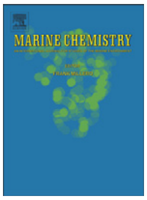
Marine Chemistry 162 (2014) 89–95

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem



Measurement of pH_T values of Tris buffers in artificial seawater at varying mole ratios of Tris:Tris·HCl

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A R T I C L E I N F O

Article history:
Received 14 December 2013
Received in revised form 5 March 2014
Accepted 7 March 2014
Available online 24 March 2014

Keywords:
Buffers
Calibration
pH
Standards
Traceability
Uncertainty

A B S T R A C T

Measurements of total pH, pH_T, in Harned cells are reported for 2-amino-2-hydroxymethyl-1,3-propanediol (Tris) buffers in artificial seawater (ASW) of salinity 35 at three molality ratios of Tris to Tris·HCl: 0.03:0.05, 0.04:0.04, and 0.05:0.03. The ASW formulation was derived from the 2008 International Association for the Physical Sciences of the Oceans (IAPSO) composition of seawater (Millero et al., 2008). The pH_T value of each buffer was measured at 288.15 K, 298.15 K, and 308.15 K (15 °C, 25 °C, and 35 °C). Measurement uncertainties compliant with the ISO GUM (JCGM, 2008) are provided for each buffer. These new formulations extend the available data for Tris buffers in ASW to pH_T values that bracket the pH_T range of natural surface seawaters at 298.15 K. The data provide a framework for future multiple-point calibrations of spectrophotometric and potentiometric pH_T measurements traceable to these new buffers.

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1. Introduction

The traceability of pH measurements of seawater to accepted standards is of critical importance in studies of climate change. The de facto standard for the pH of seawater at the present time is an equimolal buffer that consists of 2-amino-2-hydroxymethyl-1,3-propanediol ('Tris') and Tris hydrochloride, Tris·HCl, each at a molality of 0.04 mol/kg, in artificial seawater (ASW) (DelValls and Dickson, 1998; Nemzer and Dickson, 2005). The pH of this standard is obtained from measurements in $H_2|H^+$ electrochemical cells without transference (Harned cells). The result is expressed as total pH, pH_T (Dickson, 1993a; Millero et al., 1993), the sum of the contributions from free H^+ and from HSO_4^-. Such Harned cell measurements are at the highest metrological level. They form the foundation for all other seawater pH_T measurements and are thus of fundamental importance to the field.

The current state of seawater pH metrology is currently deficient in that pH_T values derived from Harned cell measurements have not been reported in the literature for Tris·H^+:Tris buffers with mole ratios other than 1:1. Furthermore, rigorous uncertainty estimates, essential for metrological traceability (JCGM, 2012), are lacking. Although the 0.04 mol/kg equimolal pH buffer is available as a certified reference material (CRM) (Dickson, 2011), that CRM and previous research (DelValls and Dickson, 1998; Ramette et al., 1977) only provide pH_T values for the equimolal formulation, with no uncertainty compliant with the International Standards Organization *Guide to the Expression of Uncertainty in Measurement* (ISO GUM) (JCGM, 2008).

Owing to this lack of multiple buffers with values assigned through Harned cell measurements, multi-point calibrations of secondary measuring systems for seawater pH_T at a high metrological level have not been possible. The spectrophotometric determination of pH_T using m-cresol purple (mCP) (Clayton and Byrne, 1993) is currently the most precise (standard deviation: 0.0004) secondary method for pH_T values in seawater. The measurement is traceable to the absorbance measurements and to the pK_a ($= -\lg K_a$, acid dissociation constant) of the mCP, which is determined in a parallel, single-point calibration using the 0.04 mol/kg Tris equimolal standard buffer. The method was originally validated (Byrne, 1987) over a range of ±0.04 pH. This range is smaller than the pH_T range of open-ocean seawater. Measurements over the entire range of pH_T applicable to seawater, using multiple standards value-assigned in Harned cells, would provide a more rigorous verification of the spectrophotometric technique and could independently confirm the reduced bias observed using mCP purified by high-pressure liquid (Liu et al., 2011) (HPLC) or flash (Patsavas et al., 2013) chromatography. Single-point calibrations of secondary potentiometric pH measurements also suffer from analogous shortcomings (Buck et al., 2002): multi-point calibrations offer similar advantages here also.

The present work is the first step in this process: characterization of the Tris buffers themselves. This paper reports measurements of the pH_T

Abbreviations: ASW, artificial seawater; CA, concentrated acid; CB, concentrated buffer; CRM, certified reference material; CASW, concentrated ASW; ERB, buffer prepared to the EMRP recipe; EMRP, European Metrology Research Programme; ISO GUM, International Standards Organization *Guide to the Expression of Uncertainty in Measurement*; SRM, Standard Reference Material®; Tris, 2 amino-2-hydroxymethyl 1,3-propanediol.

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http://dx.doi.org/10.1016/j.marchem.2014.03.003
0304-4203/Published by Elsevier B.V.

values of three Tris buffers in ASW that cover the range of pH_T currently applicable to open-ocean surface seawater samples. Each buffer was measured in a parallel series of measurements in Harned cells. Uncertainty calculations compliant with the ISO GUM are provided for each temperature. The paper also presents a general protocol for preparing an arbitrary number of Tris buffer solutions in an identical ASW matrix.

Fig. 1 summarizes in schematic form the contributions of the present article.

2. Experimental

2.1. Composition of reference ASW

In 2008, the International Association for the Physical Sciences of the Oceans (IAPSO) published an internationally-agreed reference composition for seawater (Millero et al., 2008). The molalities cited in Table 4 of that work were used as the basis for the ASW formulation used here.

The following substitutions were made to yield the reference ASW composition used for the Tris buffers. First, Cl^- replaced the buffering anions (HCO_3^-, $B(OH)_4^-$, CO_3^{2-}, F^-, and OH^-) and the Br^- in the IAPSO reference composition, according to Eq. (1):

$$b_{Cl^-} = b_{Cl^-,IAPSO} + \sum_i |z_i| b_{i,IAPSO} + b_{Br^-,IAPSO}. \tag{1}$$

In Eq. (1), b_{Cl-} is the molality of chloride in the ASW, i is the index for the above-stated buffering anions, z_i and b_i are the ionic charge and molality of the ith buffering ion, and IAPSO denotes the IAPSO reference composition. The symbol b for molality (Mills et al., 1993) avoids conflict with m, mass, used in the supplementary material.

Second, Ca^{2+} replaced Sr^{2+} in the IAPSO reference composition:

$$b_{Ca^{2+}} = b_{Ca^{2+},IAPSO} + b_{Sr^{2+},IAPSO}. \tag{2}$$

The molalities of the added salts in the ASW were calculated from Eq. (3a) through Eq. (3e), where the subscript refers to the given salt or ion. The added subscript ASW in Eq. (3a) indicates that the molality of NaCl is that of the reference ASW.

$$b_{NaCl,ASW} = b_{Cl^-}, \tag{3a}$$

$$b_{MgCl_2} = b_{Mg^{2+},IAPSO}, \tag{3b}$$

$$b_{CaCl_2} = b_{Ca^{2+}}, \tag{3c}$$

$$b_{KCl} = b_{K^+,IAPSO}, \tag{3d}$$

$$b_{Na_2SO_4} = b_{SO_4{}^{2-},IAPSO}. \tag{3e}$$

The formal ionic strength (molality basis) of the ASW, I_{ASW}, is calculated from Eq. (4):

$$I_{ASW} = b_{NaCl,ASW} + b_{KCl} + 3\left(b_{MgCl_2} + b_{CaCl_2} + b_{Na_2SO_4}\right). \tag{4}$$

Eq. (5) gives b_{Cl^-} in terms of the molalities of the component salts:

$$b_{Cl^-} = b_{NaCl,ASW} + b_{KCl} + 2\left(b_{MgCl_2} + b_{CaCl_2}\right). \tag{5}$$

This IAPSO-derived ASW composition served as the basis for the three Tris buffers.

Two separate equimolal Tris buffers, each based on a slightly different ASW formulation, served as controls in the present work. The first control was the CRM, based on the formulation of (DelValls and Dickson, 1998). The second control, based on older work (Millero, 1986; Millero et al., 1993), was prepared at NIST using separately-sourced and independently-assayed salts provided by the European Metrology Research Programme (EMRP) Project ENV05 OCEAN (Spitzer, 2012), which adopted this recipe for their work. This second control is denoted here as the "EMRP recipe buffer" (ERB).

Table 1 lists the molalities of the five component salts; I_{ASW}; b_{Cl^-}; the mass fraction of water, w_{H2O}; and $-\lg w_{H2O}$ for these three ASW formulations.

The ionic strength of the ASW based on the IAPSO reference composition agrees to within 1 part in 7000 with that of the formulation used in the CRM but is about 5 parts in 7000 lower than that in the ERB. The main difference in the ERB formulation is in the molality of $MgCl_2$, which originated (Millero; personal communication; July 11, 2011) from different titration data for $b_{Mg^{2+}}$.

2.2. Target compositions and preparation of Tris buffers and HCl solutions in ASW

To produce a set of J Tris + Tris·HCl buffers in ASW, Tris and HCl are added to the ASW such that the desired molality ratio of Tris to Tris·HCl is attained. To maintain a constant ionic strength and molality of chloride in each buffer, $b_{NaCl,ASW}$ is reduced (Dickson, 1993b) by $b_{HCl,j}$, the added molality of HCl in the jth buffer:

$$b_{NaCl,j} = b_{NaCl,ASW} - b_{HCl,j}. \tag{6}$$

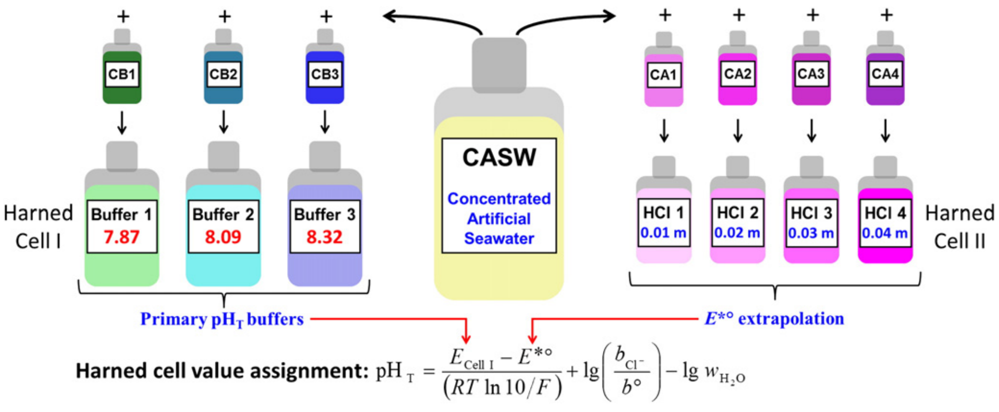

Fig. 1. Summary of synthesis protocol[a] and measurement procedure[b]. [a]CA = concentrated acid solution; CB = concentrated buffer (see text). Symbol m in the HCl solutions denotes molality of HCl in $mol \cdot kg^{-1}$. Cited pH_T values of buffers and molalities of HCl solutions are nominal. [b]Equation yields the final pH_T value assignment from the Harned cell measurement of each buffer. See text, Eqs. (9) and (10).