Reactivity of various brominating agents toward polyamide nanofiltration membranes

Huihui Zhao [a,b,c], Linyan Yang *[,a,b,c], Xueming Chen [d], Jinrui Wang [a,b,c], Lichun Bai [e] ,
Guomin Cao [a,c], Lankun Cai [a,c], Chuyang Y. Tang [f]

[a] National Engineering Laboratory for Industrial Wastewater Treatment, East China University of Science and Technology, Shanghai 200237, P.R. China

[b] Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, P. R. China

[c] School of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, P.R. China

[d] Fujian Provincial Engineering Research Center of Rural Waste Recycling Technology, College of Environment and Resources, Fuzhou University, Fuzhou, Fujian, 350116, P.R. China

[e] Key Laboratory of Traffic Safety on Track (Central South University), Ministry of Education, School of Traffic & Transportation Engineering, Central South University, Changsha 410075, P.R. China

[f] Department of Civil Engineering, University of Hong Kong, Pokfulam, Hong Kong

Corresponding Author

*Phone: +86-13270696038; e-mail: lyyang@ecust.edu.cn

Abstract

Polyamide (PA) membranes, widely used for reverse osmosis and nanofiltration, are prone to bromination under chlorinated bromide-containing water conditions. Conventional wisdom generally assumes HOBr as the only active brominating agent responsible for PA membrane degradation, while some more reactive but less abundant brominating agents (including Br_2O, BrOCl, BrCl and Br_2) under these conditions are often overlooked. The current study addresses this critical literature gap by systematically evaluating membrane degradation under various [Br^-], [Cl^-] and [HOCl] conditions. The observed pseudo-first-order rate constant of membrane degradation (k_{obs}^{m}, using change in water flux as a surrogate indicator) was found to be well correlated to [Br^-], [Cl^-] and [HOCl] (R^2>0.90). The gradual increase of [Cl^-] and [Br^-] transforms the predominant brominating agent from HOBr to BrCl and Br_2, respectively, under excessive [Br^-] conditions. The species-specific second-order reaction rate constants followed a decreasing order of k_{BrCl}^{m} (2.6×10^4 $M^{-1}\cdot s^{-1}$) > k_{BrOCl}^{m} (2.0×10^3 $M^{-1}\cdot s^{-1}$) > $k_{Br_2O}^{m}$ (9.6×10^2 $M^{-1}\cdot s^{-1}$) > $k_{Br_2}^{m}$ (1.5×10^1 $M^{-1}\cdot s^{-1}$) > k_{HOBr}^{m} (5.4×10^{-1} $M^{-1}\cdot s^{-1}$). Additional decay tests using benzanilide (BA) as a surrogate monomer compound confirmed BrCl as the most reactive species. Under typical seawater conditions (pH 8.0), the more reactive but less abundant BrCl had significantly greater contribution to membrane degradation (85%) than HOBr (3%). Under typical neutral wastewater conditions, both BrCl and HOBr contributed equally. The current study developed a novel characterization technique to assess membrane degradation by determining the kinetics of the oxidant-PA reactions.

Keywords: polyamide membranes, membrane oxidation, bromination, brominating agents, reaction kinetics

1. Introduction

Polyamide (PA)-based thin film composite (TFC) nanofiltration and reverse osmosis (NF/RO) membranes have been widely used for (waste)water treatment due to their excellent permeability and selectivity [1, 2]. The exposure of functional PA layer to oxidants (e.g., chlorine and bromine) as biofouling preventing or cleaning agents may cause membrane failure [3, 4]. The weak resistance of PA results in a disinfectant-removal step prior to NF/RO system in order to protect the downstream PA membranes, commonly practiced in seawater desalination [5].

The degradation pathways of PA membranes have been considered as N-halogenation and ring-halogenation based on the commonly accepted halogenation mechanism [4, 6]. A typical (waste)water often contains certain amount of halide ions [7, 8]. For instance, seawater contains 19.2 g/L chloride and 67 mg/L bromide, and wastewater contains 0.71 g/L chloride and 0.24 mg/L bromide[9-11]. The co-effect of free chlorine and bromide on the degradation of PA membranes has been extensively investigated [12, 13]. Bromide has been shown to make a great contribution to oxidation processes [14, 15]. A more severe decrease in membrane flux was observed after adding bromide to a chlorinated water, which is attributed to the higher reactivity of HOBr to PA than HOCl [16, 17]. The reduced water flux was a result of the enhanced compaction and/or collapse of the chains induced by the breakage of hydrogen bond, preventing the transport of water molecules though the membrane[17]. The decrease in free-volume pore size of PA membranes after chlorination was reported as well [18]. Our previous study revealed the degradation pathways of N-bromination and bromination-promoted hydrolysis under mild bromine exposure (480 mg/L·h) and the further ring-bromination under severe bromine exposure (4800−24,000 mg/L·h) at pH 7.5 [4]. In addition, the different variation of membrane performance affected by chlorine and bromine was attributed to the different incorporation efficiency and properties of active halogens, based on the conventional wisdom that assumes HOX/OX^- (X refers to Cl or Br) as the only reactive species contributing to membrane degradation [4, 16, 19]. However, the comprehensive understanding of the chemistry of aqueous halogenating agents reveals the presence of other active species in addition to HOX/OX^- formed during the chlorination of bromide-containing water [10, 20-22].

The ubiquitous presence of chloride, commonly viewed as an inert constituent, facilitates the formation of BrCl (refer to Figure 1A). Br_2O and BrOCl are formed by active bromine and chlorine. Br_2 is formed when an excess amount of bromide is present in chlorinated water, i.e., $[Br^-]_o > [HOCl]_o$, where the subscript "o" represents the initial dosage. H_2OBr^+ was excluded since its remarkable contribution may only occur under low pH conditions in the absence of chloride ions, which is out of range of interested conditions [23]. Some studies reporting the transformation of amine-containing compounds under halogenation conditions can be informative for the oxidation of polyamide membranes [10, 22, 24]. Sivey et al. verified the contribution of these reactive brominating agents (including HOBr, Br_2O, BrOCl, BrCl and Br_2) towards dimethenamid decay [10]. These species are usually overlooked owing to 4-7 orders of magnitude lower concentration than HOBr, in spite of 3-8 orders of magnitude higher inherent reactivity. For electrophilic aromatic substitutions, the poorer leaving group ability of OH^- (from HOBr) than Cl^- (from BrCl), OCl^- (from BrOCl), OBr^- (from Br_2O), and Br^- (from Br_2) may result in the weaker electrophilicity and the lower bromination rate of HOBr than the latter brominating agents [10, 22]. BrCl particularly was reported to make a much higher contribution than HOBr (62%−72% vs. 5%−16%) to anisole transformation at pH 7.0, despite its 6 orders of magnitude lower concentration, under a typical drinking water chlorination condition [22]. The species contribution to anisole transformation was evaluated by kinetic experiments under various conditions, with the obtained specific reaction rate constant and concentration of each brominating agent as inputs (see more details in Section 2.3). Interestingly, the moderate increase of “inert” chloride from 5 to 30 μM at pH 7.05 promoted 4-bromonanisole formation by around 5 times, i.e., more 4-bromonanisole was formed under a fixed reaction time, which was attributed mainly to the enhanced formation of BrCl [22].

A

	Reaction equations	Equilibrium constants
1	$HOCl + Br^- \rightleftharpoons HOBr + Cl^-$	p*K*=−5.18
2	$HOBr \rightleftharpoons OBr^- + H^+$	p*K*$_a$=8.7
3	$HOBr + Cl^- + H^+ \rightleftharpoons BrCl + H_2O$	p*K*=−4.09
4	$2HOBr \rightleftharpoons Br_2O + H_2O$	p*K*=−0.8
5	$HOBr + HOCl \rightleftharpoons BrOCl + H_2O$	p*K*=0.46
6	$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O$	p*K*=−8.4

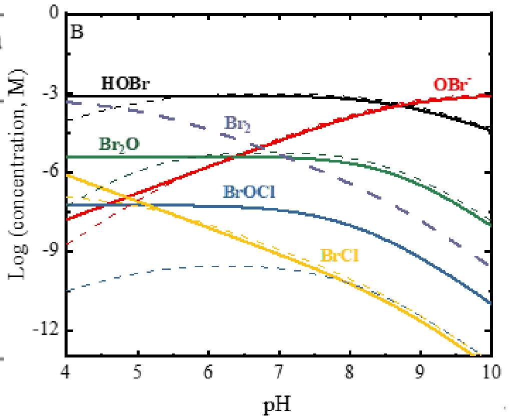

Figure 1. The reaction equations and corresponding equilibrium constants (A) [10, 24-27]. The distribution of each brominating agent under various pH (B). The species distribution was obtained under conditions of 1 mM [HOCl], 0.8 mM [Br$^-$], pH 4.0−10.0, 20 °C ([Br$^-$]$_o$<[HOCl]$_o$, solid line) and 1 mM [HOCl], 1.2 mM [Br$^-$], pH 4.0−10.0, 20 °C ([Br$^-$]$_o$>[HOCl]$_o$, dash line).

In a recent work, Huang et al. [28] evaluated the reactivity of different chlorinating agents towards benzanilide (BA, a representative monomer of PA membranes). Cl_2 was shown to be more reactive than HOCl (76 vs. 2.1×10^{-2} $M^{-1}s^{-1}$) by kinetic experiments [28, 29], which provides a novel insight towards the evaluation of brominating species. Huang et al. [7] further confirmed the higher reacitvity of Br_2O, BrOCl, BrCl and Br_2 than HOBr towards BA decay. Despite the potential similarity, the direct extrapolation of halogenation kinetics from BA monomer (homogeneous) to PA bulk material (heterogeneous) may raise uncertainties [7, 30]. The reactive species formed by chloramine and Br$^-$ appeared to have a limited influence on membrane flux but play a significant role on BA decay [30]. In addition, the different degree of hydrogen bonding in PA membranes and BA monomer may affect the degradation. Therefore, the reactivity of the brominating agents towards bulk PA membranes in addition to membrane monomers deserves to be systematically investigated, in order to fundamentally understand the membrane degradation process.

In this study, the reactivity and contribution of each brominating species (including HOBr, Br_2O, BrOCl, BrCl and Br_2) to the degradation of a PA membrane and a membrane monomer under chlorinated bromide-containing water conditions were evaluated by kinetic experiments. The effect of solution chemistry was assessed by varying pH (ranging from 4.0 to 10.0), Br^-, Cl^- and free chlorine concentrations, and ionic strength. The kinetics of membrane ageing under typical drinking water, wastewater and seawater chlorination conditions were evaluated. The current study developed a novel type of characterization technique for membrane oxidation assessment through determining the kinetics of the oxidant-PA reactions.

2. Materials and methods

2.1 Chemicals and materials

Sodium hypochlorite and sodium bromide were used to generate free chlorine and bromide, respectively. Sodium chloride and sodium nitrate were used to evaluate the effect of chloride and ionic strength on the degradation of membranes and monomers, respectively. Nitric acid and sodium hydroxide were used for pH adjustment in reactions between membranes and halogenating agents. BA (a representative PA membrane monomer, with its molecular structure shown in Supporting Information S1) was used as a model compound. BA was dissolved in methanol and stored at −18 ºC in dark. Sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10\ H_2O$) and sodium phosphate monobasic dihydrate ($NaH_2PO_4 \cdot 2\ H_2O$) were used as pH buffer solutions during the monomer kinetic experiment [31]. Sodium thiosulfate was used as a chlorine quencher to terminate reactions [7, 28]. Sodium chloride and boric acid were used to evaluate the rejection of charged and neutral solutes by virgin and halogenated membranes. The neutral species H_3BO_3 accounts for >98% of the total boron under pH 7.5 (Supporting Information S2). Azomethine-H, acetic acid, ammonium acetate, ascorbic acid, and ethylenediaminetetraacetic acid disodium were used for boron detection. The purity and supplier of these chemicals have been provided in Supporting Information S3. Deionized (DI) water (conductivity < 4.0 μs/cm and resistivity > 0.25 Ω·cm) was used in all stock solution preparations and experiments.

A commercial TFC nanofiltration membrane NF90 obtained from DuPont was investigated in this study. This fully aromatic PA membrane was prepared by m-phenylenediamine and trimesoyl chloride [32, 33]. The chemical structure of the selective layer and physicochemical properties of NF90 are shown in Supporting Information S1. The degradation of supporting layer (i.e., polysulfone) was not considered due to its superior bromine resistance compared with polyamide [4, 34]. The membranes were stored at 4 ºC in the dark before use.

2.2 Halogenation experiment

2.2.1 Membrane halogenation

The membrane coupons were soaked in DI water for 24 h to remove impurities. The synthetic exposure solutions were prepared by adding free chlorine, bromide, and chloride of various concentrations (see more details in Supporting Information S4). The adding order of these reagents followed sodium hypochlorite, sodium bromide and sodium chloride. The solution pH ranging from 4.0 to 10.0 was then adjusted by 0.1 M HNO_3 and NaOH. The pH buffer was not used for membrane degradation experiments, considering its potential interference to membrane degradation process and membrane performance. An incubation time of 0.5 h was applied to allow the formation of free bromine via oxidation of bromide by chlorine, since the transformation from Br^- to free bromine in chlorinated water is fast (half-life of seconds to minutes under different pHs) [35]. The virgin membranes were used for each oxidation condition, i. e., totally ten membranes were used to investigate the effect of exposure time at pH 7.0 (totally 5 time points, *n*=2). The reactions between membranes and brominating agents were conducted in 250 mL amber glass bottles with PTFE-lined caps, to minimize the depletion of brominating agents by natural light. These bottles were oscillated on a shaker working at a rotating speed of 120 r/min at 20 °C (HZP-250, Jinghong Laboratory Equipment, China). The membranes were collected after a predetermined reaction time and rinsed with DI water for 5 times to remove active halogen residuals. During the entire exposure duration, solution composition was not further manually adjusted except for pH (adjust to the designed value every 10 min). The filtration performance of virgin and halogenated membranes was evaluated by a membrane filtration system.

The membrane filtration system consists of four parallel rectangular cross-flow cells (CF042, Sterlitech, USA) with a channel size of 4.6 cm × 9.2 cm. The feed solution was controlled at 25 °C by a chiller (CW-5200, Teyu Electric, China). Before the filtration experiment, the virgin membranes were rinsed several times and soaked in DI water for 24 h to remove impurities. The pretreated membranes were loaded into the cells and compacted for at least 12 h to eliminate the compaction effect. Membrane filtration experiments were carried out under the conditions of a pressure of 6.9 bar, a system temperature of 25 °C, and a cross-flow rate of 1 L/min. The feedwater pH was adjusted by 1 M HNO_3 and NaOH.

Water flux, and the rejection of charged NaCl and neutral H_3BO_3 for NF90 were tested separately by three feed solutions, namely DI water, 10 mM NaCl, and 200 mg/L H_3BO_3. Water flux was measured by weighing the mass of the permeate at a predetermined time interval. Salt rejection was determined by measuring the conductivity of the feed and permeate samples. The rejection of neutral H_3BO_3 was evaluated by measuring its concentration by azomethine-H spectrophotometric method.

2.2.2 BA halogenation

The BA halogenation experiments were conducted similarly to membrane halogenation, with the main differences described below. The BA reactions were performed in 40 mL amber glass vials with PTFE-lined caps. The buffer solution ($Na_2B_4O_7 \cdot 10\ H_2O$ or $NaH_2PO_4 \cdot 2\ H_2O$) was added to the reactor to reach 10 mM to maintain a stable pH during reaction process. The BA (10 μM) and halide ions with a series of concentrations (0−1.25 mM Br^- and 0.2−4.4 mM Cl^-) were prepared in reactors with an effective volume of 30 mL. The sample after a predetermined reaction period was collected and transferred into a 2 mL vial containing excess thiosulfate ($[Na_2S_2O_3]>4\ [Cl_2]$, to quench active halogen residuals [7, 28]. The samples were manually shaken and immediately measured by high performance liquid chromatography coupled with a UV detector working at a wavelength of 260 nm (HPLC-UV, LC-20AT, Shimadzu, Japan).

2.3 Calculation of reaction rate constant of membrane material and monomer

BA halogenation experiments were performed under a pseudo-first-order condition ($[HOBr]_T>10[BA]$). $[HOBr]_T$ was assumed equal to the total concentration of brominating agents [22]. $[HOBr]_T$ was assumed equal to $[Br^-]_o$ under the condition of $[HOCl]_o>[Br^-]_o$ based on the mass balance of elemental bromine (with the coefficient determined by the number of bromine atom, Eq.1). For reactions under the condition of $[HOCl]_o<[Br^-]_o$, $[HOBr]_T$ was assumed equal to $[HOCl]_o$ based on the mass balance of free bromine (with the coefficient determined by the number of Br^+, Eq.2).

Nevertheless, these two sets of conditions did not raise significant difference for concentration calculation since Br_2 was assumed to be not formed under $[HOCl]_o>[Br^-]_o$.

$$[HOBr]_T=[BrCl]+2[Br_2]+[BrOCl]+2[Br_2O]+[HOBr]+[OBr^-] \quad (1)$$

$$[HOBr]_T=[BrCl]+[Br_2]+[BrOCl]+2[Br_2O]+[HOBr]+[OBr^-] \quad (2)$$

where [BrCl], $[Br_2]$, [BrOCl], $[Br_2O]$, [HOBr] and $[OBr^-]$ represent their equilibrium molar concentrations (M). The observed reaction rate constants (k_{obs}^{BA} , s^{-1}) were calculated from the slopes of $\ln([BA]_t/[BA]_0)$ versus time (t, h) plots. The plots were consistently linear (see section 3.3), indicating that these reactions followed the pseudo-first-order kinetics. The reaction rate of membrane monomer (r_{obs}^{BA}, $M\cdot s^{-1}$) could be described by Eq.3:

$$-\frac{d[BA]}{dt}=r_{obs}^{BA}=k_{obs}^{BA}[BA] \quad (3)$$

Inspired by the kinetic experiment of membrane monomer, we attempted to demonstrate the kinetic effect of bromination on macroscopic properties of membranes. The bromine uptake by membranes can be a proper indicator of membrane bromination. Some existing characterization technologies, e.g., X-ray photoelectron spectroscopy (XPS, from the top 0-5 nm of the surface region) and Fourier transform infrared spectroscopy (FTIR), are generally not sensitive enough to resolve the minor differences [4]. Other more sensitive techniques, e.g., Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD), allowing a depth greater than hundreds of nanometers [19, 36, 37], have been used for the characterization of both PA active layer and polysulfone support layer of membranes exposed to chlorine as a function of layer depth. However, the understanding of the kinetics of halogen uptake by PA remains superficial and its correlation with the apparent membrane performance is unclear. The membrane performance (i.e., water flux) was thus considered in the current study as a phenomenological indicator of membrane degradation to investigate reaction kinetics. The rate of water flux decline during membrane degradation could be calculated from the slopes of ln$J_{v\text{-}norm}$ versus time (t, h) plots, similar to that for BA decay. $J_{v\text{-}norm}$ is the normalized water flux, equal to J_{vt}/J_{vo}. In this study, the water flux after an exposure duration of 5 min by free halogen was set as the reference water flux J_{vo} in the corresponding calculations due to the initial increase of water flux of brominated membrane under alkaline condition (pH 10.0, see more details in Supporting Information S5). It is worth noting that using J_{vo} at 0 or 5 min did not significantly affect the kinetic results for pH 4.0 and 7.0. The pseudo-first-order kinetic model was applied during a reaction period of 0-1 h with R^2>0.92 (see more details in section 3.1), considering the limited consumption of free chlorine. The loss of free chlorine was kept <10% within an exposure time of 1 h for membrane halogenation (Supporting Information S6). The observed rate (r_{obs}^{m}, s^{-1}) and pseudo-first-order rate constant (k_{obs}^{m}, s^{-1}) of membrane materials within 1 h exposure could be described by Eq.4:

$$-\frac{dJ_{v-norm.}}{dt} = r_{obs}^{m} = k_{obs}^{m} J_{v-norm.} \tag{4}$$

In the current study, the effects of several independent variables, including [HOCl], [Cl$^-$], [Br$^-$], pH, and ionic strength, on the kinetics of membrane degradation and BA decay were systematically evaluated. The reactivity of the individual brominating agent on membrane material and monomer was evaluated by determining their corresponding reaction rate constant. The equilibrium molar concentrations for HOBr, Br_2O, BrOCl, BrCl and Br_2 were calculated based on the equilibrium constants and initial concentrations of HOCl, Cl$^-$, and Br$^-$ using Wolfram Mathematica software (Supporting Information S7). These concentrations were assumed to remain constant over the halogenation process within 1 h, considering the limited consumption of free halogen (less than 10% loss, Supporting Information S6) [10]. The k_{obs}^{BA} and k_{obs}^{m} were taken as the sum of the second-order rate constant multiplied by the molar concentration of each brominating agent (Eq. 5 and 6, respectively) [10]:

$$k_{obs}^{BA} = k_{BrCl}^{BA}[BrCl] + k_{\mathrm{Br}_2}^{BA}[Br_2] + k_{BrOCl}^{BA}[Br\mathrm{O}Cl] + k_{\mathrm{Br}_2O}^{BA}[Br_2O] + k_{HOBr}^{BA}[HOBr] \qquad (5)$$

$$k_{obs}^{m} = k_{BrCl}^{m}[BrCl] + k_{\mathrm{Br}_2}^{m}[Br_2] + k_{BrOCl}^{m}[Br\mathrm{O}Cl] + k_{\mathrm{Br}_2O}^{m}[Br_2O] + k_{HOBr}^{m}[HOBr] \qquad (6)$$

where $k_{BrCl}, k_{\mathrm{Br}_2}, k_{BrOCl}, k_{\mathrm{Br}_2O}, k_{HOBr}$ are the specific second-order reaction rate constant of each brominating agent (M$^{-1}\cdot$s^{-1}), with the superscripts “BA” and “m” representing BA decay and membrane degradation, respectively. The transformation from pseudo-first order to second-order kinetic model (reflected by the unit of rate constants) was performed in order to obtain the rate constant of each brominating agent in addition to the rate constant of total bromine. These reaction rate constants were determined based on the nonlinear least-square analyses by Matlab software, with k_{obs}^{BA}, k_{obs}^{m}, [BrCl], [Br_2], [BrOCl], [Br_2O], and [HOBr] as inputs (see details in Supporting Information S7). OBr^- was excluded from $[HOBr]_T$ for reaction rate constant calculation since it was more inert with amide N and aromatic rings relative to HOBr [10, 31].

2.4 Analytical methods

The sum of free chlorine and free bromine was determined photometrically by the dipropyl-p-phenylenediamine (DPD) method (Spectroquant® chlorine test, EPA 330.5, Merck) and reported equivalently as Cl_2. The solution pH was monitored by a pH meter (FE20 Plus, Mettler Toledo). The Cl^- and Br^- concentrations were determined by an ion chromatography (IC, Eco IC, Metrohm, Switzerland).

The BA was measured by HPLC-UV (LC-20AT, Shimadzu, Japan) coupled with a C18 column (Inertsil® ODS-SP, 4.6 mm × 250 mm, 5 μm), a method proposed by Huang et al. [28]. The mobile phase consisted of ultra-pure water (eluent A, 75%) and HPLC grade acetonitrile (eluent B, 25%). The oven temperature was kept at 40 °C. The total flow was kept at 1 mL/min. A 10 μL sample was injected and detected at a wavelength of 260 nm. The total running time was 8 min. The calibration curve (1-10 μM) with $R^2>0.999$ is shown in Supporting Information S8.

The boron was determined by azomethine-H spectrophotometry using UV-Vis spectrophotometer (UV-1800 PC, MAPADA, China). The stock solution of boric acid (10 mg/L) was prepared and stored in polyethylene vials. The stock solution of azomethine (5 g/L) was obtained by mixing azomethine-H and ascorbic acid at a weight ratio of 1/4 under 50 °C. The acetate buffer, used to keep a constant pH at 5.6, was prepared by adding 75 g ammonium acetate, 5 g ethylenediaminetetraacetic acid disodium and 37.5 ml glacial acetic acid into 110 mL pure water. Boron stock solution with a series of controlled volume was added into 10 mL colorimetric tube with plugs and diluted to 5.0 mL with pure water. The 2 mL acetate buffer and 2 mL azomethine-H were added successively to the standards, blanks and quality control samples. The pretreated samples were kept static for 90 min, transferred into 10 mm cuvette, and tested by a UV-Vis spectrophotometer at a wavelength of 420 nm. The calibration curve (0.2−2.0 mg/L) with $R^2>0.999$ is shown in Supporting Information S8.

3. Results and discussion

3.1 Determination of pseudo-first-order reaction rate constant of membrane degradation

Figure 2 presents J_{vt}/J_{v0} as a function of exposure time. The correlation coefficients of $R^2>0.92$ were observed by a linear fitting between $\ln(J_{vt}/J_{v0})$ and time, indicating that the flux decline within 1 h was well fitted by the pseudo-first-order kinetic model. The variation degree and trend for water flux, NaCl rejection and H_3BO_3 rejection was significantly different (Supporting Information S5), which may need more characterization data to clarify. The membrane reactivity revealed a strong dependence on the exposure solution pH in the presence of oxidizing agent. The control experiment shows that the effect of exposure solution pH without any oxidizing agent on water flux was insignificant (Supporting Information S9). The k_{obs}^{m} values for pH 4.0 and 7.0 were comparable at 1.8×10^{-4} s^{-1} and 1.5×10^{-4} s^{-1}, respectively. Although the halogen uptake in acidic condition is commonly reported to be higher than in neutral condition [38], using water flux may raise differences since membrane performance was a combined result of complicated physicochemical properties. In contrast, the k_{obs}^{m} at pH 10.0 was an order of magnitude lower (only 3.6×10^{-5} s^{-1}). Other studies similarly reported that chlorination of polyamide membranes at pH 4.0 is more severe than at higher pH [38, 39]. In addition to the potential different membrane degradation mechanisms by bromination and bromination-promoted reaction under varying pHs [19, 39], the different distribution and reaction rate of active bromine species could also play a significant role. More HOBr and HOCl (the stronger electrophilic oxidizing agents than OBr^- and OCl^-) were formed at pH 4.0 and 7.0 than pH 10.0 (Supporting Information S10), which might be partially responsible for the different variation degree of membrane performance. In addition, the minor change in membrane performance, including water flux, NaCl rejection and H_3BO_3 rejection, after chlorination-only may indicate the significant role of brominating species under coexistence of chlorine and bromide. In other words, the contribution of chlorinating species was negligible (Supporting Information S5). The pH-dependent concentration of other active brominating species (i.e., Br_2O, BrCl, BrOCl and Br_2), despite their 2−8 orders of magnitude lower concentration relative to HOBr (Figure 2B), may influence the overall bromination rates of membranes as well.

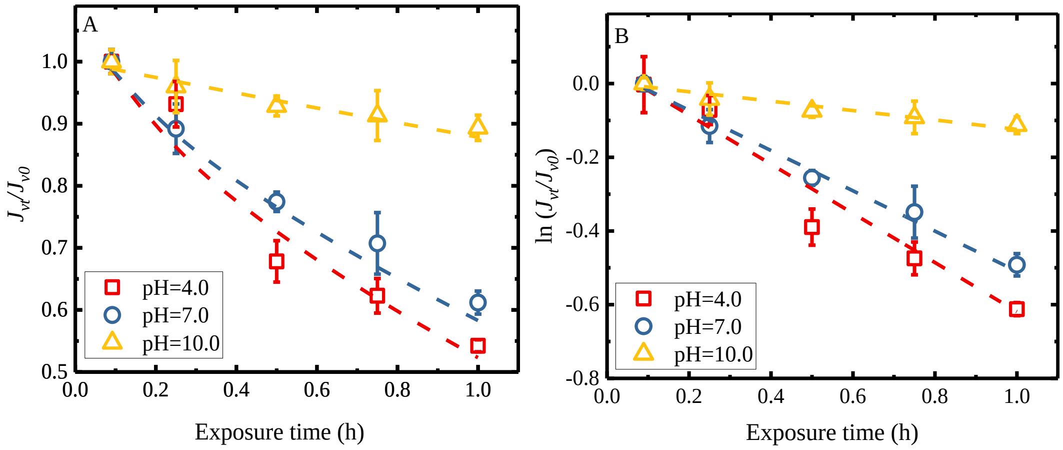

Figure 2. Effect of halogenation on membrane water flux (A, B). Membranes were exposed under conditions of 1 mM [HOCl], 0.8 mM [Br^-], pH 4.0, 7.0, 10.0, 20 °C. Membrane filtration was performed under conditions of pH 7.5, 6.9 bar, 1 L/min, DI water, 25 °C. The error bars represent the range based on two independent experiments. The dash lines represent the modeling results obtained by applying the kinetic rate constants.

3.2 Effect of exposure solution chemistry on membrane performance

To resolve the effect of the characteristics of exposure solution, the relative importance of [Br^-], [HOCl], [Cl^-], and ionic strength to membrane degradation was systematically evaluated. In addition, the effect of the excessive bromide $[Br^-]_{ex}$ (i.e., $[Br^-]_{ex} = [Br^-]_o - [HOCl]_o$ for $[Br^-]_o > [HOCl]_o$) was also determined. Water flux was relatively stable for membranes exposed under the same halogen environment but different ionic strength ranging from 0 to 4 mM (Supporting Information S11), indicating a negligible effect of ionic strength on membrane degradation.

In general, [Br$^-$], [Br$^-$]$_{ex}$, [HOCl], and [Cl$^-$] had positive linear correlations with k_{obs}^{m} (R^2>0.90, Figure 3). Under the condition of [Br$^-$]$_o$<[HOCl]$_o$ ([HOBr]$_T$=[Br$^-$]$_o$, a scenario for drinking water), k_{obs}^{m} was increased by 46%, 87% and 118% at pH 4.0, 7.0, and 10.0, respectively, with Br$^-$ varied from 0.1 to 0.8 mM (Figure 3A). The k_{obs}^{m} at pH 7.0 and 10.0 were lower than that at acidic condition, verifying a different reaction rate and/or mechanism under different pHs. In addition, the lowest slope of k_{obs}^{m} versus [Br$^-$] plots at pH 10.0 (0.42 $s^{-1}\cdot mM^{-1}$) verified the lowest dependence of reaction rate on [Br$^-$] under alkaline conditions. The distribution of brominating species under various [Br$^-$] demonstrates that more Br$^-$ contributed to more formation of total bromine (Supporting Information S12), which might be responsible for the accelerated degradation. Under the condition of [Br$^-$]$_o$>[HOCl]$_o$ ([HOBr]$_T$=[HOCl]$_o$, a scenario for seawater), free chlorine was insufficient to oxidize all bromide to form free bromine, leading to the presence of bromide residual and therefore the formation of Br_2 (Supporting Information S12). The linear response of k_{obs}^{m} as a function of [Br$^-$]$_{ex}$ revealed the positive contribution of Br_2 to membrane degradation (Figure 3B). The increase of HOCl and Cl$^-$ concentration led to the increased formation of BrOCl and BrCl, respectively, indicating their individual positive contribution to membrane degradation (Figure 3C, D, Supporting Information S12). Our results are consistent with existing reports of Br_2O, BrOCl, BrCl and Br_2 as highly reactive substances towards some aromatic organic compounds such as dimethenamid, salicylic acid, anisole, and BA [10, 22, 28, 31, 40].

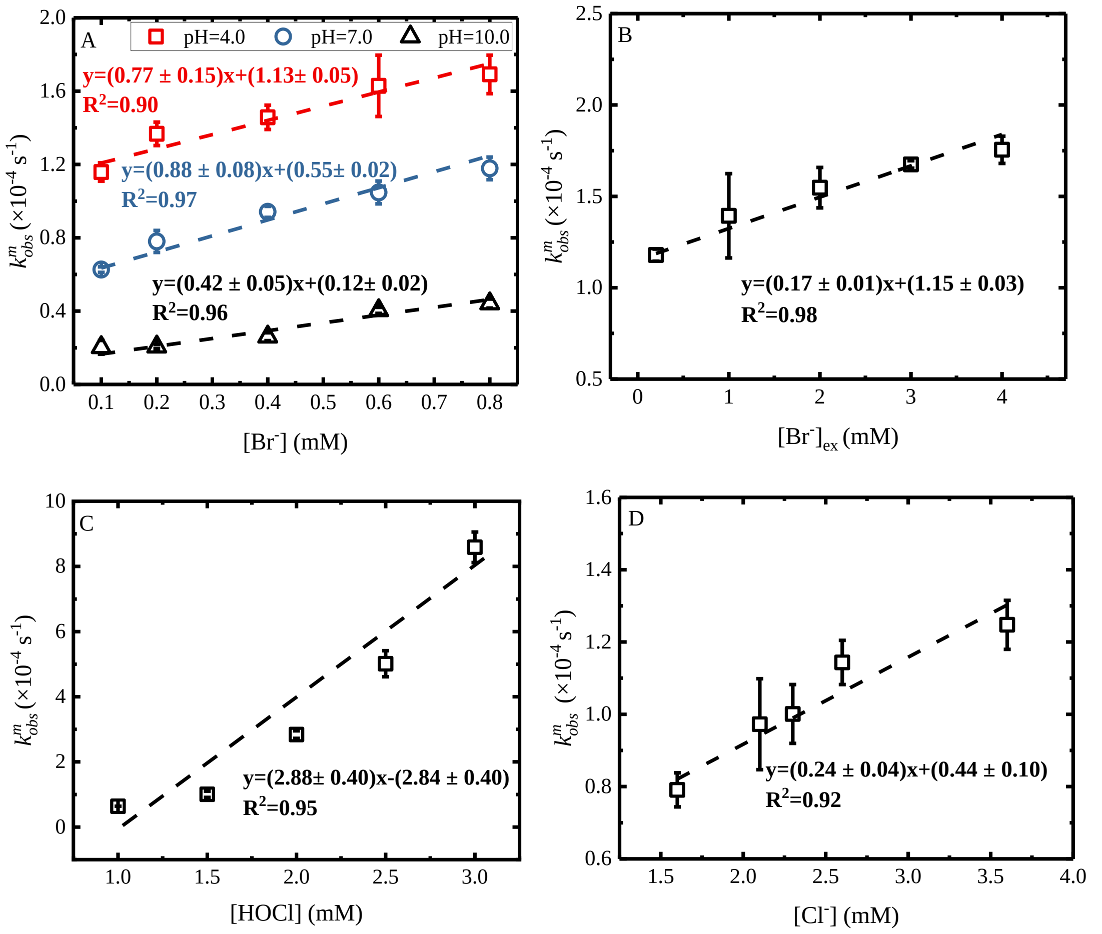

Figure 3. Effect of $[Br^-]$ (A), $[Br^-]_{ex}$ (B), [HOCl] (C), and $[Cl^-]$ (D) on k^{m}_{obs} for membrane degradation. Membranes were exposed under conditions of 1 mM [HOCl], 0.1–0.8 mM $[Br^-]$, pH 4.0, 7.0 and 10.0, 20 °C (A), 1 h; 1 mM [HOCl], 1.2–5 mM $[Br^-]$, pH 7.0, 20 °C, 1 h (B); 1–3 mM [HOCl], 0.8 mM $[Br^-]$, pH 7.0, 20 °C, 1 h (C); 1 mM [HOCl], 0.8 mM $[Br^-]$, 1.6–3.6 mM $[Cl^-]$, pH 7.0, 1 h (D). Membrane filtration was performed under conditions of pH 7.5, 6.9 bar, 1 L/min, DI water, 25 °C. The error bars represent the range based on two independent experiments.

3.3 Determination of second-order reaction rate constant of each brominating agent

In order to quantitatively evaluate the reactivity of each brominating agent to membranes, the second-order rate constants were determined by the nonlinear regression analyses (Supporting Information S8). The reactivity of each brominating species with PA membranes followed a decreasing order of k^{m}_{BrCl} ((2.6±0.2)×10^{4} $M^{-1}\cdot s^{-1}$) > k^{m}_{BrOCl} ((2.0±0.1)×10^{3} $M^{-1}\cdot s^{-1}$) > $k^{m}_{Br_2O}$ ((9.6±0.2)×10^{2} $M^{-1}\cdot s^{-1}$) > $k^{m}_{Br_2}$ ((2.8±0.5)×10^{1} $M^{-1}\cdot s^{-1}$) > k^{m}_{HOBr} ((5.4±0.3)×10^{-1} $M^{-1}\cdot s^{-1}$) (Table 1). Our observations are consistent with existing studies reporting BrCl and HOBr as the most and least reactive species, respectively, for the bromination of model aromatic compounds[7, 10, 22, 28, 31].

Table 1. Rate constant of each brominating agent towards membrane degradation and BA decay and their physicochemical properties

	Rate constant (k, $M^{-1}s^{-1}$)		Physicochemical properties of each brominating agent				
Species	Membrane	BA	BDE [a] kJ/mol	ELUMO [b] kJ/mol	Charge on Br [b]	Molar volume [c] cm^3	LogP [d]
BrCl	$(2.6±0.2)×10^4$	$(1.4±0.9)×10^4$	218.4 (Br-Cl)	64.8	+0.091	53.1	0.82
BrOCl	$(2.0±0.1)×10^3$	$(1.7±0.4)×10^3$	235.1 (Br-O)	121	+0.176	59.4	1.59
Br_2O	$(9.6±0.2)×10^2$	$(2.5±0.8)×10^0$	235.1 (Br-O)	113	+0.151	61.2	1.40
Br_2	$(1.5±0.3)×10^1$	$(9.3±0.1)×10^0$	192.9 (Br-Br)	58.2	0.00	54.8	1.93
HOBr	$(5.4±0.3)×10^{-1}$	$(1.4±1.3)×10^{-2}$	235.1 (Br-O)	279	+0.106	39.2	1.73

Notes

[a] The bonding dissociation energy (BDE) was obtained from a reference [41].

[b] The E_{LUMO} and charge on Br were obtained from a reference [22].

[c] The molar volume was calculated by ACD/ChemSketch.

[d] The oil-water partition coefficient (logP) was calculated by Chemdraw.

The halogenation experiment for BA, a representative monomer of PA membranes, was performed to further verify the relative reactivity of each brominating agent. The pseudo-first-order kinetic model for BA decay achieved an excellent fitting (R^2>0.98), with a much higher k_{obs}^{BA} at pH 6.1 than pH 9.3 (8.1×10^{-5} s^{-1} vs. 5.6×10^{-6} s^{-1}, Figure 4A, B). This trend is consistent with that obtained for membrane testing. The effects of [Br^-], [Br^-]$_{ex}$, [HOCl], [Cl^-], and ionic strength on BA decay were evaluated as well. The ionic strength had a negligible effect on BA decay (Supporting Information S13), which is similar to membrane degradation results. More [Br^-], [Br^-]$_{ex}$, [HOCl], and [Cl^-] contributed to faster BA decay (Figure 4C-F), as reflected by the positive linear responses of k_{obs}^{BA} to their concentration (R^2>0.99). The individual reaction rate constants of five brominating agents were found to follow a decreasing order of BrCl>BrOCl>Br_2>Br_2O>HOBr (Table 1), which is consistent with a previous study [30]. The absolute values of rate constants in our study were lower than those in the reference, which might be attributed to the different reaction temperature (20 vs. 25 °C). Notably, a log-linear correlation was observed between the rate constant of each brominating agent for membranes and BA (k_s^m and k_s^{BA}, with the subscript "s" referring to each brominating agent, R^2=0.80, Figure 5A). The accurate evaluation of membrane degradation should rely on k_s^m , while the rough estimation can rely on k_s^{BA} and the correlation between k_s^m and k_s^{BA} , since the reactivity of some brominating agents (Br_2O, Br_2, HOBr) towards membranes was 1-2 orders of magnitude higher than BA. The differences in brominating agent activity toward membranes and BA might be combined results of different reaction phases (heterogeneous or homogeneous) and hydrogen bonding [7, 28, 30].

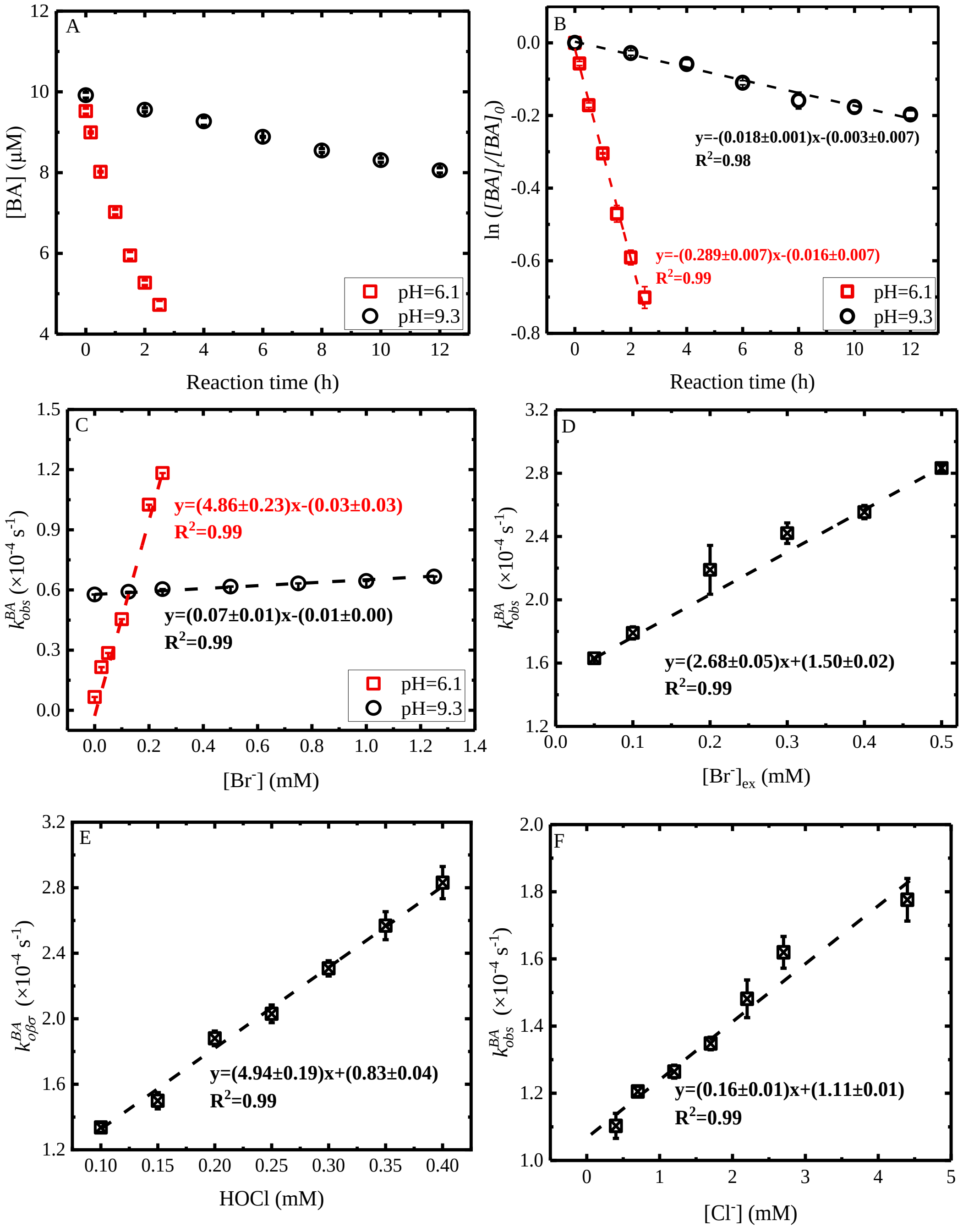

Figure 4. Effect of halogenation on BA decay (A, B) and effect of $[Br^-]$ (C), $[Br^-]_{ex}$ (D), [HOCl] (E), and $[Cl^-]$ (F) on k_{obs}^{BA}. BA decay was performed under conditions of 0.25 mM [HOCl], 0.2 mM $[Br^-]$, pH 6.1 and 9.3, 20 °C (A, B); 0.25 mM [HOCl], 0−0.2 mM $[Br^-]$, pH 6.1, 20 °C and 1.5 mM [HOCl], 0−1.25 mM $[Br^-]$, pH 9.3, 20 °C (C); 0.25

mM [HOCl], 0.3-0.75 mM [Br^-], pH 6.1 (D); 0.1−0.4 mM [HOCl], 0.2 mM [Br^-], pH 6.1, 20 °C (E); 0.25 mM [HOCl], 0.2 mM [Br^-], 0.2−4.4 mM [Cl^-], pH 6.1, 20 °C (F). The reaction time under pH 6.1 and 9.3 was 2.5 and 12 h, respectively. The error bars represent the range based on two independent experiments.

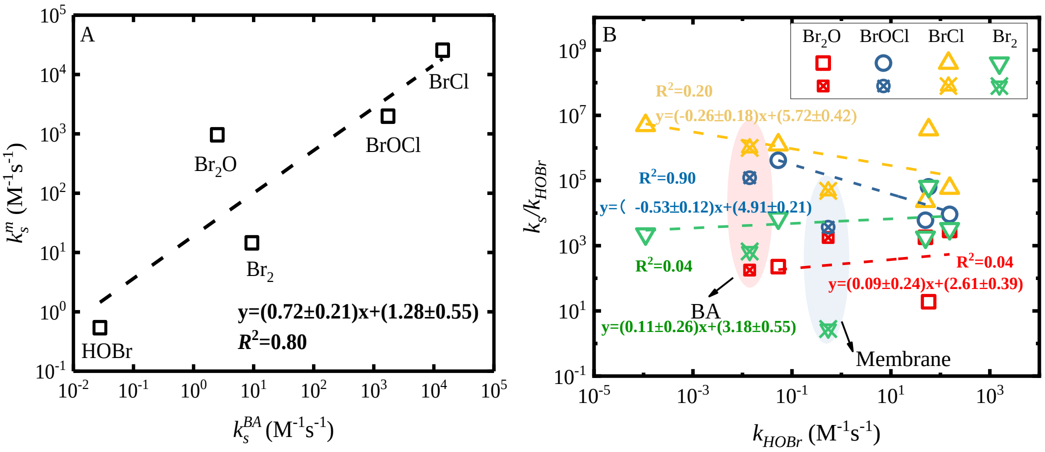

Figure 5. Correlation of rate constant for each brominating agent towards membrane and BA (A) and the reactivity-selectivity trade-off for each brominating agent (B). The second-order rate constants were obtained from this study (crossed icons) and references (hollow icons) [7, 10, 31, 40].

In order to better reflect the reactivity of BrCl, BrOCl, Br_2, and Br_2O relative to HOBr, log-log plots of k_s/k_{HOBr} (k_s refers to the reactively of each brominating species towards membranes or BA) versus k_{HOBr} were presented in Figure 5B, using data both from this study and references [7, 10, 22, 28, 31, 40]. These references only show reactions between free bromine and organic compounds, while both membrane and monomer are involved in bromination in this study. The positive values of k_s/k_{HOBr} for all brominating agents reflected their more inherent reactivity than HOBr [42]. The negative correlation between k_s/k_{HOBr} and k_{HOBr} for BrCl and BrOCl indicates that their selectivity by membranes and organic compounds decreases with the increased reactivity of HOBr. It is consistent with the reactivity-selectivity principle in halogen-involved organic chemistry [42, 43], that is a more reactive chemical compound is less selective in chemical reactions.

The reaction pathways between PA membranes and brominating agents include both N-bromination and ring-bromination via electrophilic substitution, which were based on the shift and disappearance of three characteristic bands, and the increased O/N ratio and calcium content determined by XPS and FTIR (Supporting Information S14) [4]. The bromination potential contributed by each brominating agent should be related with electrophilicity and leaving group ability [10]. A higher leaving ability implies an enhanced ability of bromine (Br^+) to accept electrons, which accelerates the halogenation process [10]. The leaving group ability decreased in the order of $Br^- > Cl^- > OBr^- > OCl^- > OH^-$ (reflected by pK_a of conjugate acids for leaving groups, a higher pK_a implies a lower leaving ability, Supporting Information S15). The energy of the lowest unoccupied molecular orbital (E_{lumo}) was also used to evaluate the electron affinity [44]. The order of electron affinity for these brominating agents based on E_{lumo} was consistent with that for leaving ability (Table 1). The lower leaving ability of OH^- may partially contribute to the lower reactivity of HOBr compared to other brominating agents. The higher reactivity of BrCl than BrOCl, Br_2O, and Br_2 could be partially attributed to its smaller molecule with lower resistance to spatial steric hindrance effect (a higher ability to diffuse into the molecular microstructure). Ling et al. similarly reported that free radical species with large size was prevented from diffusing into the separation layer, which resulted in a reduced effect on membrane oxidation [45]. The higher reactivity of BrCl might also be due to its lower bonding dissociation energy (BDE) than molecules with Br-O bonds (i.e., BrOCl, Br_2O, HOBr) [10]. Unlike Br_2, BrCl still has a positive partial charge on bromine atom. In addition, BrCl with a higher hydrophilicity ($\log P$=0.82) interacts more easily with the hydrophilic PA layer (contact angle of 53.6°, Supporting Information S1), thereby enhancing the reaction rate [46]. The higher reactivity of BrCl and BrOCl compared to the brominated analogue Br_2 and Br_2O, was attributed to the greater electrophilicity induced by the higher positive charge on bromine atom (BrCl>Br_2, BrOCl>Br_2O, Table 1) [10]. The higher reactivity of Br_2O than Br_2 towards membrane degradation could be attributed to the competing effects of positive charge enhanced reactivity over steric hindrance suppressed reactivity, as the negatively charged PA membranes were more electrostatically attractive by the positively charged brominating agent (NF90 has zeta potential of −13 mV at pH 7.5, Supporting Information S1). However, Br_2 was more reactive than Br_2O towards BA decay, indicating that steric hindrance may play a more significant role than charge. To further demonstrate the significance of physicochemical properties on species reactivity, a correlation between rate constant and physicochemical properties for each brominating agent was established (Figure 6 and Supporting Information S16). Among all the parameters, the oil-water partition coefficient ($\log P$) has the strongest correlation on the species reactivity (r=−0.91 for membrane degradation and r=−0.89 for BA oxidation), which might be related to the hydrophilic interaction between brominating agents and membrane/BA surfaces. For example, BrCl was prone to react with PA membrane, which was mainly owing to the strongest hydrophilic interaction between BrCl with the highest hydrophilicity (lowest log*P*) and the hydrophilic membrane surface. Nevertheless, some future work may be needed to verify this correlation, i.e., evaluate the variation of reaction rate by changing the hydrophilicity of membrane surfaces.

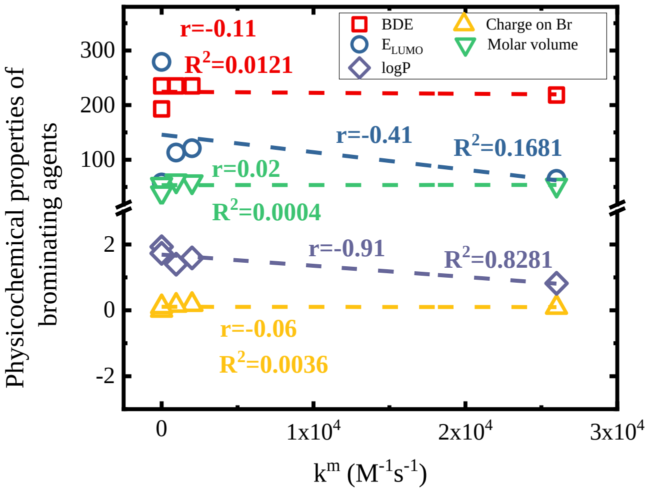

Figure 6. Correlation between rate constant and physicochemical properties for each brominating agent.

3.4 Environmental significance

The relative contribution of individual brominating agent to the overall membrane degradation was evaluated as fraction of k_{cal}^{m} ($k_{cal}^{m} = k_{BrCl}^{m}[\mathrm{BrCl}] + k_{Br_2}^{m}[\mathrm{Br_2}] + k_{BrOCl}^{m}[\mathrm{BrOCl}] + k_{Br_2O}^{m}[\mathrm{Br_2O}] + k_{HOBr}^{m}[\mathrm{HOBr}]$). These typical application scenarios are considered: drinking water, wastewater, and seawater chlorination conditions. Since the typical free chlorine for disinfection is within 1−4 mg/L [47], a concentration of 2 mg/L was used in the calculations [10, 48]. The Cl^- and Br^- concentrations are 0.3 mM and 1.25 µM for drinking water [10, 49], 20 mM and 3 µM for wastewater [9, 10], 540 mM and 840 µM for seawater [11], respectively. Other ionic and organic constituents, i.e., Ca^{2+}, organic matter, that may be present in real water matrixes have been excluded to eliminate the potential interference (e.g., scaling, formation of disinfection by-produces or other intermediates). The concentration (obtained by reaction equilibrium in Figure 1A) and reaction rate constant of each brominating agent (Table 1) were used as inputs to determine k_{cal}^{m} fraction.

Under typical drinking water conditions, k_{cal}^{m} decreased with the increase of solution pH, indicating a higher reaction rate of bromination under acidic condition (Figure 7A). BrCl is the predominant brominating agent responsible for membrane degradation at pH<5.2 (contribute more than 48%) and HOBr predominates at pH>5.2 (Figure 7B). The contribution of BrOCl is within 1%−3% for the entire pH range of 4.0−10.0. Br_2O

also plays a negligible role (<2%) owing to its lower reactivity, regardless of its sometimes even higher concentration than BrCl (Figure 7C and Table 1).

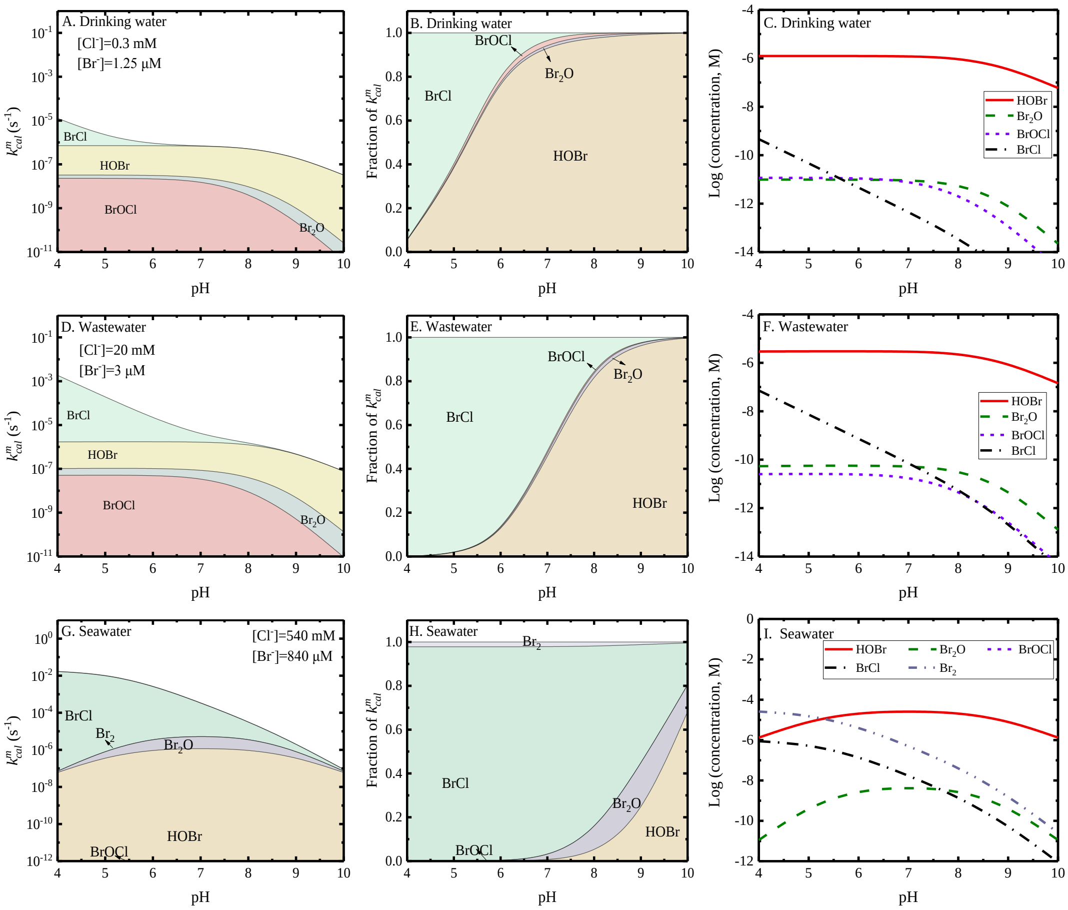

Figure 7. k^m_{cal}, fraction of k^m_{cal}, and concentration of each brominating agent as a function of pH under typical drinking water (A, B, C), wastewater (D, E, F), and seawater (G, H, I) chlorination conditions. The free chlorine of 2 mg/L was used herein. $[Br^-]$ and $[Cl^-]$ were present in figures.

$$k^m_{cal} = k^m_{BrCl}[BrCl] + k^m_{Br_2}[Br_2] + k^m_{BrOCl}[BrOCl] + k^m_{Br_2O}[Br_2O] + k^m_{HOBr}[HOBr].$$

For typical wastewater, the k^m_{cal} was significantly higher than that in drinking water due to its higher content of $[Cl^-]$ and $[Br^-]$ (20 vs. 0.3 mM for Cl^- and 3 vs. 1.25 μM for Br^-, Figure 7D). The critical point of pH to differentiate the most predominant brominating agent between BrCl and HOBr is 7.1 (Figure 7E). The two orders of magnitude higher concentration of Cl^- in wastewater than that in drinking water (20 vs. 0.3 mM) contributed to the more remarkable formation of BrCl in wastewater (7.2×10^{-8} mM vs. 4.5×10^{-10} mM at pH 7.0, Figure 7C, F), therefore a higher fraction of contribution to membrane degradation (52% vs. 2%, at pH 7.0). Thus, the introduction of Cl^- during (waste)water treatment should be avoided to minimize the formation of BrCl. For instance, $Fe_2(SO_4)_3$ should be a more suitable coagulant than $FeCl_3$ for (waste)water containing few calcium ions (membrane scaling is negligible) from the point of protecting the downstream PA membranes against degradation (less Cl^- leads to less BrCl formation) [42, 50].

For typical seawater conditions, the 2-4 orders of magnitude higher k_{cal}^{m} compared to drinking water and wastewater conditions was observed, mainly owing to the presence of excessive $[Br^-]$ and higher $[Cl^-]$ (Figure 7G). The higher $[Cl^-]$ (0.54 M) results in a remarkable contribution of BrCl to membrane degradation, particularly at pH<8.0 (contribution of more than 85%, Figure 7H). Br_2O and HOBr became dominant species to membrane degradation at pH>9.0 due to the higher concentrations in water (Figure 7I). The k_{cal}^{m} fraction of Br_2 is less than 3% for the entire pH range despite its great formation, which was attributed mainly to its lower reactivity compared to other species except for HOBr (Figure 7I). BrOCl also makes a negligible contribution at <1% due to its low formation.

Indeed, for typical wastewater treatment under neutral conditions (pH 7.0) [10], BrCl is proven to be of nearly equivalent importance compared to HOBr (Figure 7E) for membrane degradation. In addition, the contribution follows an order of BrCl (85%) > Br_2O (10%) > HOBr (3%) > Br_2 (<2%) > BrOCl (<1%) under typical seawater conditions (pH 8.0) [51]. These observations challenge the generally accepted concept that HOBr is the most significant species contributing to bromination reactions [16, 52]. It seems that Cl^- and Br^- in pending treated (waste)water play important roles on membrane degradation under chlorinated conditions. To better reflect their individual and synergistic role, a three-dimensional factor diagram was used to demonstrate the relevance between k_{cal}^{m} and halide ions (i.e., $[Cl^-]$, $[Br^-]$) at pH 7.0 (Supporting Information S17). The value of k_{cal}^{m} was significantly controlled by halide concentrations. The co-existence of Cl^- and Br^- would considerably affect k_{cal}^{m} due to the formation of BrCl with the highest reactivity and Br_2 with a moderate reactivity [7].

4. Conclusions

This study systematically investigated the reactivity of some often-overlooked brominating agents (including BrCl, BrOCl, Br_2O, and Br_2) in addition to HOBr towards PA membrane degradation in chlorinated bromide-containing water conditions. Our finding challenges the conventional wisdom assuming HOBr as the only reactive species responsible for bromination reactions. In contrast, the species-specific second-order reaction rate constants towards membrane degradation obtained from kinetic experiments followed a decreasing order of BrCl>BrOCl>Br_2O>Br_2>HOBr, with 2−5 orders of magnitude higher reactivity of these overlooked species than HOBr. Under typical seawater conditions (pH 8.0), the contribution of more reactive but less abundant BrCl (85%) to membrane degradation was significantly higher than HOBr (3%). The ubiquitous presence of Cl^- and Br^-, of which Cl^- was commonly viewed as an inert constituent, in water environment makes significant contributions to the formation of BrCl and Br_2, respectively. Thus, the proper control of halide ions is critical to extend membrane lifespan. For example, the addition of chloride-containing reagents for water pre-treatment should be avoided or minimized to reduce the formation of highly reactive BrCl. Membrane performance for real (waste)water treatment would be affected by the complicated water matrices, including disinfectant residuals, halide ions, organic matters, inorganic salts, etc. These additional potential matrix effects are pending to be systematically explored in order to effectively control and simulate the membrane process. In addition, the effect of these halogenating agents on the physicochemical properties and other filtration parameters (the permeability of neutral and charged solutes in addition to water) of PA membranes deserved to be further investigated, in order to resolve the reaction types and mechanisms that bromine species participates.

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All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

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