decay of BA+*N*-X-BA occurred in ~ 10 minutes. Figure 2-31 displays the decay of BA+*N*-X-BA and the formation of the *o*-Br-BA and *p*-Br-BA. The mass balance regarding BA is > 90% closed, where possible discrepancies were the same as the ones stated in the previous section.

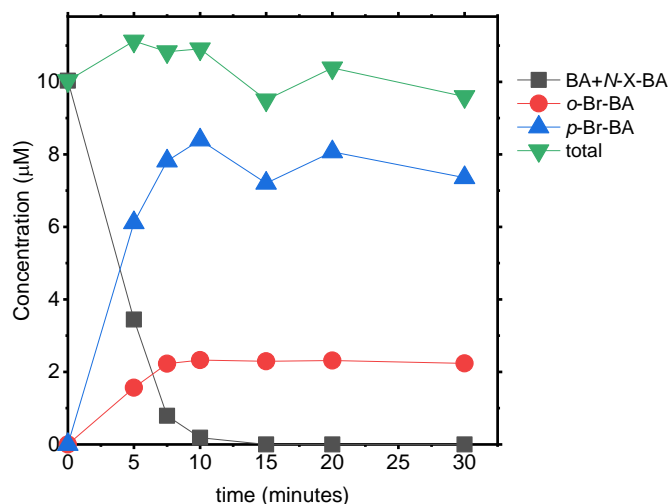


Figure 2-31. BA+N-X-BA decay and by-product formation at pH 3.92, $[BA]_0$ 10 μM , $[Cl^-]$ 540 mM, $[Br^-]$ 840 – 894 μM , $[NH_2Cl]_0$ 200 μM , $[C_{Ace}]_T$ 25 mM

The decay of BA+N-X-BA when BA was in the presence of (i) bromide (840 μM), (ii) chloride (540 mM) and trace bromide (< 54 μM), and (iii) bromide (840 μM) and chloride (540 mM) at concentrations corresponding to seawater were compared. Rate of decay of BA+N-X-BA was fastest for the system with bromide and chloride amended followed by bromide only, and lastly chloride with trace bromide. Results suggested the presence of bromide controlled the formation of a brominating agent during chloramination at low pH which led to the formation of brominated by-products for all conditions. The concentration of bromide present at seawater concentration is over 500 times lower than the concentration of chloride; therefore, it was evident that bromide in the presence of chloramines led to a much stronger halogenating agent than chloride in the presence of chloramines. Overall, the strongest halogenating agent likely occurred when both bromide and chloride were present during chloramination. It is possible that BrCl was the brominating agent that controls the BA decay and by-product formation. It was found by Huang et al.²² that BrCl was the strongest brominating agent, but this occurred when pre-formed HOBr was added to a solution containing chloride at pH 6.2; therefore, a direct comparison cannot be made. Figure 2-32 displays BA+N-X-BA decay under the previously stated conditions.

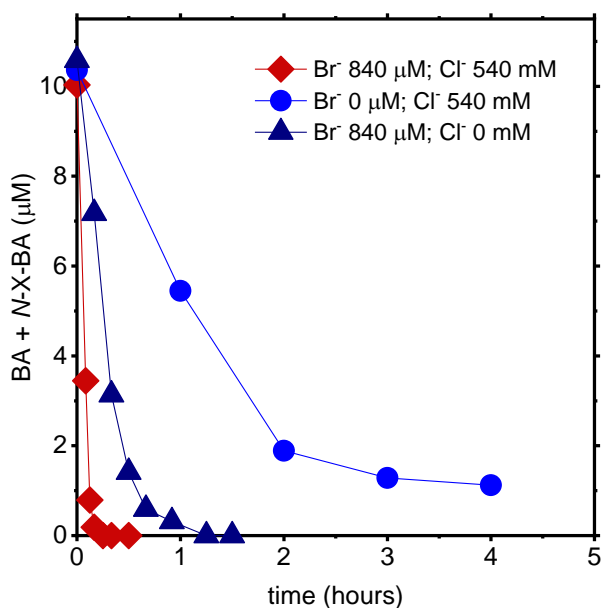


Figure 2-32. BA+N-X-BA decay pH 3.9 to 4.1, $[BA]_0$ 10 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{C}_{\text{Ace}}]_{\text{T}}$ 25 mM

At neutral pH during the chloramination of BA when bromide and chloride were both present at seawater concentrations, a more dramatic decrease in BA+N-X-BA occurred compared to when just bromide or just chloride with trace bromide were present. In fact, there was approximately a 25% decrease in BA+ N-X-BA when bromide and chloride were present. This was likely due to the formation of higher concentrations of secondary species that formed when both Cl^- and Br^- were present. Figure 2-32 displays BA+N-X-BA decay at pH 6.6 to 7.3 under varying halide conditions.

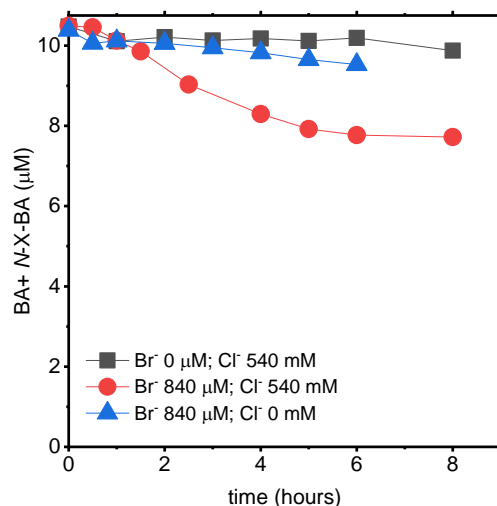


Figure 2-33. BA+ *N*-X-BA decay when $[BA]_0$ 10 μM , $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{CPO}_4]_{\text{T}}$ 25 mM

Although the addition of both bromide and chloride led to the highest decay of BA+ *N*-X-BA compared to only bromide or only chloride, there was no sign of ring halogenated by-products based on extracted ion chromatograms corresponding to 275.9, 277.9, 231, or 233 m/z . Previous literature has found that chloramines in the presence of bromide and chloride can result in *N*-halogenation followed by amide bond cleavage due to hydrolysis of the PA-RO membrane at pH 7.8 to 8.2.³⁰ Similarly, this phenomenon is known to occur during the chlorination of PA-RO membranes, especially at and above neutral pH.^{2,43} One hypothesis is when both bromide and chloride were present during chloramination, hydrolysis of the *N*-halogenated bond occurred and BA was fragmented in the yellow highlighted m/z region corresponding to 105 shown in Figure 2-34. However, 77 m/z was also extracted because it could fragment in the MS.

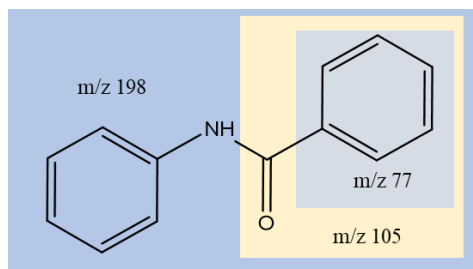


Figure 2-34. Possible ways for BA to fragment when exposed to chloramines and halides

The m/z ratios of 77 and 105 were extracted from the total ion chromatogram at time 0 and after 8 hours. The peaks in the Figure 2-35 correspond to the time-zero sample and the 8-hour sample, where the time-zero sample is green and the eight-hour sample is blue. The blue peak with the retention time at 4.9 minutes could be a fragmented by-product from BA due to the exposure of chloramines, bromide, and chloride.

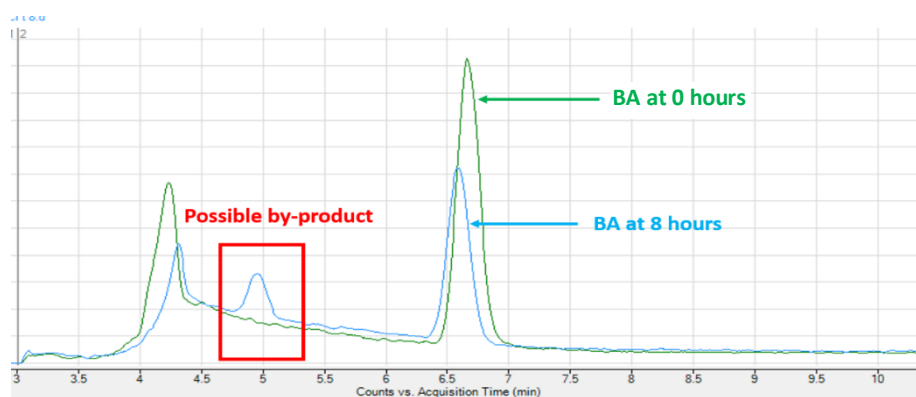


Figure 2-35. EIC 77 m/z and 105 m/z from pH 7 samples after 0 hours and 8 hours when $[BA]_0$ 10 μ M, $[NH_2Cl]_0$ 200 μ M, $[CPO_4]_T$ 25 mM

At pH 9.3, no evident change occurred during chloramination regardless of halide condition in the system. As stated in the previous paragraph, previous studies have observed and increase in carboxylic groups due to amide bond scission at high pH when the PA membrane is exposed to chlorine or chloramines under varying halide conditions, but no change was observed here. Figure 2-36 displays BA+N-X-BA decay when bromide and chloride were present along with when chloride with trace bromide was present.

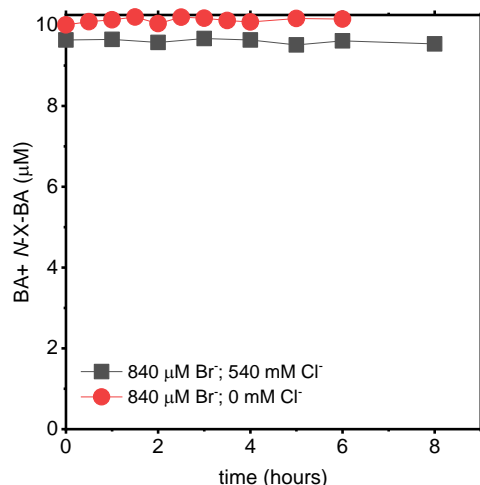


Figure 2-36. BA+N-X-BA decay at pH 9.3, $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{BA}]_0$ 10 μM , $[\text{C}_{\text{B}(\text{OH})_3}]_{\text{T}}$ 25 mM

2.5 Conclusions

This study evaluated the effects of chloramines with and without halides on the decay and by-product formation of the polyamide model monomers BA and *N*-CH₃-BA over a wide pH range. Results indicated low pH in the system and high concentration of bromide present resulted in the most dramatic decay and by-product formation of the monomer of interest. The most rapid decay of BA occurred when pH was low and bromide concentration was high. Under these conditions, BA decay could be predicted using pseudo-first order decay kinetics; however, when a low concentration of bromide was present, pseudo-first order did not describe decay as well likely because the brominating agent(s) was not in excess to BA. The concentration of pre-formed NH₂Cl and phosphate buffer concentration had negligible effects on BA+N-Br-BA decay. Results from *N*-CH₃-BA indicated that direct ring bromination occurred for *N*-CH₃-BA and likely also occurred when BA was in the presence of chloramines and bromide at low pH. However, this does not dismiss Orton Rearrangement as an alternative pathway for BA because it was still possible that both direct ring bromination and Orton Rearrangement occurred during chloramination of bromide containing waters. When BA and *N*-CH₃-BA were chloraminated under the same conditions, BA decay was substantially more rapid, which suggested that the addition of a methyl group on the amide N could lead to more chloramine resistant PA membranes.

Furthermore, when BA was chloraminated in the presence of both bromide and chloride, only ring bromination occurred, but the presence of chloride exacerbated the rate of BA+*N*-X-BA decay at pH 4 and 7 and increased the rate of ring bromination at pH 4. Overall, this study found that the addition of bromide compared to iodide or chloride led to the most dramatic change to the BA monomer and controlled ring bromination during chloramination. Future work must be done in order to find the true kinetics of BA because based on current methods the by-product *N*-Br-BA cannot be differentiated from BA. Also, future work should be done to further investigate the role of iodide on PA membranes during chloramination because of the severe implications of I-DBPs in chloraminated water containing iodide.

2.7 References

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3. CHANGES IN FLUX OF POLYAMIDE-BASED REVERSE-OSMOSIS MEMBRANES DURING THE CHLORAMINATION OF HALIDE-CONTAINING WATERS

3.1 Abstract

Flux experiments were performed using SWC4-LD polyamide based (PA) reverse osmosis (RO) membranes to determine membrane performance after exposure to (i) chlorination, (ii) chloramination, (iii) chloramination in the presence of bromide, and (iv) chloramination in the presence of bromide and chloride. Flux experiments were conducted from 6 hours to 14 days; however, most experiments were conducted over a 7-day period because 7-day experiments had the greatest change in flux. Overall, results indicated that free chlorine damaged the membrane to the highest degree and monochloramine the lowest regardless of pH. During chloramination, results suggested that the presence of bromide led to further damage to the membrane based on increased change in flux; however, the extent of damage did not reach the degree of the free chlorine only condition. At low pH, flux declined under all conditions, and it was likely due to membrane halogenation (e.g. chlorination or bromination). Halogenation of PA-RO membranes is known to result in increased membrane hydrophobicity; whereas, at high pH membrane flux increase was likely due to amide bond cleavage, which created a more open polyamide structure. However, at neutral pH, both mechanisms likely occurred, which revealed minimal change in flux for neutral pH exposure conditions except chlorination only. During chlorination at neutral pH, flux increased likely because hydrolysis of the amide bond was the dominant mechanism. Further analysis is required to evaluate the effects of both chloride and bromide during chloramination because in the presence of both halides, flux increase was never observed regardless of pH.

3.2 Introduction

Chloramines have been used as an effective disinfectant in water reuse distribution systems, and they are known to be an effective biofouling control for PA-RO membranes.^{1,2} However, further understanding is required regarding how PA-RO membranes behave when chloraminated in the presence of halides. The focus of Chapter 3 is toward changes in PA-RO membrane properties when the commercially made PA-RO membrane (SWC4-LD) was chloraminated in

halide containing waters. Previous studies focused on the effects of chlorination on commercially made PA-RO membranes, but less focus has been attributed toward chloramination of PA membranes especially in the presence of halides over a wide pH range. In previous works the effects of free chlorine and chloramination on the PA-RO membranes have used techniques that elucidate the type of damage that occur. Techniques include X-Ray Photoelectron Spectroscopy (XPS), Rutherford Back Scattering Spectroscopy (RBS), Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR), flux, and salt passage. For example, XPS is often applied to evaluate membrane characteristics in the top 7 nm of the membrane surface³; whereas, RBS is commonly used to evaluate the bulk of the membrane composite.⁴ Evaluation of flux and salt passage inform the performance of the membrane.⁵ However, conflicting evidence in literature has been presented on the change in flux and salt rejection when polyamide membranes are exposed to oxidants such as free chlorine, free bromine, and chloramines.^{3,5-8}

The following sections will provide a brief overview of chlorination and chloramination of PA-RO membranes both with and without halides and the methods by which PA-RO membrane degradation was evaluated. The following topics will be explored relating to the degradation of the PA layer (i) the effects of exposure and pH during chlorination and the corresponding degradation pathways (ii) the role of the bromide during chlorination at high and low pH (iii) effects of chloramination at pH 8, and (iv) effects of chloramination of seawater at pH 7.8 to 8.

3.2.1 Chlorination of PA-RO Membranes

PA-RO membrane degradation during exposure to free chlorine has been a topic of interest in many previous studies. During chlorination, two parameters of interest are exposure time (typically expressed as ppm as Cl_2 -hours) and pH. pH plays an important role during PA membrane chlorination because (i) pH strongly affects membrane degradation mechanisms and membrane properties, such as surface charge and hydrophobicity^{3,9-11} (ii) different chlorinating species dominate depending on pH (pK_a of HOCl/OCl^- is 7.5¹²), and (iii) the mechanisms by which the membrane degrades are dependent on the chlorine species present.^{3,13,14}

A study done by Do et al.⁸ investigated the effects of chlorine exposure and pH on the PA layer. Results based on XPS, ATR-FTIR, flux, and salt rejection experiments indicated that (i) low pH and high exposure led to the highest chlorine incorporation in the membrane matrix and (ii) high pH and high chlorine exposure promoted chlorination induced hydrolysis of the PA layer. Results

from Powell et al.¹⁰, where bulk chlorine uptake of the PA membrane was measured using RBS at various pH and exposures, supported findings from Do et al. which indicated that high free chlorine exposure and low pH result in further chlorine uptake of the PA membrane. Furthermore, another study by Do et al. showed that during chlorination an increase of carboxylic bonds appeared as a result of amide bond hydrolysis using XPS to evaluate the membrane surface.³

3.2.1.1 Disagreement Between Degradation Mechanisms During Chlorination

Despite agreement in changes in PA layer surface changes during chlorination, debate remains around the degradation pathways that occur during PA-RO membrane chlorination. As referred to in the previous chapter, the widely accepted chlorination mechanism of the PA membrane was (i) through chlorine uptake of the amide-N or the ring adjacent to the amidic nitrogen or (ii) indirectly through Orton Rearrangement. Due to the flaws in this method from a chemistry perspective stated in Chapter 2, additional studies investigated the validity of this trend. For example, Huang et al.¹³ found that ring chlorination and *N*-chlorination were separate pathways, and Stolov and Freger⁹ found that Orton Rearrangement was not able to fully explain PA-RO membrane degradation during chlorination.

3.2.2 Effect of Bromide During Chlorination of PA-RO Membranes

Bromide remains of interest due to its presence in waters treated by PA-RO membranes during desalination of seawater and brackish groundwater.¹⁵ A study on disinfection by-product (DBP) formation during the chlorination of bromide containing waters, found that the presence of bromide led to the formation of brominated organic products over chlorinated organic products.¹⁶ Because of the reactive products formed from reactions between free chlorine and bromide (Chapter 2 equations 4, 5, and 7), studies have investigated the effects of the bromide ion during the chlorination of PA-RO membranes.⁶ Kwon et al.⁶ found that chlorination of bromide containing waters led to mixed chlorination and bromination of the PA layer at pH 4 and 10 based on results from XPS and ATR-FTIR. This means that bromine, which is present due to the oxidation of bromide, bounds to the membrane surface. Furthermore, results indicated that bromine uptake on the membrane was favored even if free chlorine was in excess of bromide, which is similar to what was observed in DBP studies.^{6,16}

3.2.3 Chloramination of PA-RO Membranes

Monochloramine has also been a topic of interest because it is known to be a weaker disinfectant than free chlorine; however, the extent of PA-RO membrane damage that occurs is not fully agreed upon.^{17–19} Da Silva et al. found that although PA-RO membrane exposure to NH_2Cl led to increased flux over time, membrane exposure to free chlorine damaged the membrane more severely according to salt rejection experiments.¹⁷ Furthermore, Cran et al.¹⁹ found that when the PA membrane was in the presence of NH_2Cl , flux increased by 200% after 18 hours, but results also indicated an increase in rejection, which was hypothesized to be an effect of membrane tightening.¹⁹ Gabelich et al.¹⁸ studied the effect of ferrous iron (Fe(II)) in the presence of HOCl/OCl^- and NH_2Cl on PA-RO membranes. Results indicated that HOCl/OCl^- led to lower salt rejection than NH_2Cl over 300 hours when 2 mg/L of free chlorine or 2.5 mg/L chloramine residual was present.¹⁸ Although these studies agreed that membrane damage occurred during exposure to chloramines, effects of pH and exposure time have not been fully explored. For example, it is not yet known what chloramine species damage the membrane to the highest extent because at the pH (8 to 8.3) targeted in these studies, monochloramine was the dominant residual.

3.2.3.1 PA-RO Membranes During Chloramination of Seawater

As explored in the previous chapters, the presence of halides has implications on chloramine speciation to form brominating and iodinating species.^{20,21} In fact, some secondary species are known to react with PA based membranes resulting in further membrane degradation.^{4–7,22} Previous work has investigated the effects of chloramination of synthetic and natural seawater on PA-RO membranes.^{4,7}

First, Shemer and Semiat 2011,⁷ investigated the performance of halogen-based disinfectants including NH_2Cl , HOCl/OCl^- , and a mixture of HOCl/OCl^- and HOBr/OBr^- on PA membranes in synthetic seawater at pH 8.2. Membranes were exposed to the halogen-based disinfectants in the presence of seawater with and without bromide and evaluated for flux and salt rejection. Based on results from flux and rejection experiments, free oxidants (mixture of HOCl/OCl^- and HOBr/OBr^-) damaged the membrane to the highest degree followed by monochloramine, and lastly free chlorine.⁷

Valentino et al.⁴ performed a more comprehensive study of the effects of the chloramination of seawater to gain a better understanding of the polyamide bromination kinetics and degradation

mechanisms. PA-RO membranes were exposed to synthetic and natural seawater containing bromide and iodide at 65 mg/L and 0.06 mg/L, respectively, and then membranes were chloraminated with pre-formed NH_2Cl at 2 mg/L as Cl_2 at pH 7.8 to 8.2. The halide concentrations are consistent with the upper limit of halides present in natural seawater.¹⁵ Results revealed incorporation of bromine and iodine into the membrane, irreversible ring bromination, and an increase in carboxylic acid groups as a result of amide bond cleavage. Lastly, performance experiments (e.g. flux and rejection tests) revealed increased flux and decreased rejection, which was hypothesized to be due to an increase in carboxylic groups associated with amide bond cleavage.⁴

3.2.4 Objectives

These studies agree that the presence of halides in chloraminated waters result in damage to the PA-RO membrane.^{4,7} However, gaps remain pertaining to the role of pH on PA-RO membrane and concentration of individual halides present in the water matrix, especially corresponding to membrane flux after exposure. Furthermore, there is a large discrepancy between what concentration of chloramines are applied experimentally and the chloramine concentration applied industrially. In industrial systems, disinfectants are added at 0.2-4 ppm as Cl_2 ,²³ but in literature disinfectant concentrations range from 2 to 500 ppm as Cl_2 .^{4,17}

In this study, commercially made PA-RO membranes were exposed to pre-formed monochloramine (NH_2Cl) or free chlorine (HOCl/OCl^-) under varying water quality parameters. Membrane flux was assessed after 7 to 14 days (i) at pH ranging from 4 to 9.3 (ii) at varying halide conditions including 0 to 840 μM bromide or 840 μM bromide and 540 mM chloride with 5 mM buffer during the addition of pre-formed monochloramine or free chlorine. The initial concentrations of NH_2Cl and HOCl/OCl^- were 200 μM (14.2 ppm as Cl_2).

Experimental parameters were selected (i) for chloramine and free chlorine concentrations to be approximately five times higher than what is applied industrially to reach a high enough exposure that results in a change in flux without over saturating and (ii) for the pH range to be 4 to 9.3 because membrane cleaning procedures involve pH adjustments reaching acidic and alkaline conditions.^{24,25} This work aimed to (i) reveal the effects of pH on membrane flux during chloramination of halide containing waters and (ii) compare performance loss of PA-RO

membranes during exposure to free chlorine without halides and monochloramine in the presence of halides.

3.3 Material and Methods

3.3.1 Description of standards, reagents, and stock preparation

The standards and reagents for the experiments were purchased (i.) sodium hypochlorite 5%, glacial acetic acid, $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, $\text{NaH}_2\text{O}_5\text{C}_2$, and KI from Acros Organics, (ii) Sodium tetraborate decahydrate, NaCl, $(\text{NH}_4)_2\text{SO}_4$, and NaBr from Sigma-Aldrich. Reagent water (18.2 M Ω -cm) was from a Thermo Scientific Barnstead NANOpure water system.

The SWC4-LD polyamide membrane material was purchased from Hydronautics Nitto Group Company. Membrane parameters are listed in Table 3-1 below. The HP4750 dead-end cell was purchased from Sterlitech.

Table 3-1. SWC4-LD Membrane Parameters

Characteristics	SWC4-LD
Saline Rejection (%)	99.8
Maximum Operating Pressure (psi)	1200
Maximum Operating Temperature (°C)	45
Boron Rejection (%)	93
Maximum Chlorine (ppm)	<0.1

The procedure for NH_2Cl preparation is in Section 2.3.2, and the procedure for evaluating NH_2Cl decay in the presence of bromide is in Section 2.3.3.3.

3.3.2 Experimental procedure

Once the SWC4-LD membrane module was opened, the membrane was stored in an air-tight plastic bags in complete darkness. Membrane coupons were cut to size to fit the dead-end cell and soaked in 18.2 M Ω -cm reagent grade water for at least 24 hours before analysis. After membrane soaking, virgin flux of membranes was analyzed by (i) placing membranes into the dead-end flow cell (ii) adding 120 mL of 18.2 M Ω -cm reagent grade water to the dead-end cell (iii) pressurizing the dead-end cell to 800 psi. After this, water flowed through the cell for 15 minutes in order to allow for membrane compaction. Then the flowrate from the dead-end cell was determined

gravimetrically for 15 minutes allowing for at least 10 data points. After finding virgin flux of the membranes, membrane coupons were stored in 50 mL polypropylene centrifuge tubes containing 18.2 M Ω -cm reagent water. Centrifuge tubes containing membrane materials before or after exposure were covered in aluminum foil in order to avoid photodegradation of the membrane. After determining virgin membrane flux, membranes were exposed to water matrix of interest within 48 hours.

3.3.2.1 Set up of Exposure Conditions

Membrane exposure experiments were performed using synthetic solutions in 50 mL polypropylene centrifuge tubes for 6 hours to 14 days at room temperature (24 ± 1 °C). Membranes were placed in the centrifuge tubes before the synthetic solution was added. Synthetic solutions were buffered at various pH conditions from pH 4 to 9 with either 5 mM acetate buffer (pH 3.9-4.1), phosphate buffer (pH 6.0- 7.7), or borate buffer (pH 9.0-9.3). Halides (e.g. bromide and chloride) were amended to the solution after the addition of buffers and reagent water. Reactions were initiated by the addition of 200 to 400 μ M NH_2Cl or 200 μ M HOCl/OCl^- .

3.3.2.2 Determining Flux of Exposed Membranes

After the membranes were exposed to the water matrix for the desired length of time, they were again tested for flux. The method of analysis was the exact same as determining virgin flux. After exposure, the membrane flux was compared to its initial flux and expressed as Δ Flux as mL/min at 800 psi. All flux experiments had at least 3 replicates.

3.4 Results and Discussion

3.4.1 Determination of Experimental Time Scales

In order to determine the baseline experimental time scale for all subsequent experiments, flux experiments were conducted with membranes exposed to conditions containing pre-formed NH_2Cl with bromide at pH 4 to 9.3. Exposure times ranged from 6 hours to 14 days. Results indicated the greatest change in flux occurred after 7 days. Therefore, all experiments were carried out from 7 to 14 days. Data from flux experiments measured at different time scales is presented in Figure 3-1.

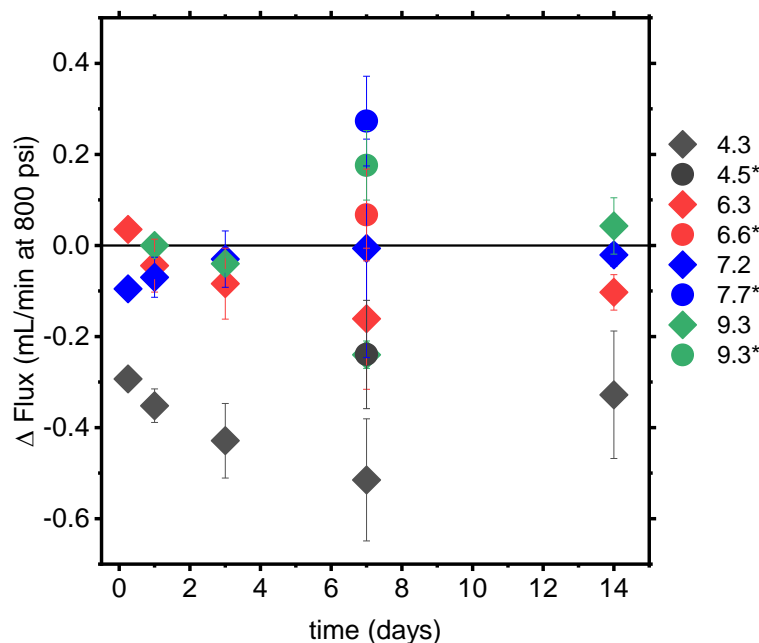


Figure 3-1. Determination of ΔFlux of SWC4-LD membranes when $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{Br}^-]$ 840 μM , $[\text{C}_{\text{Buffer}}]_{\text{T}}$ 5 mM; •* denotes membranes analyzed only one time, all other membranes analyzed many times throughout duration of experiments.

If 200 μM of the disinfectant (e.g. pre-formed NH_2Cl or HOCl/OCl^-) is applied for 7 days, the exposure can be denoted 2386 ppm as Cl_2 -hours assuming no degradation or speciation of the applied disinfectant. However, this was not an accurate way to present data particularly for chloramination of membranes due to the inherent instability of monochloramine and accelerated monochloramine decay when bromide was present in solution.^{21,26} Therefore, data in this section was not disseminated in terms of ppm as Cl_2 -hours but instead presented by stating the initial concentration of the disinfectant of interest and length of experiment. Figure 3-2 below displays NH_2Cl decay over time at pH 6.2 to 9.3 in the presence of 840 μM bromide. At pH 4, NH_2Cl decay was not experimentally determined because of the presence of many competing brominating species.

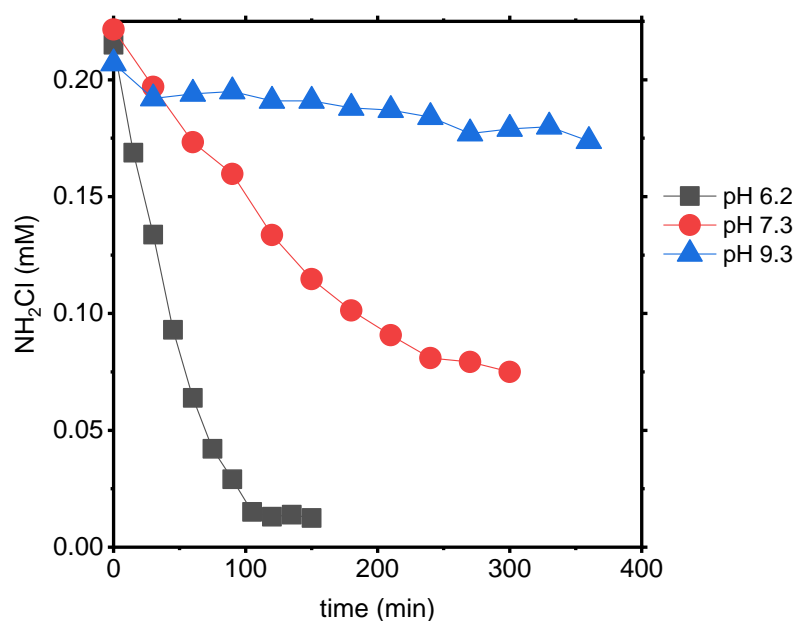


Figure 3-2. NH_2Cl decay when $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{Br}^-]$ 840 μM , and $[\text{C}_{\text{Buffer}}]_{\text{T}}$ 25 mM

3.4.2 Changes in Membrane Flux

3.4.2.1 Effects of Chlorination and Bromide Addition During Chloramination

To explore change in performance of PA-RO membranes during exposure to free chlorine, pre-formed monochloramine (200 μM), or monochloramine amended with bromide (210 or 840 μM) on the PA-RO membrane, the change in membrane flux was determined after 7 days over a wide pH range. Results indicated that the monochloramine led to the smallest change in flux; whereas, free chlorine led to the greatest change in flux at all pH evaluated. Consequently, the addition 210 μM of bromide with monochloramine resulted in a slightly larger change in flux than monochloramine. However, when 840 μM of bromide was present with monochloramine, change in flux followed a similar trend to the scenario with free chlorine. Therefore, the addition of bromide intensified the change in flux during chloramination. These results were consistent with Da Silva et al.¹⁷ which found that while NH_2Cl results in membrane damage demonstrated by an increase in flux, free chlorine is a more aggressive disinfectant.¹⁷ Flux results are presented in Figure 3-3.

3.4.2.2 Low pH

At low pH (4.1-4.5), flux decreased for all scenarios, but the intensity of the flux decline increased as $\text{NH}_2\text{Cl} < \text{NH}_2\text{Cl} + 210 \mu\text{M Br}^- < \text{NH}_2\text{Cl} + 840 \mu\text{M Br}^- < \text{HOCl/OCl}^-$. Previous studies investigated the effects of HOCl/OCl⁻ on PA-RO membranes at low pH and attributed the high decline in flux to increased membrane hydrophobicity.²⁷ Increased hydrophobicity is known to occur due to chlorine incorporation into the PA layer, which is predominantly guided by HOCl.^{3,10,27,28} It is possible incorporation of halogens (e.g. chlorine or bromine) into the membrane occurred under all conditions, which increased membrane hydrophobicity and decreased flux. However, previous studies characterizing the PA-RO membrane surface after exposure to chloramines or chloramines with bromide at low pH have not ensued. Therefore, only inferences were made regarding the mechanisms guiding the decrease in flux for chloramination scenarios with or without bromide.

However, one way to gain insight on the effects of chloramines with bromide on the PA-RO membrane is to look towards the results from the BA experiments conducted in Chapter 2. At low pH, when BA, the PA model monomer, was chloraminated in the presence of bromide, ring brominated products formed even when the solution was amended with low bromide concentration (Figure 2-11). Therefore, it is possible that the PA-RO membrane was brominated during chloramination in the presence of 210 and 840 μM bromide. Alternatively, results from experiments conducted with BA during chloramination without halides did not indicate any ring chlorination at low pH.

Furthermore, previous studies indicated that during the chlorination of PA-RO membranes at low pH, the addition of bromide resulted in membrane bromination even when only a small concentration of bromide was present (10 ppm or 125 μM).⁶ Subsequently, the addition of bromide during chlorination decreased the flux to a greater extent than chlorination only at low pH.⁶ This helps to further support the hypothesis that when the PA membrane is chloraminated in the presence of bromide at pH 4, membrane bromination occurred, which resulted in increased membrane hydrophobicity and decreased flux. However, the extent of membrane bromination during chloramination with bromide cannot be assessed by only flux experiments.

3.4.2.3 Neutral pH

At neutral pH (6.2-7.6) membrane flux increased for scenarios (i) HOCl/OCl⁻ and (ii) NH₂Cl + 840 μM Br⁻, where flux increased as NH₂Cl + 840 μM Br⁻ < HOCl/OCl⁻. However, at pH 6.5 the flux increase may not be statistically significant for the NH₂Cl + 840 μM Br⁻ condition. At pH 6.5, during the chloramination of waters containing 840 μM Br⁻, the slight change in flux could be due to competition between mechanisms, where incorporation of bromine in the PA layer occurred resulting in increased hydrophobicity and hydrolysis of the amide bond resulted in increased hydrophilicity.^{3,8} The competition of mechanisms could manifest by resulting in little to no change in flux.⁸ Based on BA experiments at pH 6 under parallel conditions in Chapter 2, ring brominated products formed after 8 hours (Figure 2-17) but below quantifiable levels. This would suggest that the PA-RO membrane could have been brominated but possibly not to an extent that dramatically affected membrane hydrophobicity.

At neutral pH when the membrane was chloraminated in the presence of 210 μM bromide, little to no change also occurred. This could be the case because (i) NH₂Cl is a weak disinfectant especially compared to free chlorine²⁹, or (ii) competing mechanisms occurred like what was hypothesized for pH 6.5 for the NH₂Cl + 840 μM Br⁻.⁸ The PA-RO membrane underwent very little change at neutral pH in the presence of monochloramine, and this was likely because NH₂Cl is a much weaker disinfectant and free chlorine.²⁹

3.4.2.4 High pH

Membrane flux increased for all four scenarios as NH₂Cl < NH₂Cl + 210 μM Br⁻ < NH₂Cl + 840 μM Br⁻ < HOCl/OCl⁻ at high pH. Similar to the increase in flux at neutral pH, the increase in flux at pH 9.3 during membrane chlorination was likely due to reduced degree in cross-linking because of chlorination-induced hydrolysis of the amide bond.^{3,8} The increase in flux during the chloramination of bromide (210 or 840 μM) containing waters was likely due to *N*-bromination followed by hydrolysis of the amide group which is known to increase in carboxylic groups on the membrane surface.⁴ It is not fully understood how the increase in bromide concentrations affected extent of amide bond hydrolysis at high pH. Based on results from this study, it was likely that an increase in bromide concentration resulted in further amide bond cleavage because more bromide (e.g. 840 μM vs. 210 μM) resulted in greater flux-increase. When experiments were conducted with the BA monomer under the similar experimental conditions in Chapter 2, results

suggested no irreversible ring bromination occurred. However, experiments conducted with BA were only over the course of 8 to 24 hours; therefore, when the PA-RO membrane was under these conditions for 7 days some ring bromination could have occurred at low levels.

The chloramination of PA membranes without the presence of bromide only slightly increased flux. However, error bars suggested this increase in flux was not significant; therefore, it was not known if the membrane was damaged by the presence of monochloramine only at the concentration present in this study. Results from Da Silva et al.¹⁷ and Cran et al.¹⁹ observed a significant increase in membrane flux at pH above 8; however, Da Silva et al. and Cran et al. added pre-formed NH_2Cl at concentrations of 500 ppm and 100 ppm NH_2Cl , respectively opposed to 14.2 ppm as Cl_2 (200 μM NH_2Cl) (i.e. the concentration used in this study). Cran et al.¹⁹ observed significant damage to the membrane in the presence of chloramines verified by FTIR, which led to the hypothesis that some damage occurred to the PA-RO membrane when 200 μM NH_2Cl was added, but it was not detected by flux experiments.

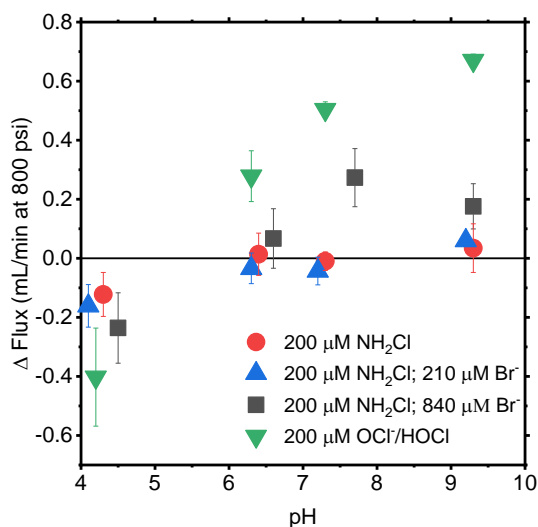


Figure 3-3. Determination of Δ Flux of SWC4-LD membranes over 7 days when $[\text{HOCl}/\text{OCl}^-]_0$ or $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{Br}^-]$ 0 to 840 μM , $[\text{C}_{\text{Buffer}}]_{\text{T}}$ 5 mM

Overall, based on these results, it was hypothesized that at low pH, the membrane became irreversibly halogenated. The degree of flux-decrease suggested that membrane halogenation occurred to the highest degree during chlorination followed by chloramination in the presence of

high bromide (840 μM). At high pH, it was hypothesized that *N*-halogenation followed by hydrolysis of the amide bond occurred which led to more carboxylic acid groups on the membrane surface and a more open polyamide structure. Thus, this phenomenon led to increased membrane flux. At neutral pH, it was hypothesized that both mechanisms occurred which led to little change in membrane flux. Figure 3-4 shows a graphical hypothesis of what occurred during chlorination and chloramination in the presence of bromide to the PA-RO membrane at high to low pH. NH_2Cl is omitted from this graphical hypothesis because change in flux was minimal. Furthermore, it is important to note that it is still not known if at low pH the irreversible ring halogenation occurred directly or if it went through Orton Rearrangement; therefore, Figure 3-4 does not show potential pathways that led to irreversible ring halogenation at low pH.

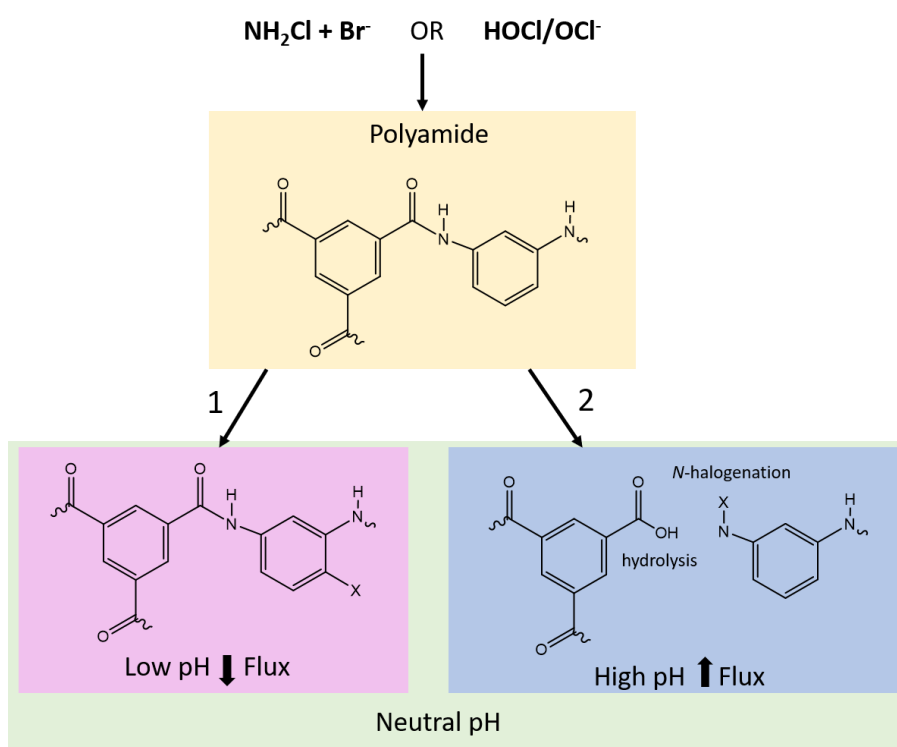


Figure 3-4. Hypothesis of Mechanisms for PA-RO Damage

3.4.3 Doubled Bromide and Pre-Formed NH_2Cl Concentrations

Figure 3-5 shows membrane flux was lower when the PA-RO membrane was in the presence of 1.68 mM bromide and chloraminated with 400 μM pre-formed NH_2Cl compared to bromide and NH_2Cl conditions of 840 and 200 μM , respectively. At pH 4.5, the doubled bromide and pre-formed NH_2Cl concentrations, 1.68 mM and 400 μM , respectively, decreased the membrane flux

to a greater extent compared to when 840 μM bromide and 200 μM pre-formed NH_2Cl were amended to the system. One hypothesis is that when more bromide and monochloramine were amended to the system, more irreversible ring bromination occurred, which increased membrane hydrophobicity and further flux-decrease.

At neutral and high pH, flux increased for all scenarios; however, the extent of flux increase is greater for the lower bromide and pre-formed NH_2Cl conditions. This could again be due to higher bromination occurring under higher exposure conditions in tandem with competing mechanisms resulting in some flux increase from amide bond cleavage. Valentino et al.⁴, found that when amended concentrations of both bromide and NH_2Cl were increased by a factor of 10, bromine uptake increased according to RBS analysis. Therefore, one possibility is that the doubling of both bromide and pre-formed NH_2Cl results in greater bromine uptake, thus, resulting in increased membrane hydrophobicity. If this were the case, then the increase in flux may not be as dramatic compared to when the lower concentrations of bromide and pre-formed NH_2Cl were amended to solution.

Although this is a possibility, further investigation is required to understand why flux-increase is not more pronounced at higher pH, where it would be expected that more bromide would result in further flux increase according to results comparing 210 μM bromide and 840 μM bromide during chloramination (Figure 3-3).

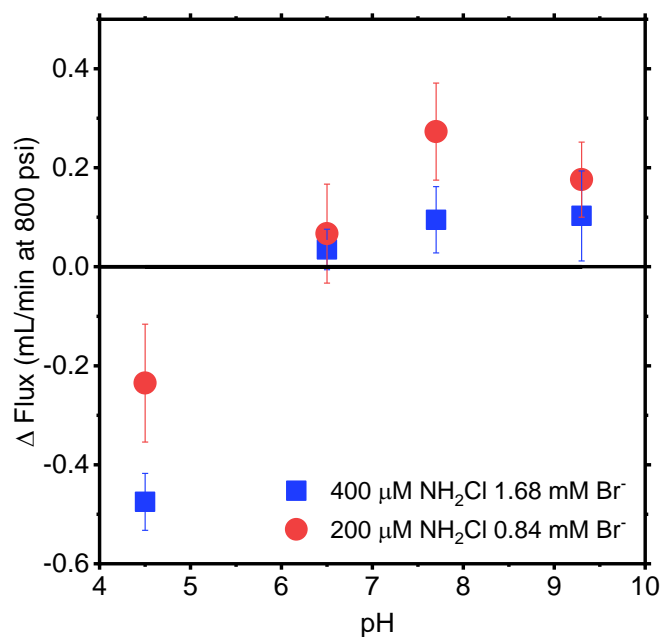


Figure 3-5. Determination of Δ Flux of SWC4-LD membranes after 7 days when $[\text{NH}_2\text{Cl}]_0$ 200-400 μM , $[\text{Br}^-]$ 0 to 840 μM , and $[\text{C}_{\text{Buffer}}]_{\text{T}}$ 5 mM

Additionally, experiments evaluating the change in flux over a 14 day period were conducted where PA-RO membranes were (i) chloraminated with 200 μM NH_2Cl in the presence of 840 μM Br^- , and (ii) chloraminated with 200 μM NH_2Cl in the presence of 840 μM Br^- at time 0 and then again after 7 days. Figure 3-6 compares the change in flux for these two conditions after 14 days. Results indicated that the flux was higher for all conditions where bromide and monochloramine were added twice (i.e. concentration doubled). This is opposite to the trend observed in Figure 3-5, where the higher bromide and monochloramine condition led to lower flux regardless of pH. One reason for this difference could be that the second addition of monochloramine and bromide possibly exacerbated already reduced polyamide cross-linking.

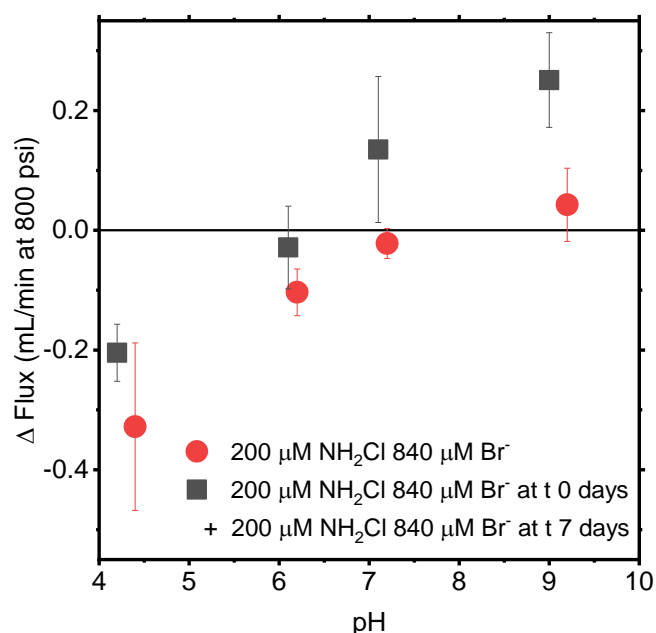


Figure 3-6. Determination of Δ Flux of SWC4-LD membranes after 14 days when (i) $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{Br}^-]$ 840 μM , $[\text{C}_{\text{Buffer}}]_{\text{T}}$ 5 mM, and (ii) $[\text{NH}_2\text{Cl}]_0$ 200 μM , $[\text{Br}^-]$ 840 μM amended at time 0 and again after 7 days, $[\text{C}_{\text{Buffer}}]_{\text{T}}$ 5 mM

3.4.4 Effects of Chloride and Bromide During Chloramination

Change in membrane flux was determined for the chloramination of PA membranes in the presence of chloride and bromide at concentrations present in seawater for pH 3.9 to 8.9. pH are lower for this experiment because the pH meter measures activity in solution, which is shifted by the high addition of chloride. Similar to when doubled bromide and pre-formed monochloramine were amended to solution, membrane flux was lower for the presence of bromide and chloride compared to bromide only during chloramination. Again, this may be due to a higher extent of halogenation, but full explanation of these results is not yet developed without further analysis by (i) isolating the effects of chloride during chloramination and testing flux and (ii) characterizing surface halogenation.

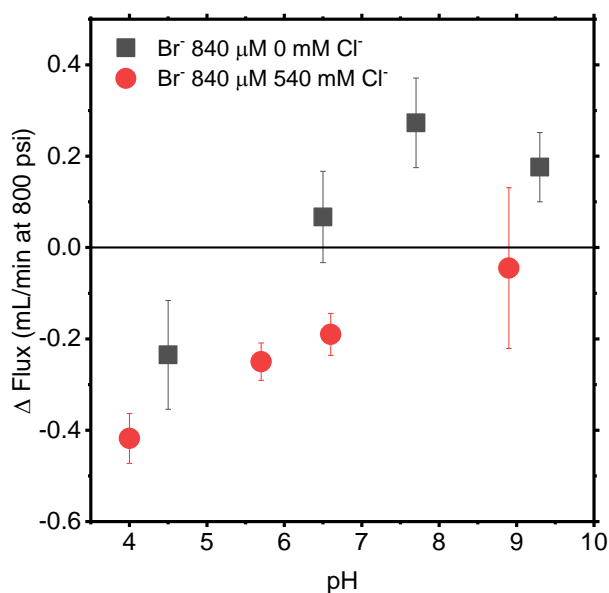


Figure 3-7. Determination of Δ Flux of SWC4-LD membranes after 7 days when $[\text{NH}_2\text{Cl}_0] = 200\text{--}400 \mu\text{M}$, $[\text{Br}^-] = 0 \text{ to } 840 \mu\text{M}$, and $[\text{C}_{\text{T,Buffer}}] = 5 \text{ mM}$

3.5 Conclusion

In this work, results from flux experiments determined changes in PA-RO membrane performance over time during exposure to varying halide (e.g. bromide or chloride) and disinfectant (e.g. pre-formed NH_2Cl or HOCl/OCl^-) combinations. Results indicated the free chlorine caused the most membrane damage, followed by monochloramine with bromide based on the greatest change in flux. Results suggested monochloramine alone could be a good replacement for free chlorine to control biofouling; however, the presence of bromide, a halide present in waters desalinated with PA-RO membranes, increases the membrane damage. However, full understanding of membrane halogenation during chloramination of bromide containing waters, especially at low pH, is not yet fully developed. Future work will aim to (i) explore surface halogenation of PA-RO membranes during the chloramination of bromide containing waters over a wide range of pH, (ii) evaluate changes in flux of PA-RO membranes during the chloramination of seawater (water containing chloride, bromide, and iodide), and (iii) determine surface halogenation of PA-RO membranes during the chloramination of seawater.

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4. RESEARCH CONTRIBUTIONS

Polyamide reverse osmosis membranes are the industry standard for water reuse and water desalination.¹ Their major limitations arise first when they undergo biofouling and furthermore when disinfectants are applied to mitigate the biofouling (e.g. free chlorine or chloramines). Overall this work aimed to explore the effects of halides present in the water matrix when chloramines were applied to PA-RO membranes. This work intended to bridge the gap between analyzing PA based monomers on an analytical scale to actual PA-RO membranes analyzed on a materials scale. Based on monomer (BA and *N*-CH₃-BA) kinetic experiments and commercial PA-RO flux experiments, results suggested that pH and the presence of bromide controlled structural changes to the PA membrane, which could eventually result in membrane failure during chloramination.

Furthermore, results indicated during chloramination in bromide, or bromide and chloride, -containing waters BA underwent irreversible ring bromination at low pH, which translates to chemical susceptibility and change in material properties on the PA-RO membrane surface. Similarly, PA-RO flux experiments indicated decrease in flux at low pH and increase in flux at high and neutral pH during the chloramination of bromide containing waters. This again suggested membrane susceptibility to damage and degradation. Additionally, the mechanisms by which membrane damage occurred were hypothesized to be dependent on pH. At low pH, PA-RO membranes likely became brominated; whereas, at high pH membrane structural properties likely began to breakdown due to *N*-bromination promoted hydrolysis of the amide bond. Regardless of mechanism, both ring bromination and amide bond cleavage are known to result in eventual membrane failure.² Results further suggested that chloramines in the presence of bromide have severe implications on any aromatic-amidic compounds during the chloramination of bromide containing waters.

This work primarily focused on the presence of bromide during chloramination because bromide occurs at relatively high concentrations in natural waters³ and can be oxidized by monochloramine to form strong brominating agents.⁴⁻⁷ On the contrary, the presence of chloride during chloramination is comparatively much higher (> 500 times) than bromide in natural seawater.³ However, chloramination of waters containing chloride do not result in highly reactive chlorinating species towards PA-RO membranes.⁵ Furthermore, iodide is highly reactive during

chloramination resulting in strong iodinating agents such as HOI.⁸ The concentration of iodide in natural waters is extremely low compared to bromide, where the concentration of bromide is over 1600 times greater than iodide.³ Therefore, bromide has both the characteristics of high reactivity in the presence of chloramines and natural presence in the environment, which make PA-RO membranes especially prone to damage.

Although this work has contributed toward elucidating the roles of halides during chloramination of the PA-RO membrane over a wide array of pH, many gaps remain. First, the pathways that occur during ring bromination and occurrence of *N*-bromination are still not fully understood because *N*-Br-BA could not be differentiated from BA due to analytical constraints. Therefore, the implementation of a novel approach is required to differentiate *N*-Br-BA from BA so that the true kinetics of BA during chloramination in bromide containing water can be evaluated. Furthermore, work should be performed to find the specific brominating agent(s) that brominate BA (i) irreversibly on the ring and (ii) on the amidic N. On the PA-RO membrane scale, further work should be conducted to (i) characterize membrane surface properties after chloramination in the presence of halides using XPS or RBS and (ii) isolate halides (e.g. bromide, chloride, and iodide) during chloramination and determine their effects on membrane performance over time. Overall, future work will aid in understanding morphological changes that occur and the pathways by which these changes occur on the PA-RO membrane during the chloramination of halide containing waters.

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VITA

EDUCATION

Master of Science (August 2017 – present) in Environmental and Ecological Engineering from Purdue University, West Lafayette, IN. Thesis Title: Chloramination of Polyamide-Based Reverse Osmosis Membranes in the Presence of Halides.

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PUBLICATIONS

Le, T.; **Haflich, H.**; Shah, A.; Chaplin, B. Energy Efficient Electrochemical Oxidation of Perfluoroalkyl Substances using Ti_4O_7 Reactive Membrane Anode. *Environ. Sci. Technol. Letters*. **In Review**.

Huang, K.; Reber, K. P.; Toomey, M. D.; **Haflich, H. M.**; Howarter, J. A.; Shah, A. D. Reactivity of the Polyamide Membrane Monomer with Free Chlorine: Reaction Kinetics, Mechanisms, and the Role of Chloride. *Environ. Sci. Technol.* **2019**. <https://doi.org/10.1021/acs.est.9b01446>.

PRESENTATIONS

Haflich, H.M.; Howarter, J. A.; Shah, A.D. Chloramination of Polyamide-Based Reverse Osmosis Membranes in Bromide Containing Waters (oral). *2019 AEESP Distinguished Lecture and 25th Annual EES Symposium*, Urbana-Champaign, Illinois, April 19, 2019.

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