The recommended dissociation constants for carboxylic acid in seawater

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Abstract. A coherent representation of carbonate dissociation constants and measured inorganic carbon species is essential for a wide range of environmentally important issues such as oceanic uptake of anthropogenic CO2 and carbon cycle depictions in ocean circulation models. Previous studies have shown varying degrees of discordance between calculated and measured CO2-system parameters. It is unclear if this is due to errors in thermodynamic models or in measurements. In this work, we address this issue using a large field dataset (15,300 water samples) covering all ocean basins. Our field data, obtained using laboratory-calibrated measurement protocols, are most consistent with calculated parameters using the dissociation constants of Mehrbach et al. [1973] as refit by Dickson and Millero [1987]. Thus, these constants are recommended for use in the synthesis of the inorganic carbon data collected during the global CO2 survey during the 1990s and for characterization of the carbonate system in seawater.

Introduction

The carbon dioxide system in seawater can be defined by specifying temperature, salinity, nutrient and boron concentrations, and two of the four inorganic CO2-system parameters: pH (log[H+]), total inorganic carbon (Ct), total alkalinity (A), and CO2 fugacity (fCO2). The CO2 fugacity is expressed by the relationship, fCO2 = [CO2]/Kw, where Kw is the solubility of CO2 and [CO2] = [CO2]aq + [H2CO3]. Measurement of all four of the CO2-system parameters allows an evaluation of the accuracy of available carboxylic acid dissociation constants by the so-called “system overdetermination.” Agreement between measurements and thermodynamic calculations (model closure) is fundamental to our understanding of important geochemical issues such as the determination of the calcium carbonate compensation depth and the distribution of fossil fuel CO2 in the oceans. It is particularly important in numerical ocean circulation models where surface ocean fCO2 is calculated from A, and Ct fields. Different carbonate-system equilibrium models yield differences in calculated fCO2 as large as 30 ppm.

Several determinations of carboxylic acid dissociation constants have been made as a function of temperature and salinity in natural seawater [Mehrbach et al., 1973] and in artificial seawater without fluoride [Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993]. Dickson and Millero [1987] refit the experimental datasets of Mehrbach et al. [1973] (referred to as MFHR-DM87) and of Hansson [1973]. Additional sets of constants have been created by fitting the pooled data of Hansson and Mehrbach et al. [Dickson and Millero, 1987], and the pooled data of Goyet and Poisson and Roy et al. [Millero, 1995]. Average differences in various equations for pK and pK are in a range of 0.001-0.008 in pK, and of 0.005-0.03 in pK, [Millero, 1995]. These differences are similar to the 2a experimental precision (0.01-0.17 in pK, and 0.015-0.026 in pK) and probably are not strongly significant. However, the different equations derived from original experimental datasets yield significant differences in calculated parameters. Here we present the equations that yield the best agreement with a large field dataset.

Over the last 10 years, significant improvements have been made in the measurement of inorganic CO2 parameters [DOE, 1994]. The use of certified reference material (CRM), developed by Dr. A. Dickson (Scripps Institution of Oceanography), greatly contributed to improved precision and accuracy in at-sea A and Ct measurements. These improvements have motivated a number of investigators to re-examine the internal consistency of the CO2 parameters measured in the laboratory [Lee et al., 1996; Murphy, 1996; Lueker, 1998] and at sea [Millero et al., 1993; Clayton et al., 1995; Lee et al., 1997; McEllicott et al., 1998; Wanninkhof et al., 1999; Byrne et al., 1999]. These studies have resulted in conflicting conclusions regarding the optimal set of carboxylic acid dissociation constants. The differing conclusions drawn from previous studies have a variety of experimental origins: (1) A measurement uncertainties; A data obtained during the U.S. JGOFS Equatorial Pacific Process Study in 1992 (EqPac92) were overestimated by about 8 µmol kg due to inaccurately assigned titrant concentrations. This affects the conclusions drawn by Millero et al. [1993]. (2) pH scale uncertainties: McEllicott et al. [1998] noted that all four CO2 parameters measured during the EqPac92 program would be internally consistent with the constants of MEHR-DM87 at 20°-25°C if spectroscopic pH values were increased by 0.0038. DeValls and Dickson [1998] determined that the pH values assigned to “tris” buffers needed to be increased by 0.0047 for all temperatures and salinities. The reported pK of the indicator m-cresol purple [Clayton and Byrne, 1993] is based on the “tris” characterization of Dickson [1993] who used the reported e.m.f.

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Paper number 1999GL002345.
0094-8276/00/1999GL002345S05.00
values of Ramette et al. [1977]. Consequently, spectroscopic pH values obtained in the laboratory [Lee et al., 1996] and in field studies [Millero et al., 1993; Clayton et al., 1995; Lee et al., 1997] may need to be revised upward by 0.0047 pH units. (3) Limited scope of previous studies: Previous investigations of thermodynamic CO₂-system consistency often involved two or three carbon system parameters over a narrow range of temperature (t) and fCO₂, or specific ocean regions.

This work is distinct from previous studies in that it uses a large, well-calibrated field dataset covering a 5°-30°C range of temperature, a 33-37 range of salinity, and a 250-1700 μm range of fCO₂. Field measurements were made in all major ocean basins from the equator to high latitudes. The data were obtained by many investigators over a four-year period. Laboratory measurements made over a similar range of temperature and f(CO₂) are also included in this analysis. The internal consistency of all data used in this study was carefully examined on a per cruise basis: A₅ and C₅ data were normalized to CRMs values [Dickson, 1997] and pH data were adjusted upward by 0.0047 pH units for consistency with the revised “tris” buffer characterization of DalValls and Dickson [1998]. This dataset, which represents our current achievable level of accuracy on a routine basis at sea and in the laboratory, is used to determine which set of carbonic acid dissociation constants is optimal for use in characterizing the oceanic CO₂-system.

Sources of Laboratory and Field Data

Laboratory measurements of all four CO₂ parameters were made on a single seawater sample (S=35) as a function of temperature (5°-35°C) and fCO₂ (300-1700 μm). The analytical techniques and data are documented in Lee et al. [1996]. Field data were obtained on cruises conducted by the National Oceanic and Atmospheric Administration/Ocean-Atmosphere Carbon Exchange Study (NOAA/OACES) in the Atlantic, Indian, and Pacific Oceans (Table 1). The NOAA/OACES CO₂ dataset is unique in that all four CO₂ parameters were measured throughout the water column from the surface to 6000 m. Samples were analyzed for f(CO₂) and C₅ at 20°C, and for A₅ and pH at 25°C except for the North Atlantic study where pH was measured at 20°C. Detailed procedures for analysis of fCO₂, pH, C₅, and A₅ can be found in DOE [1994]. Analysis protocols differed for pH and fCO₂ measurements on different cruises. The fCO₂ of discrete samples was measured by an infrared analyzer (IR) [Whimninkhof and Thoning, 1993] on the EQPAC, A20R, and P18 cruises, and by gas chromatographic analysis with flame-ionization detection (GC-FID) after catalytic reduction of CO₂ to CH₄ [Neill et al., 1997] on the 18R and P15S cruises. Spectroscopic pH measurements using the indicator m-cresol purple were made at 20°C on the A20R and at 25°C on the 18R by the University of Miami group, and at 25°C on the EQPAC, P15S, and P18 cruises by the University of South Florida group.

Results and Discussion

In this study, pH-C₅ and A₅-C₅ are used as input combinations to study the consistency between the measurements and the first and second carbonate dissociation constants. The pH-C₅ combination can be used to assess the consistency between measurements and pK₅ parameterizations by comparing measured vs. calculated fCO₂ (Fig. 1a, 1b), and the consistency between measurements and pK₅ parameterizations by comparing measured vs. calculated A₅ (Fig. 1c, 1d) [Lee et al., 1996]. The A₅-C₅ combination can be used to evaluate the consistency between measurements and log Kₐ/K₅ ratios by comparing measured fCO₂ and fCO₂ calculated from A₅-C₅ (Fig. 1c, 1d). In these calculations we have used the constants of MEHR DM87, along with equilibrium constants for other components (e.g., boric acid dissociation, solubility of CO₂, water hydrolysis, and phosphoric and silicic acid dissociation), necessary to characterize the carbonate system in seawater as recommended in Millero [1993]. Since the constants of MEHR-DM87 are expressed in terms of moles per kilogram of solution on the “seawater” scale [Dickson and Millero, 1987], all acid dissociation constants have been adjusted to the same scale. The effect of uncertainties in equilibrium constants on calculated parameters is discussed in the caption of Fig. 1.

Assessment of pK₅

The difference between measured fCO₂ and fCO₂ calculated from pH-C₅ is strongly dependent upon the pK₅. The fCO₂ residuals in Fig. 1a and 1b show the percentage error in fCO₂ (ΔfCO₂ = [(measured fCO₂ - calculated fCO₂) / measured fCO₂] × 100) for laboratory and field data. Observations are binned into fCO₂ intervals equal to 300 μm, and are shown as a function of sample fCO₂. The best agreement between measured and calculated fCO₂ was obtained using the constants of MEHR-DM87. The fCO₂ residuals for field measurements are mostly within ±1% over the entire fCO₂ range (Fig. 1a, 1b) and
dissociation constants other than MEHR-DM87 (Table 1). The pK1 measurements of Goyet and Poisson, Hansson, and Roy et al. agreed to within ±0.003 in pK1 [Millero, 1995] but they differ from MEHR-DM87 by about 0.01, which is equivalent to a 3% offset in calculated fCO2.

**Assessment of pK1.**

The difference between measured A1 and A1 calculated from pH-C1 strongly depends on the pK2. The A1 residuals (ΔA1 = measured A1 - calculated A1 in μmol kg⁻¹) for laboratory and field data are binned and are plotted as a function of sample fCO2 in Fig. 1c and 1d. The A1 residuals for laboratory and field data using the constants of MEHR-DM87 are about ±3 μmol kg⁻¹ (1σ) with little dependence on fCO2. When the constants of Roy et al. and Goyet and Poisson are used, the A1 residuals are considerably larger for samples with low fCO2. An adjustment of 0.03 in the pK1 of Roy et al. would be required to produce a near zero slope in the residuals. Such an adjustment lowers the calculated A1 by about 15 μmol kg⁻¹ for samples with fCO2 = 300 μatm and also lowers the A1 by 4 μmol kg⁻¹ for samples with fCO2 = 1600 μatm.

**Assessment of the log K1/K2 Ratio.**

Calculation of fCO2 from A1-C1 requires a reliable log K1/K2 ratio. The differences in the log K1/K2 for various parameterizations range from -0.04 to 0.06 and are primarily caused by differences in K2. Measured fCO2 values for samples with low fCO2 (<500 μatm) at t = 5-30°C are most consistent with calculations using the constants of MEHR-DM87. This is not the case at high fCO2 (>500 μatm) where fCO2 residuals become greater as fCO2 increases (Fig. 1f). The fCO2 dependence of the residuals is apparent in two independent laboratory measurements [Lee et al., 1996; Lueker, 1998], and in the field data of GC-FID based fCO2 measurements (Fig. 1f). This trend is also evident irrespective of the carbonic acid dissociation constants used. This implies that the log K1/K2 ratio calculated from these measurements varies as a function of sample fCO2, which is in contradiction with our understanding of the carbonate system. The IR based fCO2 measurements do not show this trend (Fig. 1e), and the apparent discrepancy in fCO2 measurements at high fCO2 has to be resolved before we can draw firm conclusions regarding the consistency between fCO2-A1-C1 measurements and the log K1/K2 at high fCO2. Wanninkhof et al. [1999] showed that surface underlay fCO2 measurements, made on three OACES cruises (A20R, I8R, and P18) covering a water temperature range of 5-30°C and fCO2 range of 280-450 μatm, are consistent with fCO2 calculated from A1-C1 data using the constants of MEHR-DM87. At low temperature, the constants of MEHR-DM87 and Roy et al. both give a reliable prediction of fCO2, because the difference in the log K1/K2 between Roy et al. and MEHR-DM87 at t<5°C is significantly smaller (<0.02) than at other temperatures. At 25°C the difference is as large as 0.05, which leads to differences in calculated fCO2 of 30 μatm.

**Conclusions.**

The adjustment in the pK2 of m-cresol purple suggested by DelWalls and Dickson [1998] brings calculations involving pH into optimal agreement with the other CO2-system measurements. The constants of MEHR-DM87 are most suitable for
calculations involving pH-Ar-CO₂ combinations over a range of t=0°-35°C, S=33-37, and fCO₂=250-1700 μatm. The constants of MEHR-DM87 also yield good agreement with measurements and calculations involving fCO₂-Ar-CO₂ combinations at low fCO₂. At high fCO₂, calculated fCO₂ values using the log K₁/K₂ ratio of MEHR-DM87 are less than the measured values for the laboratory and GC-FID field measurements. Definitive conclusions regarding the consistency between measurements and the log K₁/K₂ will require resolution of discrepancies in fCO₂ measurements at high fCO₂. Overall, the constants of MEHR-DM87 provide the most consistent comparisons between laboratory and field measurements over a wide range of ocean temperature, salinity, and fCO₂. This work suggests that the internal consistency of CO₂-system measurements can be achieved over long periods of time by diverse teams of investigators through the use of standard reference materials.

Acknowledgements. This work was jointly sponsored by the NOAA/OAACES program and the DOE global CO₂ survey project. We wish to thank Dr. Lisa Dilling, program manager of GCC for supporting this work. This high quality data represented here was the result of a large number of scientists who participated in the global CO₂ survey. Their contribution is gratefully acknowledged. University of Miami/CIMAS has partially supported Kitack Lee. The cruise data used in this paper can be obtained at http://www.aoml.noaa.gov/ocd/oaces. Preparation of the camera-ready copy by Gail Derr is appreciated.

References


Lueker, T.J., The ratio of the first and second dissociation constants of carbonic acid determination from the concentration of carbon dioxide in gas and seawater at equilibrium, Ph.D dissertation, 155 pp., Univ. of California at San Diego, 1998.


Murphy, P., The carbonate system in seawater: Laboratory and field studies, Ph.D dissertation, 288 pp., Univ. of Washington, 1996.


(Received April 26, 1999; revised November 10, 1999; accepted November 22, 1999.)