

pH of seawater

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ABSTRACT

An important property of aqueous solutions is pH because it affects chemical and biochemical properties such as chemical reactions, equilibrium conditions, and biological toxicity. With the increasing uptake of fossil fuel CO₂ into the oceans, a decrease in pH is important to consider at this time. Unfortunately, many different methods for assessing pH have been used by different groups. The objectives of this review were to (1) briefly examine the concept of pH as it was introduced and developed, up to the current scientific developments, assumptions, and recommendations, (2) critically assess the various approaches that different scientific groups have adopted for pH, balancing their preferences and arguments, (3) compare measuring vs. modeling pH, and (4) issue recommendations on an optimized approach or approaches for pH.

The main conclusions of this review are: (1) pH definitions and conventions are highly variable, which leads to highly variable estimates of pH. For example, for seawater at $S_A = 35.165$ g/(kg soln), $t = 25$ °C, $P = 1.0$ atm, and $fCO_2 = 3.33E-4$ atm, model calculated pH values varied from 8.08 to 8.33 on the various pH scales; (2) An acceptable nomenclature is needed to keep pH variability unambiguous, due to alternative definitions and conventions. A nomenclature example is given in this paper. It is the (still unsolved) task of international bodies such as IUPAC or IOC to develop and promote such widely recognized conventions; (3) pH can be accurately estimated based on measurement (potentiometric, spectrophotometric) and modeling approaches. Accuracy via different definitions and conventions clearly requires consistency with respect to experimental measurements, equilibrium constants, activity coefficients, and buffer solutions that are used for specific approaches; (4) "Total" pH accuracy that includes the Bates–Guggenheim convention is ± 0.01 pH units. Removing the Bates–Guggenheim convention from the accuracy calculation can lead to "conventional" accuracies of ± 0.004 pH units; (5) pH extensions to high solution concentrations are capable using the Pitzer modeling approach. Modeling can, in principle, lead to pH estimates that are more accurate than measurements, which is illustrated with two Pitzer models for natural waters made up of the major components of seawater. But this principle still needs to be proven; (6) It is recommended that ocean scientists use the free concentration or activity of the proton to examine the effect of pH on processes in the oceans.

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1. Introduction

An important property of aqueous solutions is pH because it affects chemical and biochemical properties such as chemical reactions, equilibrium conditions, and biological toxicity (Bates, 1982; Dickson, 1984, 1993a,b; Herczeg et al., 1985; ISO, 2007; Millero et al., 2009b). Especially important for seawater pH are acid–base systems that are functions of pH (Millero, 2001). With the increasing uptake of fossil fuel CO₂ into the oceans, the effect of a decrease in pH is important to

consider at this time (Marion et al., 2009; Millero et al., 2009b). Unfortunately, many different methods for assessing pH have been used by different groups. In this study, we will focus on pH that is independent of kinetic processes. Also pH can either be measured or modeled, or some combination of these two approaches. According to Dickson (1984): "The field of pH scales and the study of proton-transfer reactions in seawater is one of the most confused areas of marine chemistry." Twenty-seven years later, it still remains confusing, both to insiders and outsiders.

The objectives of this review were to

- (1) Briefly examine the concept of pH as it was introduced and developed, up to the current scientific developments, assumptions, and recommendations

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- (2) Critically assess the various approaches that different scientific groups have adopted for pH, balancing their preferences and arguments
- (3) Compare measuring vs. modeling pH
- (4) Issue recommendations on an optimized approach or approaches for pH.

In this review, we are primarily considering the pH of natural waters (rivers, estuaries, seawater and brines) that are made up of the major components of seawater (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Sr^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , Br^- , CO_3^{2-} , $\text{B}(\text{OH})_4^-$, F^- , OH^- , $\text{B}(\text{OH})_3$, and CO_2 ; Millero et al., 2008).

2. Concepts, definitions, and conventions

One of the more confusing aspects of pH is the fact that, despite its unique notional definition, $\text{pH} = -\log(a_{\text{H}^+})$ (the negative logarithm of the H^+ ion activity), the term “pH” has been used by various groups in association with different meanings (scales) and with different measurement procedures and assumptions (Bates, 1982; Dickson, 1984, 1993a,b; Millero, 1986; Dickson and Millero, 1987; UNESCO, 1987; Lewis and Wallace, 1998; Millero, 2001, 2007, 2010; Dickson et al., 2007; ISO, 2007; Schuster et al., 2009; van Heuven et al., 2009). For example:

$$\text{pH}_F = -\log([\text{H}^+]/\text{m}^0) \quad (1)$$

$$\text{pH} = -\log(a_{\text{H}^+}) = -\log(m_{\text{H}^+} \gamma_{\text{H}^+}/\text{m}^0) \quad (2)$$

$$\text{pH}_T = -\log([\text{H}^+] + [\text{HSO}_4^-])/\text{m}^0 \quad (3)$$

$$\text{pH}_{\text{SWS}} = -\log([\text{H}^+] + [\text{HSO}_4^-] + [\text{HF}])/\text{m}^0 \quad (4)$$

where brackets [] refer to concentrations. To make the concentration values unitless, it is divided, depending on the units in which it is expressed, by $\text{m}^0 = 1 \text{ mol}/(\text{kg H}_2\text{O})$, $\text{c}^0 = 1 \text{ mol}/(\text{kg soln})$, or $\text{M}^0 = 1 \text{ mol}/\text{l}$. Later we will discuss these alternative concentration units. In these equations, “F” refers to free, “T” refers to total, and “SWS” refers to seawater scale. Eq. (1) was the original definition of pH by Sorensen (1909), >100 years ago, which has since evolved (Eqs. (2)–(4)). The right-hand version of Eq. (2) is based on the molal concentration (m), the molal activity coefficient (γ), and the standard molality ($\text{m}^0 = 1 \text{ mol}/(\text{kg H}_2\text{O})$), which is how pH is defined for the IUPAC standard (Buck et al., 2002). What we are calling pH in Eq. (2) (an abstract concept) is sometimes referred to as pH_{NBS} (an operational procedure), where NBS refers to the National Bureau of Standards (now called NIST, National Institute of Standards and Technology). For some, Eq. (2) is equivalent to pH_{NBS} (e.g., UNESCO, 1987; Lewis and Wallace, 1998), while for others pH_{NBS} only refers to pH defined for dilute solutions ($I \leq 0.1 \text{ m}$) where pH can be accurately estimated (e.g., Millero, 2001). We prefer to define pH_{NBS} only for dilute solutions that are traceable to dilute buffers, discussed below. Because of these different pH descriptions, we will define pH (Eq. (2)) as simply the negative decimal logarithm of the activity of the proton ion for both dilute and concentrated solutions.

Given an absolute salinity = 35.165 g/(kg soln), equivalent to a practical salinity (S_A) (S_P) = 35.00, at 25 °C with molal concentrations, calculated $\text{pH} = 8.332$, $\text{pH}_F = 8.195$, $\text{pH}_T = 8.087$, and $\text{pH}_{\text{SWS}} = 8.078$. We will discuss the various pH scales and their uncertainty (ISO/IEC, 2008) later in the paper.

The pH concentration units are mol/(kg H_2O) (molality), mol/(kg soln), or mol/l (molarity). For example, the definition of pH by UNESCO (1987) distinguished pH_{SWS} by using $^T\text{m}_{\text{H}}$ for the H species in Eq. (4) that have molal (m) concentrations:

$$\text{pH}_{\text{SWS,H}} = -\log(^T\text{m}_{\text{H}}) \quad (5)$$

and $^T[\text{H}]$ for mol/(kg soln):

$$\text{pH}_{\text{SWS}} = -\log(^T[\text{H}]) \quad (6)$$

In these two equations, the “T” value refers to total, which differs from our definition in Eq. (3). These two SWS equations are one of those issues mentioned above that leads to confusion and should not be used.

Unfortunately, there is no consistency in how these pH concentration options are best defined (Bates, 1982; Dickson, 1984, 1993a,b; Millero, 1986; Dickson and Millero, 1987; UNESCO, 1987; Lewis and Wallace, 1998; Millero, 2001, 2007, 2010; Buck et al., 2002; Dickson et al., 2007; ISO, 2007; van Heuven et al., 2009). Therefore, in what follows, we will use “m” as a superscript on the left sides of Eqs. (1)–(4) for molal concentrations [e.g., pH^m or pH_{SWS}^m], a superscript of “c” for mol/(kg soln) [e.g., pH^c or pH_{SWS}^c], and “M” as a superscript for molar concentrations (e.g., pH^M or pH_{SWS}^M). The following equations can be used to convert between pH^m and pH^c :

$$\text{pH}^m = \text{pH}^c + \log\left(\frac{1000 - S_A}{1000}\right) \quad (7)$$

and between pH_M and pH_c :

$$\text{pH}^M = \text{pH}^c - \log(\rho) \quad (8)$$

where S_A is absolute salinity that is related to practical salinity (S_P) by $S_A = S_P(35.165/35.00)$ (Millero et al., 2008) and ρ is solution density (g/cm^3). Comparing these concentration definitions (m, M, and c), the pH values with different concentration scales for average seawater ($S_A = 35.165 \text{ g}/(\text{kg soln})$) at 25 °C are $\text{pH}^m = 8.332$, $\text{pH}^M = 8.338$, and $\text{pH}^c = 8.348$. Similarly, pH_{SWS} on these three concentration scales are 8.078, 8.084, and 8.094, respectively. Compared to the previously discussed pH definitions (Eqs. (1)–(4)) and their calculated pH values (8.078–8.332), these concentration scales (m, M, and c) have a minor influence on pH (± 0.016). Therefore, in what follows, we will largely rely on the molal scale.

While some ion concentrations can be measured unambiguously (e.g., K^+ , Cl^-), this is not the case for H^+ ions because they form associations with other constituents (e.g., CO_3^{2-} , F^- , SO_4^{2-}). Furthermore, single ion activities cannot be measured unambiguously (Bates, 1982; Covington and Whitfield, 1988; Pitzer, 1995; Millero, 2001; Buck et al., 2002). The situation becomes particularly difficult when dealing with complex matrices, e.g. seawater; but even in dilute, nearer to ideal electrolytic solutions, it has been, for a while, far from satisfactory, since international recommendation bodies, e.g. IUPAC, were not definitive on their recommendations. This led to the revision of the nonconclusive IUPAC 1985 recommendations with the publication of the currently enforced ones based on a metrological approach with hierarchical levels of target uncertainty (Ellison et al., 2000) attached to the assessed pH value according to the selected measurement procedure (Buck et al., 2002). The intention is that, from this common scientific basis, application and extension to specified fields will be developed in a harmonized and consistent way. Eq. (2) can be rewritten as:

$$\begin{aligned} \text{pH}^m &= -\log(a_{\text{H}^+}) = -\log(m_{\text{H}^+} \cdot \gamma_{\text{H}^+}/\text{m}^0) \\ &= -\log(f_{\text{H}^+} \cdot [m_{\text{H}^+} + m_{\text{HSO}_4^-} + m_{\text{HF}}]/\text{m}^0) \end{aligned} \quad (9)$$

for the molal (m) case, where a_{H^+} is the hydrogen ion activity, γ_{H^+} and f_{H^+} are activity coefficients of the hydrogen species in their respective proton scales. pH can be measured based on multiple assumptions, which we will discuss below. Also, chemical equilibrium models can be used to calculate activity coefficients and solution concentrations, which allow estimation of pH. We will also demonstrate how this can be done below.

While individual ion activities cannot be measured unambiguously, activity products such as a_{HCl} can be measured or modeled. For example, the activity product for HCl is

$$a_{\text{HCl}} = (a_{\pm\text{HCl}})^{1/2} = [(\gamma_{\text{H}^+})(\gamma_{\text{Cl}^-})(m_{\text{H}^+})(m_{\text{Cl}^-})]^{1/2} \quad (10)$$

or

$$a_{\text{HCl}} = [(a_{\text{H}^+})(\gamma_{\text{Cl}^-})(m_{\text{Cl}^-})]^{1/2} \quad (11)$$

The Harned cell potential (see description below) can measure a_{HCl} , m_{Cl^-} is also measurable, and γ_{Cl^-} is based on the Bates and Robinson (1980) standard values at a molality of 0.01 m. Therefore, three of the terms in Eq. (11) are estimable allowing the calculation of pH via

$$(a_{\text{H}^+}) = (a_{\text{HCl}})^2 / [(\gamma_{\text{Cl}^-})(m_{\text{Cl}^-})]. \quad (12)$$

A convention that is sometimes used to define pH through the activity coefficient for Cl^- is called the MacInnes (1919) convention that dates back >90 years that states

$$\gamma_{\text{K}^+} = \gamma_{\text{Cl}^-} = \gamma_{\pm\text{KCl}} \quad (13)$$

because the ion size and mobility of K^+ and Cl^- are nearly equivalent in dilute solutions. In this case, the activity coefficients for K^+ and Cl^- are equal to the mean activity coefficient for KCl at all ionic strengths. This assumption leads to the equation:

$$\gamma_{\text{H}^+}(\text{MacInnes}) = [(\gamma_{\text{H}^+}(\text{alternative}))(\gamma_{\text{Cl}^-}(\text{alternative}))] / \gamma_{\pm\text{KCl}}. \quad (14)$$

The “alternative” is simply a way of estimating activity coefficients (e.g., Pitzer modeling). Eq. (14) leads to variation in the calculated pH because the γ_{H^+} values are different between the MacInnes and Pitzer approaches, which we will discuss later. The Pitzer equation for pure NaCl solutions also yields a value of the activity coefficient for Na^+ equal to the value for Cl^- ($\gamma_{\text{Na}^+} = \gamma_{\text{Cl}^-} = \gamma_{\pm\text{NaCl}}$). But this result only works for pure NaCl solutions, while Eq. (13) is a function of ionic strength that can contain many other ions than K^+ and Cl^- .

A convention used to define pH traceable to the SI system is the Bates–Guggenheim convention that is defined by the Debye–Hückel equation:

$$\log(\gamma_{\text{Cl}^-}) = \frac{-A I^{1/2}}{[1 + 1.5 I^{1/2}]} \quad (15)$$

where A is the Debye–Hückel constant and I is the ionic strength (Bates and Guggenheim, 1960; Buck et al., 2002). Definitions and conventions, as outlined above, can lead to substantially different pH values as we will further examine below.

3. Environmental ranges for pH

Below we will discuss several measurement and modeling approaches for estimating pH. A critical factor in interpreting how useful different approaches are will be environmental limits. For example, the IUPAC (Buck et al., 2002) ranges for estimating pH with primary standards are ionic strengths (I) $\leq 0.1 \text{ mol kg}^{-1}$, temperatures from 0 to 50 °C, and the pH range from 3 to 10 (Guiomar et al., 2005). While this approach may have defined the state-of-the-art for determining dilute solution pH, it would not work, as presently structured, for seawater where $I = 0.72 \text{ mol kg}^{-1}$ (at SP = 35), which is substantially above the IUPAC limit of $I \leq 0.1 \text{ mol kg}^{-1}$. On the other hand, pH limits for seawater are for salinities of 5 ($I = 0.10 \text{ mol kg}^{-1}$) to 45 ($I = 0.93 \text{ mol kg}^{-1}$), temperatures of 0 to 50 °C, and pH ranges of 7.4 to 9.6 (Millero, 1986; UNESCO, 1987; Millero and Roy, 1997; Millero and Pierrot, 1998; Caldeira and Wickett, 2003). Such ranges

cover most seawater on Earth. Another factor not mentioned above is pressure, which is especially important for deep seawater applications. The effect of pressure on pH in seawater is estimated using experimentally measured and molal volume estimates of how pressure affects the dissociation of carbonic acid, boric acid, water, H_2S , HF, HSO_4 , etc. (Millero, 2001). Is there any approach that can optimize the accuracy of pH determinations across broad ranges of environmental factors? Is there even any method that can accurately determine pH at all? We will address these questions next.

4. Measurement approaches

There are primarily two cells that are used for measuring pH in aqueous solutions by potentiometric methods. The Harned cell is a gas hydrogen cell that does not have transference (of ions), and is the only cell for state-of-the-art assignment of primary pH standards using IUPAC standards (Buck et al., 2002). This is the basis of the primary method, only of concern to metrological institutes and physical-chemistry research groups (Mariassy et al., 2009). Their use only becomes relevant when associated with proper control of the sources of uncertainty, which do not pertain to most practical applications (Lito et al., 2006; Guiomar et al., 2007). Nevertheless they constitute references to which a traceability chain (establishment of a calibration hierarchy) should be ensured (P. de Bièvre, “Metrological traceability of measurement results in chemistry” <http://www.iupac.org/projects/2001/2001-010-3-500.html>). Combination glass electrodes, on the other hand, are the preferred cell for practical pH measurements (UNESCO, 1987; Nordstrom et al., 2000; Buck et al., 2002; ISO, 2007). A shortfall of these cells is that they have liquid junction potentials that affect pH measurements. There are experimental ways of minimizing liquid junction potentials (UNESCO, 1987; Covington and Whitfield, 1988; Millero and Roy, 1997; Millero, 1986, 2001; Buck et al., 2002; ISO, 2007); but the latter problem is a major source of uncertainty in quantifying the pH of aqueous solutions (Leito et al., 2002).

One way to minimize pH uncertainties is with pH buffers, used to calibrate pH electrodes that are similar in ionic strength to the sample. IUPAC has classified pH buffers as primary that cover the pH range of 3 to 10, and secondary buffers that cover the pH range of 1.7 to 13.4 (see Tables 1 and 2 in Buck et al., 2002). Primary buffers have values based on Harned cells that are accepted without reference to other standards of the same quality, while secondary buffers are assigned values by comparison to primary buffers (Buck et al., 2002). But as pointed out above and below, the IUPAC standards only have full meaning for I values $\leq 0.1 \text{ m}$.

Seawater specialists, on the other hand, prefer using Tris [tris (hydroxymethyl)aminomethane] buffers. Tris buffers have pH values around 8.2 that are close to seawater pH, plus one can add seawater with associated salts to these buffers. Actually, one can add seawater to any buffer with the objective of having calibrants and samples with matching ionic strengths, thereby minimizing differences in activity coefficients. Calibration curves in terms of activity or in terms of concentration would be parallel, which is useful in terms of analytical response. This is similar to what is done with TISAB (total ionic strength adjustment buffer) for fluoride analysis. The concern about adding seawater to buffers is mainly the chemical interactions and changes in equilibrium, hence in species and corresponding concentrations and activities it may promote. The choice of recommended buffers (bracketing procedure) has to take this into account. It is highly recommended that pH in seawater be calibrated with Tris buffers in solutions of known composition similar to seawater (Ramette et al., 1977; Millero, 1986; UNESCO, 1987; Covington and Whitfield, 1988; Dickson, 1993b; Millero and Roy, 1997; Millero, 2001; Millero et al., 2009a, 2009b). Fortunately, Tris buffers can be traced back to primary pH buffers by comparison measurements (Buck et al., 2002).

The bulk of water samples relies on measurement of pH based on calibration with buffered pH solutions. Because (a_{H^+}) cannot be measured unambiguously, assumptions are necessary. IUPAC (International Union of Pure and Applied Chemistry) recommends Eq. (2) as the definition for pH in dilute solutions (Buck et al., 2002). Their primary pH method relies on measurements in a Harned cell that leads to the equation:

$$E = E^0 - [(RT/F)\ln 10] \log[(m_{H^+} \gamma_{H^+} / m^0)(m_{Cl^-} \gamma_{Cl^-} / m^0)] \quad (16)$$

where E is the potential of cell, E^0 is the standard potential of cell, R is the molar gas constant, T is absolute temperature, F is the Faraday constant, and m^0 is the standard molality (1 mol/kg). This cell can unambiguously measure HCl activity. The molal Cl^- concentration is experimentally measured, and γ_{Cl^-} in dilute solutions is based on the Bates and Robinson standard values at 0.01 m (Eq. (11)). Substituting m_{Cl^-} and γ_{Cl^-} into Eq. (16) or Eq. (12) allows an estimate of $a_{H^+} = m_{H^+} \gamma_{H^+}$, the only unknown in these equations. But the IUPAC pH standard is only valid to $I \leq 0.1$ m because of the limits of Eq. (12).

Potentially this approach could be extended to higher concentrations (e.g., seawater at $I = 0.72$ m) by using the Pitzer equations for defining activity coefficients at higher concentrations:

$$\ln(\gamma_X) = z_X^2 F + \sum m_c (2B_{cX} + ZC_{cX}) + \sum m_a (2\Phi_{Xa} + \sum m_c \Psi_{cXa}) + \sum \sum m_c m_{c'} \Psi_{cc'X} + |z_X| \sum \sum m_c m_a C_{ca} + 2 \sum m_n \lambda_{nX} \quad (17)$$

$$+ \sum \sum m_n m_{c'} \zeta_{ncX}$$

where B , C , Φ , Ψ , λ and ζ are Pitzer-equation interaction parameters (Pitzer, 1991, 1995) among cations (c), anions (a), and neutral species (n), m_i is the molal concentration, and F and Z are equation functions. F in Eq. (17) is a function of f^γ :

$$f^\gamma = -A_\phi \left[\frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right], \quad (18)$$

which is similar to Eq. (15). But, Eq. (17) (Pitzer model) is a better model for estimating activity coefficients over a much broader range of ionic strengths (up to ≈ 20 m, Marion and Kargel, 2008). This approach could easily extend the validity of the IUPAC model to concentrations > 0.1 m based on Pitzer-based models such as the Miami models (Millero and Roy, 1997; Millero and Pierrot, 1998) and the FREZCHEM model (Marion and Kargel, 2008) that were used to show the differences in determining the activity coefficient of HCl to higher concentrations (Fig. 1). The standard error (statistical term, Steel et al., 1997) in HCl activity coefficients between the Pitzer estimate (Eq. (17)) and the Robinson and Stokes (1970) experimental measurement over the HCl range from 0.001 to 0.1 in Fig. 1 is ± 0.004 , which is an improvement over the Debye–Hückel (Eq. (15)) standard error of ± 0.008 . Furthermore, the Pitzer standard error over the HCl range from 0.001 to 8.0 m is only ± 0.0175 , which means one could extend the IUPAC range from 0.1 to 8.0 m HCl with a standard error of ≈ 0.02 , which would be very useful for many environments on Earth such as seawater and extreme acidities.

On the other hand, many seawater chemists prefer using Eq. (4) (pH_{SWS}) as the definition of pH (Dickson, 1984; Millero, 1986; Dickson and Millero, 1987; Millero, 2001) or pH based on the “free” hydrogen ion (Eq. (1), pH_F) (Millero et al., 2009a; Millero, 2010). Furthermore, Eq. (4), based on concentration, is preferred rather than Eq. (9), based on activity, because the f_{H^+} activity coefficient in Eq. (9) is a function of solution phase properties and junction potentials in pH electrode systems that are difficult to quantify or reproduce (Dickson and Millero, 1987; Millero, 2001). These very different definitions of pH require that care be taken to assure that equilibrium constants, activity coefficients, and buffer solutions are consistent with pH definitions. For example, many seawater equilibrium constants are

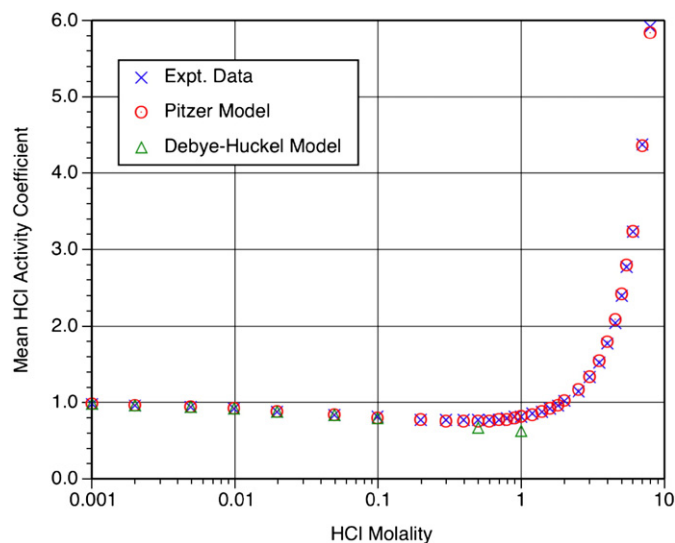


Fig. 1. The mean HCl activity coefficient at 25 °C for the concentration range from 0.001 to 8.0 m, calculated with Pitzer (Eq. (17)) and Debye–Hückel (Eq. (15)) equations, and compared to experimental data (Robinson and Stokes, 1970).

based on stoichiometric concentrations that are functions of salinity (S_p) and temperature (T), which is different from models like FREZCHEM and Miami that are based on activity products that are independent of S_p . Ideally pH electrodes should be calibrated with buffer solutions that have similar ionic media to the test solutions (e.g., seawater) (Covington and Whitfield, 1988; Dickson, 1993a; Millero and Roy, 1997; Millero, 2001). Fortunately, model calculations based on equilibrium constants are in good agreement with measured values (Millero and Pierrot, 1998). Also in oceanographic studies the effects of temperature and pressure on pH can be estimated by measuring the total alkalinity and dissolved inorganic carbon that are independent of temperature and pressure (Millero, 2007).

Two major factors that can lead to serious miscalculation of pH measurements in natural environments are due to temperature and the partial pressure of CO_2 (pCO_2) that strongly affect the pH of alkaline systems (e.g., seawater) through reactions such as:



For example, the pH^m values of a seawater sample ($S_A = 35.165$ g/(kg soln)) at 25 °C with $pCO_2 = 3.80E-4$ atm or $pCO_2 = 1.00E-3$ atm are 8.293 and 7.934, respectively. When the temperature is 0 °C, the pH values are 8.223 and 7.827, respectively. Ideally, pH should be measured when the sample is taken. If this is not possible, then collected samples need to minimize exchange of CO_2 with the atmosphere and minimize microbial processes that can affect CO_2 concentrations. See Dickson et al. (2007) and ISO (2007) for instructions on how sampling/measurement errors can be minimized.

A number of workers have also developed in situ systems that measure pH using spectroscopic indicators (Byrne et al., 1999). Spectrophotometric techniques are a very different measurement approach that is used to estimate seawater pH using colorimetric indicators such as: bromocresol green, cresol red, m-cresol purple, and phenol red (Roberto-Baldo et al., 1985; Byrne and Breland, 1989; King and Kester, 1989; Breland and Byrne, 1993; Clayton and Byrne, 1993; Dickson, 1993a; Yao and Byrne, 2001; Ohline et al., 2007; Millero, 2007; Millero et al., 2009a; Schuster et al., 2009). For example, in the paper by Roberto-Baldo et al. (1985) that used phenol red, they developed pH bounds for $33 \leq S_p \leq 37$ and $273 K \leq T \leq 303 K$ at 1 atm total pressure with an average residual pH uncertainty of ± 0.004 . In a recent paper by Millero et al. (2009a) that used m-cresol purple, they developed a

model for NaCl solutions from 5 to 45 °C and ionic strengths from 0.03 to 5.5 m with an average pH uncertainty of ± 0.003 .

5. Modeling approaches

Modeling is of fundamental importance for experimental pH measurements. The Debye–Hückel equation (Eq. (15)) is used to calculate γ_{Cl^-} at low concentrations ($I \leq 0.1$ m) that can then be used to estimate pH through Eq. (12). This equation is how pH is defined for buffer solutions. Buffer solutions, in turn, are used to calibrate pH electrodes for field applications. In principle, using the Pitzer approach one could extend the concentration range of the IUPAC standard to much higher values (Fig. 1) as previously discussed.

There are two terms used in modeling that can be confusing: model and code. A chemical model is defined as a “theoretical construct that permits the calculation of physiochemical properties and processes of substances” (Nordstrom and Munoz, 1994). Codes refer specifically to models that are written in technical codes such as Fortran and C++. In this section, we will discuss specifically “FREZCHEM” and “Miami” versions that are coded models, with theoretical concepts and Fortran codes. On the other hand, the Pitzer model is a theoretical concept without a technical code. But our discussion below/above refers to FREZCHEM and Miami as simply “models,” rather than “coded models.”

A very different approach to pH estimation is based completely on modeling (Herczeg et al., 1985; Millero and Roy, 1997; Lewis and Wallace, 1998; Millero and Pierrot, 1998; Dickson et al., 2007; Marion and Kargel, 2008; van Heuven et al., 2009). In natural waters with $\text{pH} > 4.5$, there are four properties that can be measured: (1) pH, (2) the partial pressure of CO_2 ($p\text{CO}_2$) or the equivalent fugacity of CO_2 ($f\text{CO}_2$), (3) total alkalinity (T_A), and (4) dissolved inorganic carbon (DIC). Given any two of these measured properties, it is possible to calculate the remaining two properties. Using a model to calculate pH, then you can specify $p\text{CO}_2$ - T_A , $p\text{CO}_2$ -DIC, or T_A -DIC. The Miami model can be used with inputs of any two of these carbon properties, and the results are internally consistent to $\pm 0.003 \mu\text{mol kg}^{-1}$ in T_A and DIC, ± 0.003 in pH, and $\pm 5 \mu\text{atm}$ in $p\text{CO}_2$. Herczeg et al. (1985) recommend $p\text{CO}_2$ -DIC as a good approach for assessing pH in natural waters. The FREZCHEM model (Marion and Kargel, 2008), on the other hand, relies on $p\text{CO}_2$ - T_A as the method for calculating pH. Here is how that approach works for seawater. The following charge balance exists for cations and anions in seawater:

$$\begin{aligned} [H^+] + [Na^+] + [K^+] + [MgOH^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + 2[Sr^{2+}] \\ = [HCO_3^-] + 2[CO_3^{2-}] + [HSO_4^-] + 2[SO_4^{2-}] + [Cl^-] + [OH^-] + [Br^-] \\ + [B(OH)_4^-] + [F^-] \end{aligned} \quad (20)$$

where brackets refer to concentrations. This system can be rewritten as:

$$\Delta_i = \frac{K_H K_1 f_{\text{CO}_2} a_w}{(H^+)(\gamma_{\text{HCO}_3})} + \frac{2K_H K_1 K_2 f_{\text{CO}_2} a_w}{(H^+)^2 (\gamma_{\text{CO}_3^{2-}})} + \frac{K_w a_w}{(\gamma_{\text{OH}^-})(H^+)} \quad (21)$$

where:

$$\begin{aligned} \Delta_i = [H^+] + [Na^+] + [K^+] + [MgOH^+] + 2[Mg^{2+}] + 2[Ca^{2+}] \\ + 2[Sr^{2+}] - [HSO_4^-] - 2[SO_4^{2-}] - [Cl^-] - [Br^-] - [B(OH)_4^-] - [F^-] \end{aligned} \quad (22)$$

K_H is the Henry's law constant for CO_2 , K_1 and K_2 are the first and second dissociation constants for carbonic acid, K_w is the dissociation constant for water, (H^+) is the activity of the hydrogen ion, $f\text{CO}_2$ is the fugacity of CO_2 , a_w is the activity of water, γ values are activity coefficients, and Δ_i is the difference in non-carbonate species that are either measured directly (e.g., Na^+ or Cl^-) or estimated mathematically with algorithms for minor species (e.g., MgOH^+ , HSO_4^- , F^- , and B(OH)_4^-). The three terms on the right side of Eq. (21) represent $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, and $[\text{OH}^-]$, respectively. Given the $f\text{CO}_2$, γ values and a_w from the Pitzer equations, equilibrium constants, and Δ_i , Eq. (21) can be exactly solved by successive approximations for (H^+) (the only unknown), which leads to $\text{pH} = -\log(a_{H^+})$. This specific application is limited to pH values > 4.5 . An alternative approach for estimating pH exists for strong acid cases based on measured aqueous acid molality [e.g., HCl (Fig. 1), HNO_3 , H_2SO_4] or partial pressures of acids (e.g., pHCl , pHNO_3 , pH_2SO_4) (see Marion and Kargel, 2008). In what follows with respect to modeling, we will largely focus on the Miami and FREZCHEM models because these models are focused on seawater, especially the Miami model.

The Pitzer-based FREZCHEM model contains all principal soluble species of standard seawater (see Table 4 in Millero et al., 2008). In Fig. 2, we estimated the pH values (molality scale) of seawater as a function of salinity according to Eqs. (1), (2) and (4). At $S_A = 35.165$ g/(kg soln) ($S_p = 35.00$), $t = 25$ °C, and $f\text{CO}_2 = 3.33\text{E-}4$ atm (this atmospheric concentration relates to 1976, which was used to partition the seawater composition in Table 4 of Millero et al., 2008), the calculated pH based on (a_{H^+}) (Eq. (2)) was 8.332 that dropped to 8.195 when divided by γ_{H^+} (0.729) (Eq. (1)). Adding HSO_4^- and HF to Eq. (1) dropped the pH further to 8.078 (Eq. (4)). Also included in Fig. 2 are estimates of pH using Eq. (2) with the MacInnes convention. At $S_A = 5.024$ g/kg, the calculated pH values for pH^m and $\text{pH}_{\text{MacInnes}}^m$ are 7.697 and 7.682, respectively. The maximum differences occur at $S_A = 40.189$ g/kg, where pH^m and $\text{pH}_{\text{MacInnes}}^m$ are 8.365 and 8.310, respectively. These differences are simply due to how γ_{H^+} is defined in Eq. (4) ($\gamma_{H^+}(\text{MacInnes})$ vs. $\gamma_{H^+}(\text{alternative})$).

Also included in Fig. 2 are similar estimates for Eqs. (2) and (4) generated by the Pitzer-based Miami model (Millero and Pierrot, 1998). The two model estimates of pH (Eq. (2)) differ by 0.010 at $S_A = 5.024$ g/(kg soln) and by 0.001 at $S_A = 40.19$ g/(kg soln); similarly, the two estimates of pH_{SWS} (Eq. (4)) differ by 0.005 at $S_A = 5.024$ and by 0.001 at $S_A = 40.19$ g/(kg soln). Overall, maximum differences occurred at low salinities and minimal differences occurred at high salinities.

Do these model comparisons prove that these models now make accurate pH calculations? Not exactly. Our initial attempt to make comparisons between these two models led to a maximum error of $\text{pH}_{\text{SWS}} = 0.046$ at $S_A = 40.19$ g/(kg soln). What brought the two models into better agreement was due to changes in several relatively

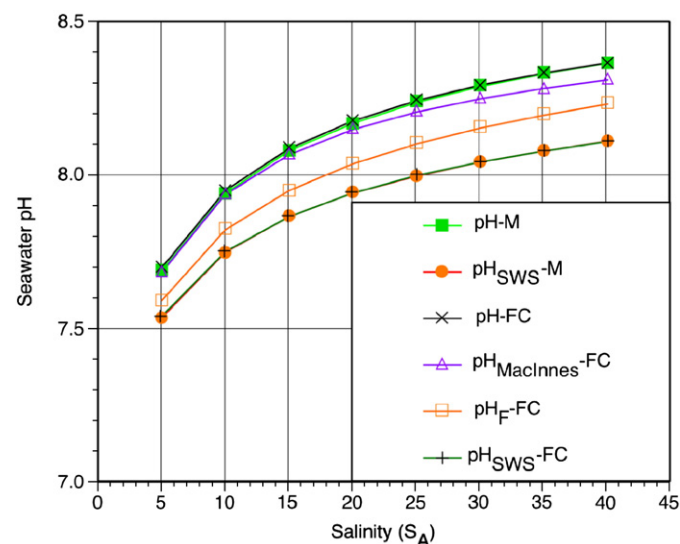


Fig. 2. Model-calculated pH values for seawater (molal concentrations, m) based on the FREZCHEM model (FC) compared to the Miami model (M). $T = 25$ °C, $f\text{CO}_2 = 3.33\text{E-}4$ atm.

minor pH components, especially with respect to the FREZCHEM model that is not, per se, a predominantly seawater model like the Miami model. For example, the FREZCHEM model Pitzer equations for H–Cl interactions were developed for HCl concentrations ranging from 0 to 12 m over the temperature range from -93 to 25 °C (Marion, 2002) that provide good fits to experimental data across a broad range of concentrations (Fig. 1). However, the comparable equations in the Miami model provide better fits to experimental data at lower concentrations ($\text{HCl} \leq 1$ m). Replacing the FREZCHEM model HCl interaction parameters with the Miami model parameters brought pH calculations into better agreement. Another change dealt with how to cope with the minor fluoride ion (F^-) that affects pH_{SWS} (Eq. (4)). In an earlier FREZCHEM model, F^- was simply added to the Cl^- concentration. In the Miami model, F^- was a function of Pitzer parameterizations for NaF and KF interactions, and CaF and MgF complexes. Adding the latter fluoride equations into FREZCHEM improved the model pH comparisons. And finally, the model Pitzer parameterization for CaCO_3 ion-pairs in FREZCHEM was changed, which brought the two models into excellent agreement (Fig. 2). These changes were not speculative, but based on sound reasoning. While these two independent models were in excellent agreement with respect to equilibrium constants (Fig. 3), it was minor component that changes largely affecting activity coefficients that led to a better comparative fit for calculated pH (Fig. 2). Accuracy of models depends fundamentally on constituent compositions and equilibrium constants (Eqs. (20) and (21), Fig. 3). To demonstrate the accuracy of such models will ultimately require comparisons to definitive experimental data from major environments such as seawater.

6. Traceability and target uncertainties

There are many studies that trace how pH was measured, generally with estimates of the accuracy (agrees with the standard value) or precision (agrees with their mean) of these measurements (e.g., Pearson et al., 1978; Covington and Whitfield, 1988; Dickson, 1993a; Lewis and Wallace, 1998; Nordstrom et al., 2000; Buck et al., 2002; Naumann et al., 2002; Spitzer and Werner, 2002; Spitzer, 2005; Meinrath et al., 2006; ISO, 2007; Millero, 2007; Dickson et al., 2007; Millero et al., 2009a; Schuster et al., 2009; van Heuven et al., 2009). The IUPAC standard pH (Buck et al., 2002), which is probably the most accurate pH system, gives target uncertainty values obtained for primary buffer standards, secondary buffer standards, and glass

electrode calibrations and routine measurements. The pH recommended target uncertainties for primary standards ranged from 0.0015 to 0.004 (see their Table 4 at 25 °C). Similar target uncertainties for secondary standards ranged from 0.004 to 0.02. Glass electrode calibrations with 1-point, 2-point, or 5-point buffers have target uncertainties of 0.3, 0.02–0.03, and 0.01–0.03 pH values, respectively. But these estimates ignore the uncertainty associated with the Bates–Guggenheim convention (Eq. (15)), which has an uncertainty term of 0.012 in estimating pH (Buck et al., 2002). Since all primary standards, secondary standards, and glass electrode measurements are related, directly or indirectly (metrological pyramid), to the Bates–Guggenheim convention, this means that pH values cannot be accurately known better than ± 0.01 pH units, albeit, the precision values can be much lower. And this assumption includes spectrophotoscopic techniques that claim a pH_{SWS} accuracy of ± 0.003 (Millero, 2001) as these values are also a function of the Bates–Guggenheim convention because they rely on the same chloride ion containing buffer solutions.

To prevent confusion within the pH literature, it would be best to define accuracy based on the Bates–Guggenheim convention as “total” accuracy since this is a traceable approach dealing with SI standards (Buck et al., 2002). Alternatively, the Bates–Guggenheim convention can be ignored in estimating accuracy, which leads to “conventional” accuracy, which is how pH accuracy is listed in most cases (e.g., Dickson, 1993a; Millero, 2001, 2007; Buck et al., 2002; Schuster et al., 2009). For more details, see the Buck et al. (2002) discussion of this accuracy uncertainty issue.

The three model estimates of pH at 25 °C with $S_A = 35.165$ g/(kg soln) for pH^m , pH^f , and pH_{SWS}^m were 8.332, 8.195, and 8.078 (Fig. 2); these pH values would be significantly different given an optimal “total” accuracy of ± 0.01 pH units. But this would not be the case in comparing pH values that are only different with respect to concentrations units (mol/(kg H_2O), mol/(kg soln), and mol/l), where we showed previously were only different by ± 0.016 pH units. Accuracy and precision of practical measurements, on the other hand, can easily be different by several tenths of a pH unit due largely to temperature, pCO_2 , and microbial activity between sampling and analysis as discussed previously under “Measurement Approaches”. Such large practical sampling/measurement errors may, or may not, be important depending on the study. See Dickson et al. (2007) and ISO (2007) for instructions on how sampling/measurement errors can be minimized. But the main focus of this paper was on what are the state-of-the-art accuracies of pH, especially in seawater, which appear to be ± 0.01 pH units for “total” accuracy, and ± 0.004 pH units for “conventional” accuracy.

7. Future directions and conclusions

It seems unlikely that one could get all aqueous chemists to agree on a preferred definition for pH (Eqs. (1)–(4)). Values of pH should be fit for the purpose, but no better than required. Rather, the way out is to select the quantity that is significant to the particular system and study of interest. One has to unambiguously define the measurand and from there onwards progress to the assignment of reference values and produce recommendations, according to the principles of the Measurement Science. On the other hand, there are arguments for Eq. (1) $[\text{H}^+]$ and Eq. (2) (a_{H^+}) because on a molecular level it is the free concentration or activity of the proton that affects equilibrium and kinetic processes in natural waters (Millero et al., 2009a; Millero, 2010).

Also, hopefully we can agree on a common nomenclature, so that whenever pH values are published, their definition is unambiguous (Eqs. (1)–(4), Fig. 2). For example, the pH_{SWS}^m data in Fig. 2 are based on molal concentrations (mol/(kg H_2O)). On the other hand, a recent CO_2 model defined pH_{SWS}^m data in mol/(kg soln) (Lewis and Wallace, 1998). These two definitions of pH_{SWS} (Eq. (7)) differ by about 0.016 pH units at $S_A = 35.165$ g/(kg soln) (Lewis and Wallace, 1998), which

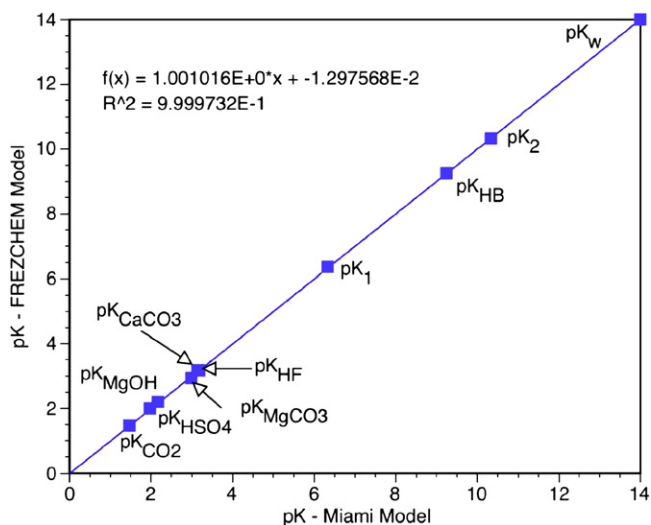


Fig. 3. A comparison of aqueous-phase equilibrium constants at 25 °C in the FREZCHEM and Miami models affecting H^+ ion activities in alkaline seawater.

is why we need accepted nomenclature that clearly and unambiguously defines pH, especially when we want to optimize accuracy.

There are a number of thermodynamic models that define seawater properties as a function of S_A (or S_P), T , and P (e.g., Feistel, 2003, 2008; Feistel and Marion, 2007; IOC et al., 2010). It should be possible to reconcile differences in Pitzer seawater models that are a function of individual constituents (such as the Miami and FREZCHEM models used in Fig. 2), refine their accuracy, and redevelop these models to predict seawater pH as a function of S_A (or S_P), T , P , and pCO_2 . For example, in running the FREZCHEM model to calculate pH using different definitions in Eqs. (1), (2) and (4), the standard concentrations of major seawater components were inputted into the program and then divided (or multiplied) by constants to simulate alternative salinities (e.g., $S_A = 35.165/7 = 5.024$ g salt/(kg soln) and $Cl = 0.56576/7 = 0.08082$ m). While such a model would work well for seawater (the overwhelmingly dominant natural water on Earth), it would only work for other aqueous solutions where complete solution components were known, which is the case in some scientific studies. In that case, Pitzer approaches such as the Miami and FREZCHEM models could be directly used to estimate pH. As alluded to earlier by workers (Dickson, 1984; Herczeg et al., 1985; Buck et al., 2002) such thermodynamic models should, in principle, be more accurate than pH electrode measurements. But this concept needs to be clearly demonstrated; Fig. 2 hints at this possibility. Given the importance of pH on biological viability and chemical processes, such models would vastly improve our understanding of aqueous solutions on Earth, now and in the future as global climate and associated pCO_2 values change.

The main conclusions of this study are:

- 1) pH definitions and conventions are highly variable, which leads to highly variable estimates of pH. For example, for seawater at $S_A = 35.165$ g/(kg soln), $t = 25$ °C, $P = 1.0$ atm, and $fCO_2 = 3.33E-4$ atm, calculated pH values for the different definitions Eqs. (1)–(4) varied from 8.08 to 8.33 (Fig. 2).
- 2) An acceptable nomenclature is needed to keep pH variability less ambiguous, due to alternative definitions and conventions. A nomenclature example is given in this paper. It is the (still unsolved) task of international bodies such as IUPAC or IOC to develop and promote such widely recognized conventions.
- 3) pH can be accurately estimated based on measurement (potentiometric, spectrophotometric) and modeling approaches. Accuracy via different definitions and conventions clearly requires consistency with respect to experimental measurements, equilibrium constants, activity coefficients, and buffer solutions that are used for specific approaches.
- 4) “Total” pH accuracy that includes the Bates–Guggenheim convention is ± 0.01 pH units. Removing the Bates–Guggenheim convention from the accuracy calculation can lead to “conventional” accuracies of ± 0.004 pH units (Buck et al., 2002).
- 5) Extensions to high solution concentrations are capable using the Pitzer modeling approach. Modeling can, in principle, lead to pH estimates that are more accurate than measurements (Fig. 2; Dickson, 1984; Herczeg et al., 1985; Buck et al., 2002). But this principle still needs to be proven.
- 6) It is recommended that ocean scientists use the free concentration or activity of the proton to examine the effect of pH on processes in the oceans.

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