Spectrophotometric determination of bicarbonate dissociation constants (K2) for freshwater, estuarine, and marine waters over a wide range of temperatures

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Project
» Spectrophotometric Determinations of Carbonic Acid Dissociation Constants for Estuarine Conditions (Spectrophotometric K1K2)

Contributors	Affiliation	Role
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Abstract
This dataset presents the first spectrophotometric data of K2 at estuarine conditions ($0 \leq Sp \leq 20$; where Sp is practical salinity) and over a broad range of temperatures ($275.15 \leq T \leq 308.15$ K; where T is temperature in Kelvin). The spectrophotometric data from Schockman and Byrne (2021) and Schockman et al. (2024) were combined with the low-salinity data. This dataset was used to produce a set of pK2 (i.e., –log K2) values for the salinity range $0 \leq Sp \leq 41$ and temperature range $275.15 \leq T \leq 308.15$ K. The resulting set of pK2 values presented in the dataset was fitted as a function of Sp and T to obtain a new pK2 parameterization on the total pH scale (Martín-Mayor et al., in review).

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Coverage

Location: Lab experiment (using seawater batches collected from surface waters of the northeastern Gulf of Mexico off the West Florida Shelf)
Temporal Extent: 2022-04-03 - 2023-10-31

Methods & Sampling

The aqueous carbon dioxide (CO_2) system stoichiometric dissociation constants K_1 and K_2 express the relative concentrations of CO_2, HCO_3^- (bicarbonate), and CO_3^{2-} (carbonate) in terms of pH. These constants are critical in the study of seawater and the oceans because any mathematical expression that relates the four major CO_2 system parameters requires the use of K_1 and K_2.

The seawater CO_2 system can be described using four measurable parameters: total alkalinity (A_T), total dissolved inorganic carbon (C_T), pH (here expressed on the total hydrogen ion concentration scale, pH_T) and CO_2 fugacity (fCO_2).

This dataset presents the first spectrophotometric data of K_2 at estuarine conditions ($0 \leq S_p \leq 20$; where S_p is practical salinity) and over a broad range of temperatures ($275.15 \leq T \leq 308.15$ K; where T is temperature in Kelvin). The low-salinity data were combined with the spectrophotometric data from Schockman and Byrne (2021) and Schockman et al. (2024).

Seawater batches collected from surface waters of the northeastern Gulf of Mexico off the West Florida Shelf were diluted with Milli-Q water to produce salinities within the range of 0 to 20, representing conditions ranging from freshwater to brackish water, respectively. Each seawater batch was prepared immediately prior to use in the lab experiment.

Spectrophotometric pH_T measurements were done following Clayton & Byrne (1993) and Dickson et al. (2007). Samples were measured in two-window 10cm cylindrical optical glass spectrophotometric cells using an Agilent 8453 diode array spectrophotometer with the UV light lamp turned off. Absorbance was taken at 434, 578, and 730 nanometers (nm) before and after adding 10 microliters (µL) of purified meta-Cresol Purple (mCP) indicator. The pH_T was calculated using 578/434 nm absorbance ratio, with 730 nm for baseline correction, using the model of Müller & Rehder (2018).

First, the pH_T was adjusted with HCl or NaOH to match the expected pH_T^0 based on the sample's salinity (S_p) and temperature (T). Once pH_T was near pH_T^0, five replicate pH_T readings were taken and averaged to get $pH_{initial}$. Then, a known amount of NaHCO₃ (or KHCO₃) was added to the sample and shaken thoroughly. Subsequently, the cell was placed back in the spectrophotometer and five pH_T replicates were recorded and averaged as pH_{final}. Next, the sample's temperature in the spectrophotometric cell was recorded using a digital thermometer (Ertco-Eutechnics Model 4400). Iterative adjustments were made if $pH_{final} \neq pH_{initial}$. The next sample's $pH_{initial}$ was adjusted to better approximate pH_T^0.

After the daily samples were measured, seawater salinity for each individual sample was measured with a Guildline Portasal 8410A Laboratory Salinometer. S_{final} denotes the salinity of each individual sample (i.e., salinity after bicarbonate salt addition), and $S_{initial}$ is the salinity of diluted seawater batch. Note: NaHCO₃ additions increase salinity, especially when $S_p < 5$.

For experiments in which $t < 15$ ºC (where t is temperature in ºC), the setup was moved to an environmental room for additional temperature control (Harris Environmental Systems).

For a more detailed description of the methodology, please refer to Schockman and Byrne (2021) and Martin-Mayor et al. (2025, in review).

The resulting set of pK_2 values presented in this dataset was fitted as a function of S_P and T to obtain a new pK_2 parameterization for the salinity range $0 \leq S_p \leq 41$ and temperature range $275.15 \leq T \leq 308.15$ K (Martín-Mayor et al. 2025, in review).

Data Processing Description

The resulting set of pK_2 values presented in this dataset was fitted as a function of practical salinity (S_p) and temperature (T) to obtain a new pK_2 parameterization for the salinity range $0 \leq S_p \leq 41$ and temperature range $275.15 \leq T \leq 308.15$ K (Martín-Mayor et al. 2025, in review).

BCO-DMO Processing Description

- Imported data from source file "Martin-Mayor_Spec_pK2_S0-40_t2-35_FINAL.xlsx" sheet name "All data combined" into the BCO-DMO data system.
- Modified parameter (column) names to conform with BCO-DMO naming conventions.

Data Files

File
962304_v1_spectrophotometric_pk2.csv (Comma Separated Values (.csv), 4.85 KB) MD5:9ae4084bd0a21abc7fe575ba1f00b3c9 Spectrophotometric data for experimental pK2. Primary data file for dataset ID 962304, version 1.

Supplemental Files

File	
Table 1.1 from Martin-Mayor et al. 2025.pdf	(Portable Document Format (.pdf), 355.91 KB) MD5:c84eaa6a38d3f91aa838af7cc098e49b
Table 1.1: Measured Sp, t, R-ratio, calculated pHT values using Muller and Rehder (2018), pK1 from Waters et al. (2013, 2014), and exp-pK2 values (i.e., experimentally derived values from Martin-Mayor et al. (2025) Equation 14).	
Table 1.2 from compiled Schockman papers.pdf	(Portable Document Format (.pdf), 367.22 KB) MD5:70ec9729e3fc515a531510dffc3725ca
Table 1.2: Data from Schockman and Byrne (2021) and Schockman et al. (2024) with Φ = 0.9993. Shown are (a) the highest pHinitial for which the NaHCO3 addition increased the pH and its associated pHfinal, and (b) the lowest pHinitial for which the NaHCO3 addition lowered the pH and its associated pHfinal, measured SP, t, R-ratio, calculated pHT values using Muller and Rehder (2018), pK1 from Waters et al. (2013, 2014), and exp-pK2 values (i.e., experimentally derived values from Martin-Mayor et al. (2025) Eq 14). Also shown are the pHT0 values for each (SP and t) pair with standard deviation of the four pHT values.	

Related Publications

Clayton, T. D., & Byrne, R. H. (1993). Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Research Part I: Oceanographic Research Papers, 40(10), 2115–2129. doi:10.1016/0967-0637(93)90048-8
Methods

Dickson, A.G.; Sabine, C.L. and Christian, J.R. (eds) (2007) Guide to best practices for ocean CO2 measurement. Sidney, British Columbia, North Pacific Marine Science Organization, 191pp. (PICES Special Publication 3; IOCCP Report 8). DOI: https://doi.org/10.25607/OBP-1342
Methods

Martin-Mayor, M.; Byrne, R; Schockman K.; Liu, X. (2025). Spectrophotometric determination of the bicarbonate dissociation constant (K2) in estuarine waters and a model for all natural waters. Geochimica et Cosmochimica Acta (in review).
Results

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Methods

Müller, J. D., & Rehder, G. (2018). Metrology of pH Measurements in Brackish Waters—Part 2: Experimental Characterization of Purified meta-Cresol Purple for Spectrophotometric pHT Measurements. Frontiers in Marine

Science, 5. doi:10.3389/fmars.2018.00177
Methods

Schockman, K. M., & Byrne, R. H. (2021). Spectrophotometric determination of the bicarbonate dissociation constant in seawater. Geochimica et Cosmochimica Acta, 300, 231–245. https://doi.org/[10.1016/j.gca.2021.02.008](10.1016/j.gca.2021.02.008)
Results
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Methods

Schockman, K. M., Byrne, R. H., Carter, B. R., & Feely, R. A. (2024). Spectrophotometrically derived seawater CO2-system assessments: Parameter calculations using pH do not require measurements at standard temperatures. Limnology and Oceanography, 69(7), 1508–1520. Portico. https://doi.org/[10.1002/lno.12593](10.1002/lno.12593)
Results

Waters, J. F., & Millero, F. J. (2013). The free proton concentration scale for seawater pH. Marine Chemistry, 149, 8–22. https://doi.org/10.1016/j.marchem.2012.11.003
Methods

Waters, J., Millero, F. J., & Woosley, R. J. (2014). Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8–22]. Marine Chemistry, 165, 66–67. https://doi.org/10.1016/j.marchem.2014.07.004
Methods

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Parameters

Parameter	Description	Units
Target_Temp	Target temperature in degrees Celsius	degrees Celsius (°C)
Target_Sp	Target practical salinity	dimensionless
Sp	Practical salinity	dimensionless
Temperature	Measured temperature in degrees Celsius	degrees Celsius (°C)
pH_T0	pH value in the total scale at which pH = 1/2 (pK1 + pK2). See Schockman and Byrne (2021) Eq. (14).	dimensionless
pH_T0_std_n4	standard deviation of the pHT measurement where n=4	dimensionless
pK2_experimental	experimental pK2 (from experimental pHT0 and pK1 from Waters et al. (2014))	dimensionless
pK2_with_parameterization	value for pK2 using the new parameterization shown in Martin-Mayor et al. (2025)	dimensionless
pK2_residuals	value of experimental pK2 minus parameterized pK2 using the Martin-Mayor et al. (2025) equation.	dimensionless

Instruments

Dataset-specific Instrument Name	Diode array spectrophotometer (Agilent 8453) with the UV light lamp turned off
Generic Instrument Name	Agilent 8453 UV-visible spectrophotometer
Dataset-specific Description	Samples were measured in two-window 10cm cylindrical optical glass spectrophotometric cells using an Agilent 8453 diode array spectrophotometer with the UV light lamp turned off.
Generic Instrument Description	The Agilent 8453 spectrophotometer is a laboratory optical instrument for chemical analysis to extract spectral information in the ultraviolet (UV) and visible light. The instrument radiates a single light beam by optically combining two source lamps: a deuterium-discharge lamp for the UV wavelength range and a tungsten lamp for the visible and short wave near-infrared (SWNIR) wavelength range. The beam passes through the sample, is focused and dispersed within the spectrograph lens, slit and grating, and reaches the diode array in the form of a spectral image. The diode array samples a wavelength range of 190 to 1100 nm at a mean sampling interval of 0.9 nm. The nominal spectral slit width is 1 nm and the stray light is less than 0.03%.

Dataset-specific Instrument Name	Digital hand-held thermometer (Ertco-Eutechnics Model 4400)
Generic Instrument Name	digital thermometer
Dataset-specific Description	The sample's temperature in the spectrophotometric cell was recorded using a digital thermometer (Ertco-Eutechnics Model 4400).
Generic Instrument Description	An instrument that measures temperature digitally.

Dataset-specific Instrument Name	Guildline Portasal 8410A Laboratory Salinometer
Generic Instrument Name	Guildline 8410A Portasal
Dataset-specific Description	Seawater salinity for each individual sample was measured with a Guildline Portasal 8410A Laboratory Salinometer.
Generic Instrument Description	Portasal Salinometer 8410A Guildline 8410A Portasal is a truly portable, high precision instrument from the world leader in salinometers. The Portasal will deliver salinity calculations on-board ship with laboratory level accuracy. It measures accurate conductivity ratios and displays calculated salinity directly as well as measured parameters. http://www.osil.co.uk/Products/Ignore/tabid/56/agentType/View/PropertyID...

Dataset-specific Instrument Name	Harris Environmental System environmental room
Generic Instrument Name	Test chamber
Dataset-specific Description	Environmental room for additional temperature control (Harris Environmental Systems) was used for experiments in which t
Generic Instrument Description	A test chamber is a controlled environment where specific conditions (temperature, humidity, light, etc.) are maintained for testing and research purposes. Also called climatic chamber, environmental chamber, environmental room, or environmental enclosure

Project Information

Spectrophotometric Determinations of Carbonic Acid Dissociation Constants for Estuarine Conditions (Spectrophotometric K1K2)

NSF Award Abstract
Human health and well-being are linked in many ways to the health of our estuaries and coastal ocean waters. Yet surprisingly, we know less about some aspects of these important waters than we do the more distant waters of the deep ocean. This project will use state-of-the-art spectrophotometric methods (that is, light- and color-based methods) to advance our understanding of the fundamental and ever-changing chemistry of these waters and, eventually, the effects of these changes on marine life. The focus of this study will be to understand the chemistry of carbon dioxide in seawater. The new tools we will use are recently characterized pH indicators — chemicals that change color in seawater depending on the acidity of that water. These specially selected, purified indicators can be used to measure pH with unsurpassed precision and accuracy. We will use the indicators in laboratory experiments to determine how a critical parameter of the carbon dioxide system (a dissociation constant known as "K2") changes depending on the temperature and salinity of the water. Characterizing K2 has been a goal of marine chemists for more than 50 years. The better we know K2, the better we can understand and predict how carbon moves through and cycles within natural waters. These measurements will expand our understanding of not only K2 but also the many other seawater characteristics that can be calculated from K2. Ultimately, this work will facilitate the interpretation and prediction of many ocean processes relevant to human health and coastal economies, such as ocean acidification (the lowering of ocean pH due to increasing carbon dioxide in the atmosphere) and calcium carbonate dissolution (the resulting dissolution of seashell material). The results will thus lay the groundwork for new perspectives on how ocean acidification affects the various shelled organisms that serve as food for economically important marine animals/fisheries and for people. The results of this work will also help to improve models of carbon dioxide dynamics in lakes, rivers, underground pore waters, and physiological fluids. As regards broader impacts, this work will help the PI continue to transfer his knowledge on this important topic to the next generation via his training of graduate, undergraduate, and high school students. This project would support one graduate and one undergraduate student, as well as help the current research projects of two minority doctoral students. Lastly, the PI plans to continue his involvement in the Bridge to the Doctoral Program aimed at getting minority students involved in the sciences.

In seawater, two carbonic acid dissociation constants (K1 and K2) describe the relationship between solution pH and the relative concentrations of dissolved carbonate ions, bicarbonate ions, and dissolved carbon dioxide. Accurate characterization of these CO2-system constants over broad ranges of environmental conditions has been a much sought-after goal for more than 50 years because knowledge of these terms is essential for quantitatively interpreting and predicting the biogeochemical cycling of carbon in all natural aqueous systems. The accuracy of CO2-system calculations is especially sensitive to uncertainties in K2, the equilibrium constant that describes the dissociation of bicarbonate ions to produce hydrogen ions and carbonate ions. This research project is designed to use spectrophotometric pH measurements (solely) to characterize this important constant. The purified pH indicators to be used in this work provide seawater pH

measurements of unsurpassed precision and accuracy. Using select indicators whose properties have recently been characterized over freshwater-to-seawater ranges of salinity and temperature, we will determine K2 over similar ranges so as to improve the accuracy of CO2-system calculations in estuaries and coastal ocean waters. The resulting insight into equilibrium characteristics will facilitate interpretations and predictions of pH buffering in aqueous systems, provide an improved understanding of calcium carbonate solubility behavior, and lead to improved models of CO2-system behavior in freshwater lakes, rivers, soil and sediment pore waters, and physiological fluids. The longer-term benefits of this project will extend to assessments of the influence of ocean acidification on the life cycles of carbonate-bearing organisms that serve as food for economically important marine organisms.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-2042935