EPA Public Access

Author manuscript

Environ Eng Sci. Author manuscript; available in PMC 2020 March 14.

About author manuscripts

Submit a manuscript

Published in final edited form as:

Environ Eng Sci. 2019 March 14; 36(3): 283–294. doi:10.1089/ees.2018.0387.

A Drinking Water Relevant Water Chemistry Model for the Free Chlorine and Cyanuric Acid System from 5 to 35 °C

David G. Wahman¹ and Matthew T. Alexander²

¹Corresponding author, United States Environmental Protection Agency, Office of Research and Development, 26 W. Martin Luther King Dr., Cincinnati, OH 45268. Phone: (513) 569–7733. Fax: (513) 487–2543. wahman.david@epa.gov ²United States Environmental Protection Agency, Office of Ground Water & Drinking Water, 26 W. Martin Luther King Dr., Cincinnati, OH 45268. Phone: (513) 569–7380. Fax: (513) 487–2543. alexander.matthew@epa.gov

Abstract

In the United States, approved methods to measure free chlorine concentrations in drinking water systems adding sodium dichloroisocyanurate (dichlor) or trichloroisocyanuric acid (trichlor) as chlorine sources exhibit measurement bias from chlorinated cyanurate presence, leading to overestimated free chlorine concentrations for regulatory compliance. One option to overcome this limitation is to estimate free chlorine concentrations using an established water chemistry model (full model), but the full model has only been determined for 25 °C. The current research used a simplified version of the full model (simple model) and estimated the unknown temperature dependence (5 to 35 °C) of the two remaining equilibrium constants (K_{7a} and K_{9a}) required for the simple model. At 0 M ionic strength (μ), $\ln K_{7a} = -\frac{4,671}{T_K} + 4.95$ or $\text{p}K_{7a} = \frac{2,028}{T_K} - 2.15$,

$$\Delta H_{7a}^0 = 38.8 \pm 6.0 \text{ kJ mol}^{-1} \text{ (95\% confidence interval, CI), } \ln K_{9a} = -\frac{5,133}{T_K} + 3.79 \text{ or}$$

$$\text{p}K_{9a} = \frac{2,229}{T_K} - 1.65, \text{ and } \Delta H_{9a}^0 = 42.7 \pm 3.0 \text{ kJ mol}^{-1} \text{ (95\% CI). At 25 °C and } \mu \text{ of 0 M, the simple}$$

model estimated $\text{p}K_{7a}$ and $\text{p}K_{9a}$ are 4.65 ± 0.059 (95% CI) and 5.83 ± 0.020 (95% CI), respectively. As an example of temperature's impact, the free chlorine concentration for a 2 mg $\text{Cl}_2 \text{ L}^{-1}$ dichlor addition (pH 7.0) decreases from 0.90 mg $\text{Cl}_2 \text{ L}^{-1}$ free chlorine at 25 °C to 0.60 mg $\text{Cl}_2 \text{ L}^{-1}$ free chlorine at 5 °C. If temperature was not considered, a system operating at 5 °C would overestimate their free chlorine concentration by 50%, which could have significant implications for understanding disinfection efficacy, illustrating the developed model's significance.

To whom correspondence should be directed: David G. Wahman, United States Environmental Protection Agency, Office of Research and Development, 26 W. Martin Luther King Dr., Cincinnati, OH 45268. Phone: (513) 569–7733. Fax: (513) 487–2543. wahman.david@epa.gov.

Author Disclosure Statement

All the authors confirm that no competing financial interests exist.

Keywords

dichlor; trichlor; cyanuric acid; temperature; equilibrium model

Introduction

In July 2001, dichlor (anhydrous sodium dichloroisocyanurate, $C_3Cl_2N_3NaO_3$, or sodium dichloroisocyanurate dihydrate, $C_3Cl_2N_3NaO_3 \cdot 2H_2O$) and trichlor (trichloroisocyanuric acid, $C_3Cl_3N_3O_3$) use for the routine treatment of drinking water in the United States (US) was first approved under the Federal Insecticide, Fungicide, and Rodenticide Registration Act (FIFRA) (Kuechler, 2009). Subsequently, several manufacturers have achieved NSF 60 certification for various dichlor or trichlor products for drinking water addition (NSF International, 2018). Ultimately, in the US, dichlor or trichlor may be approved by Safe Drinking Water Act (SDWA) primacy agencies for use in drinking water. In addition to use in US drinking water systems, the World Health Organization (WHO) provides guidelines on the use of dichlor in drinking water (World Health Organization, 2007; 2011), and dichlor has been suggested as a form of chlorine for household point-of-use water treatment (Clasen and Edmondson, 2006). Kuechler (2009) summarizes the stated advantages for using dichlor or trichlor as free chlorine sources in drinking water, including that they are high percent chlorine chemicals (55–92%) and solid chlorine forms that (i) require simpler handling than liquid or gas chlorine forms, (ii) have storage stabilities on the order of years, and (iii) do not add calcium to the water.

Dichlor or trichlor addition to drinking water is equivalent to adding free chlorine (hypochlorous acid (HOCl) plus hypochlorite ion (OCl^-)) and cyanuric acid ($C_3H_3N_3O_3$) in a fixed proportion. The $C_3N_3O_3$ moiety (126.05 molecular weight) is typically denoted as Cy; therefore, cyanuric acid is represented as H_3Cy , Cl_3Cy is trichlor, and $NaCl_2Cy$ is dichlor. For context and assuming 100% chemical purity, each $mg\ Cl_2\ L^{-1}$ added of dichlor or trichlor adds 0.89 or 0.59 $mg\ Cy\ L^{-1}$ (126.05 molecular weight), respectively. Regardless of how cyanuric acid becomes present in water with free chlorine (i.e., through addition of dichlor, trichlor, or free chlorine and cyanuric acid individually), a rapid equilibrium (Matte et al., 1990) is obtained between H_3Cy and its three dissociation products, HOCl, and chlorinated cyanurates (Fig. 1) that has been established at 25 °C by O'Brien (1972) and O'Brien et al. (1974), referred to herein as the full model (Table 1). The resulting free chlorine concentration present in the water (assuming no ammonia is present) is dependent on (i) temperature, (ii) pH, (iii) chemical added (i.e., dichlor or trichlor), (iv) chemical dose which determines the total chlorine (sum of chlorine in free chlorine and chlorinated cyanurates, TOTCl) and the total cyanurate added (sum of the cyanurate in H_3Cy and its three dissociation products and chlorinated cyanurates, TOTCy), and (v) extent of chlorine demand that has occurred which determines the remaining TOTCl concentration (Wahman, 2018a).

Because of the combination of a fast equilibrium (Matte et al., 1990) between H_3Cy and its three dissociation products, HOCl, and chlorinated cyanurates (Fig. 1 and Table 1) and the possibility of direct reactions with method reagents (Jensen and Johnson, 1990), typical wet

chemistry methods (e.g., N,N-diethyl-p-phenylenediamine (DPD) based methods and amperometric titration) used to measure the free chlorine concentration in drinking water systems adding dichlor or trichlor exhibit measurement bias from chlorinated cyanurate presence (Canelli, 1980; Jensen and Johnson, 1990; Wahman et al., 2017; Wajon and Morris, 1980; Whittle, 1970). Therefore, when TOTCy is greater than zero and no ammonia is present to form chloramines, the free chlorine concentration is overestimated which is important because the effective disinfectant in systems where chlorinated cyanurates and free chlorine are present is considered to be free chlorine, specifically HOCl (Canelli, 1974; Engel et al., 1983; Murphy et al., 2015; Wojtowicz, 1996; Yamashita et al., 1988).

Currently, the inability to accurately determine free chlorine concentrations in systems adding dichlor or trichlor prohibits determination of disinfection efficacy, including compliance with US primary disinfection requirements or numeric free chlorine distribution system residual (i.e., greater than detectable) requirements required by several states (Wahman and Pressman, 2015). The current issue with free chlorine measurement is highlighted in the State of Utah's plan review policy for dichlor and trichlor installations (Utah Division of Drinking Water, 2017) and a recent memorandum from the US Environmental Protection Agency (USEPA, 2018).

To overcome the inability to directly measure free chlorine in systems using dichlor or trichlor, one option is to simulate free chlorine concentrations using the established equilibrium water chemistry of the free chlorine and cyanuric acid system. For example, a web-based application has recently been developed to estimate free chlorine concentrations using this concept (Wahman, 2017). A limitation with the water chemistry estimate is that it is currently only applicable to 25 °C, limiting its usefulness in actual drinking water systems where temperature may vary over a wide range (e.g., 5 to 35 °C). In addition, O'Brien (1972) and O'Brien et al. (1974) used chemical concentrations one to two orders of magnitude greater than would be seen in drinking (e.g., 149 mg Cl₂ L⁻¹ TOTCl and 378 mg Cy L⁻¹ TOTCy) to estimate the equilibrium constants evaluated herein. Therefore, extending the water chemistry model to include temperatures from 5 to 35 °C and evaluating it under drinking water relevant conditions is an immediate need.

If pH, TOTCy, and TOTCl are known, the full model for the free chlorine and cyanuric acid system consists of ten independent equilibrium expressions that are temperature dependent, two mass balance equations for TOTCl and TOTCy, and 12 unknown chemical concentrations (Table 1 and Fig. 1) (O'Brien et al., 1974). As described in Wahman (2018a) and for drinking water samples, pH and TOTCl can be directly measured, and TOTCy can be conservatively calculated based on the dichlor or trichlor mass originally dosed. Fortunately, under relevant drinking water conditions (i.e., 6.5 ≤ pH ≤ 9.5, TOTCl ≤ 10 mg Cl₂ L⁻¹, and TOTCy ≤ 10 mg Cy L⁻¹), the system is reduced to six chemicals present at meaningful concentrations (Fig. 1) because of the pH range and TOTCl and TOTCy concentrations. Therefore, only four (K , K_6 , K_{7a} , and K_{9a}) temperature dependent equilibrium expressions (Table 1 and Fig. 1) are required along with the TOTCl and TOTCy mass balances. The resulting model is herein termed the simple model (Table 1).

Fig. 2 displays the impact of using the simple model versus the full model to simulate free chlorine concentrations at 25 °C and was generated using drinking water relevant combinations (13,671 total simulations) of pH (6.5 to 9.5 every 0.1 units), TOTCl (0 to 10 mg Cl₂ L⁻¹ every 0.5 mg Cl₂ L⁻¹), and TOTCy (0 to 10 mg Cy L⁻¹ every 0.5 mg Cy L⁻¹). For most conditions, the simple model simulated free chlorine concentrations were slightly greater than those from the full model, and the differences were generally less than 0.05 mg Cl₂ L⁻¹, reaching a maximum of 0.20 mg Cl₂ L⁻¹ at pH 9.5 (Fig. 2A). In the worst-case scenario (pH 9.5), the deviation of the simple model was only 6% of the full model simulated free chlorine concentration (Fig. 2B). Furthermore, Supplementary Fig. S1 shows that for the conditions evaluated in the current research (Table 2), the full and simple models simulate essentially the same free chlorine concentrations, assuming 25 °C.

In the simple model, two of the four required equilibrium expressions (Table 1 and Fig. 1) represent the acid-base chemistry of free chlorine (HOCl and OCl⁻, K) and cyanuric acid (H₃Cy and H₂Cy⁻, K₆) whose temperature dependence in Kelvin (T_K) have been established (Equations 1 and 2, respectively, 0 M ionic strength (μ)) (Morris, 1966; Wahman, 2018b).

$$\text{pK} = \frac{3,000}{T_K} - 10.0686 + 0.0253T_K \quad (1)$$

$$\text{pK}_6 = \frac{1,743}{T_K} + 1.12 \quad (2)$$

Using the reported K and K₆ relationships, only the temperature dependence of two equilibrium constants (K_{7a} and K_{9a}) involving chlorinated cyanurates are required to expand the simple model to a range of relevant drinking water temperatures. Therefore, the goal of the current research was to determine the temperature dependence of K_{7a} and K_{9a} from 5 to 35 °C. With K_{7a} and K_{9a}'s temperature dependence determined, the simple model's temperature dependence is complete, providing the necessary information to simulate free chlorine concentrations in drinking water systems using dichlor or trichlor over a range of practical temperatures (e.g., updating the existing web-based application to incorporate temperature).

In addition to the previously described drinking water application, the simple model developed in the current research may have broader applications. For instance, cyanuric acid, dichlor, and trichlor have been used as disinfectants and algicides in cooling towers (Hammond et al., 1986) and added to outdoor swimming pools since 1958 to stabilize chlorine residual by minimizing sunlight related degradation (Canelli, 1974).

Materials and methods

Reagent and glassware preparation

Solutions were prepared in ultra-pure water (18.2 M Ω -cm, Barnstead NANOpure Diamond). Stock cyanuric acid solutions (1,000 mg L⁻¹ of H₃Cy, pH > 9, 129.07 molecular weight) were prepared from reagent grade cyanuric acid (Acros Organics), accounting for reagent purity of 98%. Free chlorine and OCl⁻ solutions were prepared from reagent grade sodium hypochlorite (Fisher Chemical). Carbonate buffers were made from sodium bicarbonate (Fisher Chemical) and adjusted to the target pH with 0.05 and 0.5 N hydrochloric acid (HCl) or sodium hydroxide (NaOH) as required. All glassware was treated to make it chlorine-demand free prior to use (Summers et al., 1996).

Analytical methods

Spectrophotometric measurements (292 nm) were conducted with a 10-cm pathlength quartz cuvette using a Hach DR/4000U Spectrophotometer. The spectrophotometer was blanked with ultra-pure water prior to use. Triplicate absorbance measurements were taken and averaged for any measured sample.

The sample pH and temperature were measured immediately prior to each spectrophotometric measurement with an Orion pH electrode with automatic temperature compensation connected to an Orion Star A211 pH meter that had been calibrated with nominal pH standards of 4, 7, and 10 per manufacturer's instructions. Free and total chlorine colorimetric DPD samples were analyzed in parallel with each spectrophotometric measurement using a Hach SL1000 Portable Parallel Analyzer (Hach Company, 2015; 2017).

Absorbance verification experiments

Morris (1966) estimated molar absorptivity values for HOCl and OCl⁻ from 230 to 300 nm between 5 and 35 °C, demonstrating that a linear relationship between absorbance and HOCl and OCl⁻ concentrations existed at each temperature and wavelength studied, and the relationship did not change substantially with temperature. In the current research, absorbance was measured at 292 nm because (i) at the TOTCl and TOTCy concentrations used in the experiments, HOCl and OCl⁻ are the only two chemicals present in the experimental water that meaningfully absorb at 292 nm (Morris, 1966; O'Brien, 1972; O'Brien et al., 1974) (see Supplementary Data for confirmation, Absorbance Interference Check at 292 nm), (ii) the maximum molar absorptivity for OCl⁻ at 292 nm is approximately 3.5 times that of HOCl at 230 nm (Morris, 1966), and (iii) at the pH values evaluated in the current research, OCl⁻ is present at approximately the same or greater concentration than HOCl. Therefore, 292 nm represented the wavelength providing the maximum absorbance that could be attributed to free chlorine and not subject to interference from other chemical species present.

As subsequently discussed (see Equilibrium Constant Experiments), the molar absorptivity values for HOCl and OCl⁻ at 292 nm are not required for data analysis. Rather, only verification of a linear relationship exists between concentration and absorbance at 292 nm

from 5 to 35 °C on the current spectroscopy equipment is required. Therefore, 0, 0.25, 0.50, 1, 2, and 4 mg Cl₂ L⁻¹ OCl⁻ (pH 10) standards were prepared in duplicate at 5, 20, and 35 °C and measured at 292 nm to verify that the current equipment could produce results comparable to Morris (1966). OCl⁻ was chosen to demonstrate spectroscopy equipment linearity at the various temperatures because it was simpler to create solutions of OCl⁻ versus HOCl, and OCl⁻ has a greater molar absorptivity, allowing TOTCl concentrations (0 to 4 mg Cl₂ L⁻¹) to be used that were relevant to the current research.

Equilibrium constant determination experiments

Equilibrium constant experiments.—All experiments and associated measurements were conducted in a temperature controlled chamber maintained nominally at either 5, 10, 15, 20, 25, 30, or 35 °C. Duplicate experiments were conducted at 5, 20, and 35 °C. To acquire the required data to allow estimation of K_{7a} and K_{9a} temperature dependence, solutions of free chlorine only and free chlorine with cyanuric acid additions of either 1, 2, 3, or 4 mg L⁻¹ cyanuric acid were created in 0.004 M carbonate buffer at pHs 7.5, 8.3, and 9.0 at each experimental temperature and for two TOTCl concentrations (1.9 and 3.7 mg Cl₂ L⁻¹).

A sample's free chlorine concentration was determined using a combination of spectrophotometry and colorimetric methods. In a solution containing only free chlorine (i.e., no cyanuric acid addition and designated as Solution #1) at a fixed pH and temperature, the 292-nm absorbance is proportional to HOCl and OCl⁻ concentrations (Equation 3).

$$Abs_1 = \epsilon_{HOCl} l \alpha_0 TOTFree_1 + \epsilon_{OCl} l \alpha_1 TOTFree_1 = \epsilon_{HOCl} l \alpha_0 TOTCl + \epsilon_{OCl} l \alpha_1 TOTCl \quad (3)$$

In Equation 3, Abs₁ is the measured total absorbance at 292 nm in Solution #1; α₀ and α₁ are the fractions of free chlorine that are HOCl and OCl⁻, respectively; ε_{HOCl} and ε_{OCl} are the molar absorptivities of HOCl and OCl⁻ at 292 nm, respectively; l is the pathlength of the absorbance cell; and TOTFree₁ is the free chlorine concentration in Solution #1 which equals the TOTCl concentration in Solution #1.

Adding some mass of cyanuric acid to Solution #1 creates Solution #2 where the absorbance at 292 nm is now related by Equation 4. Note that the only difference between Solution #1 and Solution #2 is the presence of cyanuric acid in Solution #2 (i.e., Solution #2 has the same pH, temperature, and TOTCl concentration as Solution #1). Therefore, α₀ and α₁ are also the same between Solution #1 and Solution #2. In Equation 4, Abs₂ is the measured total absorbance at 292 nm in Solution #2 and TOTFree₂ is the free chlorine concentration in Solution #2. Because some TOTCl is now bound as chlorinated cyanurates in Solution #2, TOTFree₂ is less than TOTCl.

$$Abs_2 = \epsilon_{HOCl} l \alpha_0 TOTFree_2 + \epsilon_{OCl^-} l \alpha_1 TOTFree_2 \quad (4)$$

Taking the absorbance ratio for Solution #1 and Solution #2 results in Equation 5 which relates the absorbance ratio to the fraction of free chlorine in Solution #2 and becomes independent of HOCl and OCl⁻ molar absorptivities.

$$\frac{Abs_2}{Abs_1} = \frac{\epsilon_{HOCl} l \alpha_0 TOTFree_2 + \epsilon_{OCl^-} l \alpha_1 TOTFree_2}{\epsilon_{HOCl} l \alpha_0 TOTCl + \epsilon_{OCl^-} l \alpha_1 TOTCl} = \frac{TOTFree_2}{TOTCl} \quad (5)$$

TOTFree₂ can be calculated using Equation 5 and the measured (by an appropriate method such as colorimetric DPD) free or total chlorine concentration in Solution #1 as shown by Equation 6.

$$TOTFree_2 = \frac{Abs_2}{Abs_1} (TOTCl) = \frac{Abs_2}{Abs_1} (TOTFree_1) \quad (6)$$

Equation 6 does not require knowledge of the HOCl and OCl⁻ molar absorptivities. Rather, the only requirement for Equation 6 is that at each temperature, HOCl and OCl⁻ have a constant molar absorptivity (i.e., that concentration is proportional to absorbance) as has been determined by Morris (1966).

Simple model.—Equation 7 represents a third-order polynomial equation derived from the simple model in terms of total free chlorine (TOTFree) concentration (see Supplementary Data Derivation of Equation 7 from the Simple Model). In Equation 7, α_0 is the concentration fraction of TOTFree that is HOCl (Supplementary Equation S1); $\{H^+\}$ is hydrogen ion activity which equals 10^{-pH} ; K_{6c} is the concentration based cyanuric acid first equilibrium constant calculated from K_6 (Supplementary Equation S4); and K_{7a} and K_{9a} are chlorinated cyanurate equilibrium constants. Equation 7 was used along with experimentally determined TOTFree concentrations (Equation 6) to estimate the temperature dependence of K_{7a} and K_{9a} as subsequently discussed (Equilibrium constant temperature dependence and Parameter estimation).

$$\begin{aligned}
 & \left(\frac{K_{6C} \alpha_0^2}{K_{7a} K_{9a} \{H^+\}} \right) \text{TOTFree}^3 + \left(2\text{TOTCy} \frac{K_{6C} \alpha_0^2}{K_{7a} K_{9a} \{H^+\}} + \frac{K_{6C} \alpha_0}{K_{9a} \{H^+\}} - \text{TOTCl} \frac{K_{6C} \alpha_0^2}{K_{7a} K_{9a} \{H^+\}} \right. \\
 & \left. \right) \text{TOTFree}^2 + \\
 & \left(\text{TOTCy} \frac{K_{6C} \alpha_0}{K_{9a} \{H^+\}} + 1 + \frac{K_{6C}}{\{H^+\}} - \text{TOTCl} \frac{K_{6C} \alpha_0}{K_{9a} \{H^+\}} \right) \text{TOTFree} - \text{TOTCl} \left(1 + \frac{K_{6C}}{\{H^+\}} \right) = 0
 \end{aligned}
 \tag{7}$$

Ionic strength and activity corrections for K6 and K.—To determine the concentration based equilibrium constants K_c and K_{6c} from K and K_6 (Supplementary Equations S1 and S4), the range of μ for the experimental conditions was calculated using Equation 8 based on known chemical additions, the measured pH and temperature, and a charge balance to account for the acid or base addition required to obtain the measured pH (Wahman, 2018b). For the μ calculations, relationships for carbonate and water ionization constants with temperature were taken from Goldberg et al. (2002) and Stumm and Morgan (1996), respectively.

$$\mu = \frac{1}{2} \sum_{\text{all ions}} c_i z_i^2 \tag{8}$$

Subsequently, μ was used to calculate the single charge ion ($z = 1$) activity coefficient (γ_1) from the Davies equation using Equation 9 (Benjamin, 2002). In Equation 9, the term A_{DH} is determined from Equation 10 at the specified T_K (Benjamin, 2002) and in Equation 10, the dielectric constant for water (ϵ_{water}) is determined at the specified temperature in $^{\circ}\text{C}$ (T_c) from Equation 11 (Malmberg and Maryott, 1956).

$$\log \gamma_z = -A_{DH} z^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu \right) \tag{9}$$

$$A_{DH} = 1.82 \times 10^6 (\epsilon_{\text{water}} T_K)^{-3/2} \tag{10}$$

$$\epsilon_{\text{water}} = 87.740 - 0.40008 T_c + 9.398 \times 10^{-4} T_c^2 - 1.410 \times 10^{-6} T_c^3 \tag{11}$$

The determined range of μ (0.0040 to 0.0045 M) and corresponding γ_1 (0.928 to 0.935) values covered a narrow range. Because γ_1 was identical to two significant figures over its entire range, γ_1 was fixed at 0.93 for all experimental conditions to simplify analysis, representing at worst a 0.5% deviance from the actual γ_1 .

Equilibrium constant temperature dependence.—The basic relationship between an equilibrium constant (K_{eq}) with T_K is shown by Equation 12 (Stumm and Morgan, 1996). In Equation 12, H^0 is the standard enthalpy change of the reaction while R is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$). If H^0 is assumed to be independent of T_K , Equation 13 results. Equation 13 can be further simplified to Equation 14 or Equation 15. Using Equation 14, specific relationships for K_{7a} and K_{9a} with T_K are represented by Equations 16 and 17. Equations 1, 2, 7, 16, and 17 were used for parameter estimation, and A_{7a} , A_{9a} , B_{7a} , and B_{9a} represent constants estimated during parameter estimation with $A_{7a} = \frac{\Delta H^0_{7a}}{R}$ and $A_{9a} = \frac{\Delta H^0_{9a}}{R}$.

$$\frac{d \ln K_{eq}}{dT_K} = \frac{\Delta H^0}{RT_K^2} \quad (12)$$

$$\ln \frac{K_{eq, T_{K2}}}{K_{eq, T_{K1}}} = \int_{T_{K1}}^{T_{K2}} \frac{\Delta H^0}{RT_K^2} dT_K = \frac{\Delta H^0}{R} \left(\frac{1}{T_{K1}} - \frac{1}{T_{K2}} \right) \quad (13)$$

$$\ln K_{eq, T_K} = \frac{\Delta H^0}{RT_K} + \text{constant} = -\frac{A}{T_K} + B \quad (14)$$

$$pK_{eq, T_K} = \frac{A}{(\ln 10)(T_K)} - \frac{B}{\ln 10} \quad (15)$$

$$\ln K_{7a, T_K} = -\frac{A_{7a}}{T_K} + B_{7a} \quad (16)$$

$$\ln K_{9a,T_K} = -\frac{A_{9a}}{T_K} + B_{9a} \quad (17)$$

Parameter estimation.—Estimation of A_{7a} , A_{9a} , B_{7a} , and B_{9a} and corresponding determinations of K_{7a,T_K} , K_{9a,T_K} , H^0_{7a} , and H^0_{9a} were accomplished in R, a freeware language and environment for statistical computing and graphics available for download at <http://www.r-project.org/> (R Core Team, 2017). R's capabilities were extended through the use of the *polynom* package, a free user-contributed package downloaded through the R software, to numerically solve Equation 7 for the TOTFree concentration (Venables et al., 2016). In the R software, the function *optim()* was used to vary estimates of A_{7a} , A_{9a} , B_{7a} , and B_{9a} by minimizing the residual sum of squares between all ($n = 208$) the experimentally measured TOTFree concentrations and the TOTFree concentrations required to solve Equation 7. To provide an estimate of uncertainty in the parameter estimates, bootstrapping with sample replacement ($n = 10,000$) was used.

Results and discussion

Absorbance verification experiments

Fig. 3 presents results demonstrating the verification of a linear relationship ($R^2 = 0.999$) between concentration and absorbance on the current equipment at 292 nm over the range of temperatures evaluated in the current research, using OCl^- as the demonstration chemical. For each temperature, similar slopes (345 to $356 \text{ M}^{-1} \text{ cm}^{-1}$ molar absorptivity) were determined, verifying the current equipment can reproduce similar results of Morris (1966). Based on variability in the lowest standard ($0.25 \text{ mg Cl}_2 \text{ L}^{-1}$), the detection limit corresponded to an absorbance of 0.002 with a 10-cm cell (APHA et al., 2005). To provide a measure of safety, the minimum absorbance values used for any sample used in parameter estimation was set to 0.020 with a 10-cm cell.

Equilibrium constant determination experiments

Source data.—Experimental data obtained from the equilibrium constant determination experiments are summarized in Supplementary Table S1, consisting of 208 data points. A summary of the experimental conditions is provided in Table 2. For each temperature, 24 possible samples containing both free chlorine and cyanuric acid were created for analysis. The lower number of samples shown in Table 2 at each temperature is a result of samples whose absorbance were below 0.020 and removed from subsequent analyses. As temperature decreased, a greater number of samples did not achieve the 0.020 absorbance threshold which is a result of lower concentrations of free chlorine being present as temperature decreased.

Full model (without temperature dependence) representation of experimental data.—To evaluate the need to incorporate temperature into the water chemistry model, a comparison of the experimentally determined free chlorine concentrations (Supplementary Table S1) to the simulated free chlorine concentrations using the full model (Table 1) was

conducted (Fig. 4A). If there was no impact with temperature, the experimentally measured and model simulated concentrations would fall on the 1:1 line displayed in Fig. 4A. It is clear in Fig. 4A that as temperatures decreased below 25 °C, the full model (without temperature dependence) overestimated the free chlorine concentrations. To understand the discrepancy between the measured free chlorine concentrations and the full model simulated free chlorine concentration, Supplementary Fig. S2 displays the difference on a concentration (Supplementary Fig. S2A) and percentage basis (Supplementary Fig. S2B). Differences of up to 1.2 mg Cl₂ L⁻¹ are evident with percentages reaching nearly 60% of the simulated value. Taken together, these results indicated that temperature must be considered to properly represent the experimental data.

Simple model estimated parameters.—Using the data presented in Supplementary Table S1, A_{7a}, A_{9a}, B_{7a}, and B_{9a} were estimated using Equations 7, 16, and 17 to determine K_{7a} and K_{9a} at various temperatures. No apparent pattern is evident in the simple model residuals (experimentally measured minus model simulated free chlorine concentrations) associated with the parameter estimation (Supplementary Fig. S3). A comparison of the simple model simulated and experimentally measured free chlorine concentrations is summarized in Fig. 4B. If the simple model simulated and experimentally measured free chlorine concentrations were identical, the points shown in Fig. 4B would form a line with a slope of one passing through the origin. The linear regression results in a line with a slope that is not significantly different than one (0.99 ± 0.010 , 95% confidence interval (CI)), an intercept not significantly different from zero (0.018 ± 0.021 , 95% CI), and excellent R² (0.994), indicating that the simple model is representing the experimental data extremely well and that the assumption of constant H⁰ (Equation 13) was justified.

A summary of the estimates of A_{7a}, A_{9a}, B_{7a}, and B_{9a} and corresponding pK_{7a} and pK_{9a} values ranging from 5 to 35 °C is provided in Table 3 along with comparisons with the 25 °C O'Brien et al. (1974) estimates adjusted to $\mu = 0$ M (refer to Supplementary Data, Adjustment of O'Brien et al. (1974) Equilibrium Constants). From the estimated values of A_{7a} and A_{9a}, $\Delta H_{7a}^0 = 38.8 \pm 6.0$ kJ mol⁻¹ (95% CI) and $\Delta H_{9a}^0 = 42.7 \pm 3.0$ kJ mol⁻¹ (95% CI). Supplementary Fig. S4 shows histograms of the bootstrap results for A_{7a}, A_{9a}, B_{7a}, and B_{9a} that were used to determine their reported uncertainty in Table 3, indicating normally distributed estimates. In addition, Fig. 5 presents the paired estimates of A_{7a} and B_{7a} (Fig. 5A) and A_{9a} and B_{9a} (Fig. 5B) from the bootstrap results, detailing the correlation between each estimated pair and corresponding joint uncertainty which is expected based on the linear relationship (Equations 16 and 17). The correlation would need to be incorporated if a future uncertainty analysis on the simple model is conducted to determine safety factors so that free chlorine concentration is not overestimated by the simple model to ensure conservative estimates when estimating disinfectant efficacy in dichlor or trichlor systems.

Using the reported standard deviations from O'Brien et al. (1974) and after adjusting their estimates determined at $\mu = 0.020$ M to $\mu = 0$ M with the experimental data provided in O'Brien (1972) (pK_{7a} = 4.45–4.57 and pK_{9a} = 5.64–5.71; 95% CI), the current 25 °C simple model estimates (pK_{7a} = 4.59–4.71 and pK_{9a} = 5.81–5.85; 95% CI) are comparable yet significantly different than the full model estimates of O'Brien et al. (1974). The differences

between the current estimates of pK_{7a} and pK_{9a} and those of O'Brien et al. (1974) may be a result of the different experimental conditions, methods used to estimate equilibrium constants, or models implemented (i.e., simple versus full). The current research conducted experiments under conditions representative of drinking water (pH 7.5 to 9.0, $< 4 \text{ mg Cl}_2 \text{ L}^{-1}$ TOTCl, and $< 4 \text{ mg Cy L}^{-1}$ TOTCy), used a simplified model that only included chemical species important under drinking water conditions, and simultaneously estimated two equilibrium constants (K_{7a} and K_{9a}) using all the data collected from 5 to 35 °C.

To estimate K_{9a} , O'Brien (1972) and O'Brien et al. (1974) used pHs from 9.4 to 10.6, chemical concentrations one to two orders of magnitude greater than the current research (149 $\text{mg Cl}_2 \text{ L}^{-1}$ TOTCl and 378 mg Cy L^{-1} TOTCy), and relied on two estimated equilibrium constants from the full model (Table 1; K_8 and K_{10}) to estimate K_{9a} . In addition, O'Brien (1972) discussed an apparent linear trend with the experimental pH for individual K_{9a} estimates used to determine the reported K_{9a} and associated uncertainty, noting that further experimental work should be conducted to investigate the pH trend as it should not exist. The O'Brien (1972) linear trend with pH ($R^2 = 0.96$) is illustrated in Supplementary Fig. S5 where the O'Brien (1972) individual pK_{9a} estimates increased as the experimental pH under which the pK_{9a} estimates were determined decreased. If the O'Brien (1972) pK_{9a} estimates (5.75 and 5.77) at the lowest experimental pH (9.45) are more representative of the actual pK_{9a} value, then the current research estimated pK_{9a} (5.81–5.85) corresponds better with these previous results. For K_{7a} , O'Brien (1972) and O'Brien et al. (1974) did not conduct specific experiments to estimate K_{7a} . Rather, K_{7a} was calculated from three estimated equilibrium constants (Fig. 1 and Table 1; K_2 , K_{3a} , and K_4) that were determined with TOTCl and TOTCy concentrations like those used to estimate K_{9a} . Regardless of the differences between the current estimates and those of O'Brien (1972) and O'Brien et al. (1974), the simple model presented herein represented the entire data set extremely well.

Practical implications

With the addition of K_{7a} and K_{9a} 's temperature dependence to the known temperature dependence of K and K_6 , a drinking water relevant chemistry model for the free chlorine and cyanuric acid system (i.e., systems using dichlor or trichlor) has been determined over a practical range of drinking water temperatures (5 to 35 °C), allowing estimation of free chlorine concentrations. Fig. 6 summarizes the temperature impact on the percent free chlorine for a 2 $\text{mg Cl}_2 \text{ L}^{-1}$ dichlor addition (1.8 mg Cy L^{-1} TOTCy) at 5, 15, 25, and 35 °C. The percent free chlorine decreases with decreasing temperature at all pH values simulated, highlighting the importance of accounting for temperature so as not to overestimate free chlorine concentration which is the true disinfectant. For example and at pH 7.0, the percent free chlorine decreases from 45% (0.90 $\text{mg Cl}_2 \text{ L}^{-1}$ free chlorine) at 25 °C to 31% (0.60 $\text{mg Cl}_2 \text{ L}^{-1}$ free chlorine) at 5 °C. If temperature was not considered, a system operating at 5 °C would overestimate their free chlorine concentration by 50%, which could have significant implications for understanding disinfection efficacy (e.g., compliance with US primary disinfection requirements).

Summary

A simplified version of the free chlorine and cyanuric acid equilibrium water chemistry model (simple model) was used to estimate the unknown temperature dependence (5 to 35 °C) of the two remaining equilibrium constants (K_{7a} and K_{9a}) required for the simple model. At 0 M ionic strength (μ), the estimated equilibrium constants were

$$\ln K_{7a} = -\frac{4,671}{T_K} + 4.95 \text{ or } pK_{7a} = \frac{2,028}{T_K} - 2.15 \text{ and } \ln K_{9a} = -\frac{5,133}{T_K} + 3.79 \text{ or}$$

$$pK_{9a} = \frac{2,229}{T_K} - 1.65. \text{ The corresponding estimated standard enthalpy change of the reactions}$$

were $\Delta H_{7a}^0 = 38.8 \pm 6.0 \text{ kJ mol}^{-1}$ and $\Delta H_{9a}^0 = 42.7 \pm 3.0 \text{ kJ mol}^{-1}$ (95% CI). With the incorporation of temperature dependence, the completed simple model is now capable of simulating free chlorine concentrations to allow assessment of disinfection efficacy, including US primary disinfection or numeric free chlorine distribution system residual (i.e., greater than detectable) requirements.

To apply the simple model in drinking water practice, one would follow the methodology outlined by Wahman (2018a) with the addition of temperature as another required measurement. Therefore, for a water sample, one needs to know the pH, TOTCl, TOTCy, and temperature as inputs to the simple model. As discussed in Wahman (2018a), pH, TOTCl, and now temperature could be measured directly on the water sample while the TOTCy concentration could be calculated from the total mass of dichlor or trichlor that was dosed into the water system, accounting for chemical purity. Because chlorine demand may have occurred, TOTCy cannot be calculated from the measured TOTCl in the water sample and dichlor or trichlor's chemical formula. Doing so would lead to an underestimation of TOTCy and an overestimation of the actual free chlorine concentration. With pH, TOTCl, TOTCy, and temperature known, the simple model provides an estimate of the sample's actual free chlorine concentration.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

The authors acknowledge the technical assistance provided by Meridith Bartley of Neptune and Company for the implementation of the bootstrapping analysis in R and Richard Falk for fruitful discussions on relevant chemistry. This work has been subjected to the United States Environmental Protection Agency's (Agency's) review and has been approved for publication. The views expressed in this manuscript are those of the author and do not necessarily represent the views or policies of the Agency. Any mention of trade names, products, or services does not imply an endorsement by the Agency. The Agency does not endorse any commercial products, services, or enterprises. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

- APHA, AWWA, and WEF. (2005). Standard Methods for the Examination of Water and Wastewater. American Public Health Association : American Water Works Association : Water Environment Federation, Washington, D.C.
- Benjamin MM (2002). Water Chemistry. McGraw-Hill, New York, NY.

- Canelli E (1974). Chemical, bacteriological, and toxicological properties of cyanuric acid and chlorinated isocyanurates as applied to swimming pool disinfection – A Review. *Am. J. Public Health* 64, 155. [PubMed: 4594286]
- Canelli E (1980). Evaluation of a portable bare-electrode amperometric analyzer for determining free chlorine in potable and swimming-pool waters. *Water Res.* 14, 1533.
- Clasen T, and Edmondson P (2006). Sodium dichloroisocyanurate (NaDCC) tablets as an alternative to sodium hypochlorite for the routine treatment of drinking water at the household level. *Int. J. Hyg. Environ. Health* 209, 173. [PubMed: 16387550]
- Engel JP, Rubin AJ, and Sproul OJ (1983). Inactivation of *Naegleria gruberi* cysts by chlorinated cyanurates. *Appl. Environ. Microbiol.* 46, 1157. [PubMed: 6316851]
- Goldberg RN, Kishore N, and Lennen RM (2002). Thermodynamic Quantities for the Ionization Reactions of Buffers. *J. Phys. Chem. Ref. Data* 31, 231.
- Hach Company. (2015). Method 10260, Free Chlorine. USEPA DPD Method, Chemkey Reagents, 0.12 to 4.6 mg/L as Cl₂. Hach Company, Loveland, Colorado.
- Hach Company. (2017). Method 10260, Total Chlorine. USEPA DPD Method, Chemkey Reagents, 0.04 to 10.0 mg/L as Cl₂. Hach Company, Loveland, Colorado.
- Hammond BG, Barbee SJ, Inoue T, Ishida N, Levinskas GJ, Stevens MW, Wheeler AG, and Cascieri T (1986). A Review of Toxicology Studies on Cyanurate and Its Chlorinated Derivatives. *Environ. Health Perspect.* 69, 287. [PubMed: 3545805]
- Jensen JN, and Johnson JD (1990). Interferences by monochloramine and organic chloramines in free available chlorine methods. 2. N,N-Diethyl-p-phenylenediamine. *Environ. Sci. Technol.* 24, 985.
- Kuechler TC (2009). Use Of Chlorinated Isocyanurates For Drinking Water Chlorination. *Proceedings of the Water Environment Federation* 2009, 799.
- Malmberg CG, and Maryott AA (1956). Dielectric constant of water from 0° to 100° C. *J. Res. Natl. Bur. Stand.* 56, 1.
- Matte D, Solastiouk B, Merlin A, and Deglise X (1990). Étude cinétique de la N-chloration de l'acide cyanurique en phase aqueuse. *Can. J. Chem.* 68, 307.
- Morris JC (1966). The acid ionization constant of HOCl from 5 to 35C. *J. Phys. Chem.* 70, 3798.
- Murphy JL, Arrowood MJ, Lu X, Hlavsa MC, Beach MJ, and Hill VR (2015). Effect of cyanuric acid on the inactivation of *Cryptosporidium parvum* under hyperchlorination conditions. *Environ. Sci. Technol.* 49, 7348. [PubMed: 26042636]
- NSF International, Search for NSF Certified Drinking Water Treatment Chemicals, <http://info.nsf.org/Certified/PwsChemicals/>, (accessed Date Accessed: January 11, 2018).
- O'Brien JE, 1972 Hydrolytic and Ionization Equilibria of Chlorinated Isocyanurate in Water. Dissertation, Harvard University, Cambridge, Massachusetts.
- O'Brien JE, Morris JC, and Butler JN (1974). Equilibria in Aqueous Solutions of Chlorinated Isocyanurate In Chemistry of Water Supply, Treatment, and Distribution. Rubin AJ, ed. Ann Arbor Science Publishers, Inc., Ann Arbor, MI pp 333–358.
- R Core Team. (2017). R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.
- Stumm W, and Morgan JJ (1996). Aquatic chemistry chemical equilibria and rates in natural waters. Wiley, Hoboken, New Jersey.
- Summers RS, Hooper SM, Shukairy HM, Solarik G, and Owen D (1996). Assessing the DBP yield: Uniform formation conditions. *J. Am. Water Works Ass.* 88, 80.
- USEPA, Memorandum – Compliance Determination for Inactivation Requirements of the National Primary Drinking Water Regulations when a Public Water Systems Uses Dichlor and Trichlor for Primary Disinfection (4 18, 2018), <https://asdwa.files.wordpress.com/2018/04/dichlor-trichlor-memo-2018-04-18.pdf>, (accessed August 27, 2018).
- Utah Division of Drinking Water, Plan Review Policy for Dichlor and Trichlor Installations (DDW–Eng–0032 April 27, 2017), <https://documents.deq.utah.gov/drinking-water/engineering/new-facilities-new-public-water-systems/DDW-2017-001930.pdf>, (accessed August 27, 2018).
- Venables B, Hornik K, and Maechler M (2016). polynom: A Collection of Functions to Implement a Class for Univariate Polynomial Manipulations. R package version 1.3–9.

- Wahman DG (2017). Free chlorine and cyanuric acid simulator application description – Version 0.50, EPA/600/S-17/165. United States Environmental Protection Agency, Washington, DC.
- Wahman DG (2018a). Chlorinated Cyanurates: Review of Water Chemistry and Associated Drinking Water Implications. J. Am. Water Works Ass. DOI: 10.1002/awwa.1086, E1.
- Wahman DG (2018b). First Acid Ionization Constant of the Drinking Water Relevant Chemical Cyanuric Acid from 5 to 35 °C. Environ. Sci. Water Res. Technol. 4, 1522.
- Wahman DG, Alexander M, and Dugan AG (2017). Chlorinated Cyanurates: Method Interferences and Application Implications In 2017 Water Quality Technology Conference. American Water Works Association, Portland, Oregon.
- Wahman DG, and Pressman JG (2015). Distribution System Residuals–Is “Detectable” Still Acceptable for Chloramines? J. Am. Water Works Ass. 107, 53.
- Wajon JE, and Morris JC (1980). The analysis of free chlorine in the presence of nitrogenous organic compounds. Environ. Int. 3, 41.
- Whittle GP (1970). Recent advances in determining free chlorine. In National Specialty Conference on Disinfection Amherst, MA.
- Wojtowicz JA (1996). Relative bactericidal effectiveness of hypochlorous acid and chloroisocyanurates. Journal of the Swimming Pool and Spa Industry 2, 34.
- World Health Organization. (2007). Sodium Dichloroisocyanurate in Drinking–water Background document for development of WHO Guidelines of Drinking–Water Quality. World Health Organization, Geneva, Switzerland.
- World Health Organization. (2011). Guidelines for drinking–water quality. World Health Organization, Geneva, Switzerland.
- Yamashita T, Sakae K, Ishihara Y, Isomura S, and Inoue H (1988). Virucidal effect of chlorinated water containing cyanuric acid. Epidemiol. Infect. 101, 631. [PubMed: 2850940]

FIG. 1.

Hypochlorous acid, cyanuric acid, cyanuric acid ionization products, and chlorinated cyanurate equilibria for the full model. Grey shaded regions indicate chemicals and reactions that are relevant under drinking water conditions and chemical dosages and are those included in the simple model. Hydrogen ion for dissociation reactions and water and hypochlorous acid for hydrolysis reactions are not shown for clarity, and required full reactions for the full and simple models are shown in Table 1. Adapted with permission from Brady et al. (1963) Copyright 1963 American Chemical Society.

FIG. 2.

Comparison of the difference in simulated free chlorine concentrations at 25 °C between the full model of O'Brien et al. (1974) and the proposed simple model over a range of drinking water relevant conditions (6.5 pH 9.5, $\text{TOTCl} = 10 \text{ mg Cl}_2 \text{ L}^{-1}$, and $\text{TOTCy} = 10 \text{ mg Cy L}^{-1}$) on a concentration (A) and percent (B) basis. $\Delta \text{ Free Chlorine (mg Cl}_2 \text{ L}^{-1}) = \text{simple model} - \text{full model}$ and $\Delta \text{ Free Chlorine (\%)} = (\text{simple model} - \text{full model}) / \text{full model}$. Equilibrium constants used for all simulations are those shown in Table 1.

FIG. 3.

Linearity verification between concentration and absorbance at 292 nm and 5 (A), 20 (B), or 35 (C) °C. Note that the ordinate has been normalized to a 1-cm pathlength and 1 mg Cl₂ L⁻¹ = 1.41 × 10⁻⁵ M.

FIG. 4.

Comparison of model simulated versus experimentally determined free chlorine concentrations for the full model (A) and simple model (B). Full model simulations conducted using equilibrium constants shown in Table 1. Simple model simulations conducted using equilibrium constants determined in the current research.

FIG. 5. Paired bootstrap estimates ($n = 10,000$) of parameters for K_{7a} (A) and K_{9a} (B).

FIG. 6.

Simple model simulation of percent free chlorine concentration at various temperatures for a 2 mg $\text{Cl}_2 \text{ L}^{-1}$ dichlor addition (i.e., 2 mg $\text{Cl}_2 \text{ L}^{-1}$ total chlorine). Simulations conducted using equilibrium constants determined in the current research. Percent free chlorine = $100 \times \text{actual free chlorine} / \text{total chlorine}$.

Table 1.

Summary of required equilibria to simulate chlorinated cyanurate water chemistry for the full and simple models and associated equilibrium constants as noted

Stoichiometry	Constant	pK ^a	Equilibrium Included	
			Full Model	Simple Model
$\text{Cl}_3\text{Cy} + \text{H}_2\text{O} \rightleftharpoons \text{HCl}_2\text{Cy} + \text{HOCl}$	K_{1a}	1.8	✓	
$\text{HCl}_2\text{Cy} \rightleftharpoons \text{Cl}_2\text{Cy}^- + \text{H}^+$	K_2	3.75	✓	
$\text{H}_2\text{ClCy} \rightleftharpoons \text{HClCy}^- + \text{H}^+$	K_4	5.33	✓	
$\text{H}_3\text{Cy} \rightleftharpoons \text{H}_2\text{Cy}^- + \text{H}^+$	K_6	6.88	✓	✓
$\text{Cl}_2\text{Cy}^- + \text{H}_2\text{O} \rightleftharpoons \text{HClCy}^- + \text{HOCl}$	K_{7a}	4.51	✓	✓
$\text{HClCy}^- \rightleftharpoons \text{ClCy}^{2-} + \text{H}^+$	K_8	10.12	✓	
$\text{HClCy}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{Cy}^- + \text{HOCl}$	K_{9a}	5.62	*	✓
$\text{H}_2\text{Cy}^- \rightleftharpoons \text{HCy}^{2-} + \text{H}^+$	K_{10}	11.40	✓	
$\text{ClCy}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCy}^{2-} + \text{HOCl}$	K_{11a}	6.90	✓	
$\text{HCy}^{2-} \rightleftharpoons \text{Cy}^{3-} + \text{H}^+$	K_{12}	13.5	✓	
$\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$	K	7.54 ^b	✓	✓

* Determined by O'Brien et al. (1974) but not required in the full model implementation

^a O'Brien et al. (1974) at 0.020 M ionic strength and 25 °C unless otherwise noted

^b Morris (1966) at 0 M ionic strength and 25 °C

Table 2.

Summary of experimental conditions (208 total samples)

Value $\pm$ Standard Deviation (number of samples with absorbance > 0.020 with a 10-cm cell)			
Temperature (°C)	pH	Total Chlorine (mg Cl ₂ L ⁻¹)	Dosed Cyanuric Acid (mg L ⁻¹ H ₃ Cy)
4.3 $\pm$ 0.13 (18)	7.50 $\pm$ 0.003 (54)	1.87 $\pm$ 0.054 (90)	1 (60)
5.3 $\pm$ 0.28 (18)	8.30 $\pm$ 0.004 (74)	3.70 $\pm$ 0.10 (118)	2 (55)
9.0 $\pm$ 0.19 (19)	9.00 $\pm$ 0.003 (80)		3 (48)
15.3 $\pm$ 0.24 (21)			4 (45)
19.8 $\pm$ 0.076 (21)			
20.6 $\pm$ 0.10 (22)			
24.4 $\pm$ 0.075 (22)			
30.2 $\pm$ 0.14 (22)			
34.2 $\pm$ 0.14 (22)			
34.5 $\pm$ 0.26 (23)			

Table 3.

Summary of estimated equilibrium constants K_{7a} and K_{9a} and associated parameters from 5 to 35 °C determined in the current research unless otherwise noted

Temperature (°C)	Value $\pm$ 95% Confidence Interval ($\mu = 0$ M)	
	pK_{7a}	pK_{9a}
5	5.14 ± 0.061	6.37 ± 0.041
10	5.01 ± 0.050	6.23 ± 0.033
15	4.89 ± 0.047	6.09 ± 0.026
20	4.77 ± 0.051	5.96 ± 0.021
25	4.65 ± 0.059	5.83 ± 0.020
25 ^a	4.51 ± 0.058 ^a	5.68 ± 0.035 ^a
30	4.54 ± 0.071	5.71 ± 0.022
35	4.43 ± 0.084	5.59 ± 0.027

Parameter (Units)	Value $\pm$ 95% Confidence Interval ($\mu = 0$ M)	
	K_{7a}	K_{9a}
A (K)	$4,671 \pm 725$	$5,133 \pm 363$
B	4.95 ± 2.52	3.79 ± 1.22
H ⁰ (kJ mol ⁻¹)	38.8 ± 6.0	42.7 ± 3.0

^aO'Brien et al. (1974) after adjusting to 0 M ionic strength and converting the reported standard deviations to 95% confidence intervals using the experimental data from O'Brien (1972)