Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Marine Chemistry 100 (2006) 80–94

MARINE CHEMISTRY

www.elsevier.com/locate/marchem

Dissociation constants of carbonic acid in seawater as a function of salinity and temperature

Frank J. Millero *, Taylor B. Graham, Fen Huang, Héctor Bustos-Serrano, Denis Pierrot

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, United States

Received 17 June 2005; received in revised form 2 December 2005; accepted 2 December 2005
Available online 31 January 2006

Abstract

Potentiometric measurements of the stoichiometric constants on the seawater pH scale for the dissociation of carbonic acid in seawater ($K_1^*=[H^+][HCO_3^-]/[CO_2]$ and $K_2^*=[H^+][CO_3^{2-}]/[HCO_3^-]$) have been made as a function of salinity (1 to 50) and temperature (0 to 50 °C). The results have been fitted to the equations (T/K)

$$pK_i - pK_i^0 = A_i + B_i/T + C_i \ln T.$$

The values of pK_i^0 in pure water are taken from the early work of Harned and Davis (1943) and Harned and Scholes (1941)

$$pK_1^0 = -126.34048 + 6320.813/T + 19.568224 \ln T$$

$$pK_2^0 = -90.18333 + 5143.692/T + 14.613358 \ln T.$$

The value of the adjustable parameters A_i, B_i and C_i for pK_1^* are given by ($\sigma=0.0054$ and $N=466$)

$$A_1 = 13.4191 S^{0.5} + 0.0331 S - 5.33E-05 S^2$$

$$B_1 = -530.123 S^{0.5} - 6.103 S$$

$$C_1 = -2.06950 S^{0.5}.$$

For pK_2^* the parameters are given by ($\sigma=0.011$ and $N=458$)

$$A_2 = 21.0894 S^{0.5} + 0.1248 S - 3.687E-04 S^2$$

$$B_2 = -772.483 S^{0.5} - 20.051 S$$

$$C_2 = -3.3336 S^{0.5}.$$

---

* Corresponding author.
E-mail address: fmillero@rsmas.miami.edu (F.J. Millero).

doi:10.1016/j.marchem.2005.12.001

The values of pK_1^* and pK_2^* determined in this study are in good agreement with the seawater (SW) measurements of Mehrbach et al. (1973) and Mojica-Prieto and Millero (2002) from $S=15$ to 45 and 0 to 40 °C. The values of pK_1^* near $S=35$ are also in reasonable agreement with the measurements in artificial seawater (ASW) of Goyet and Poisson (1989) and Roy et al. (1993) from 0 to 35 °C. The values of pK_2^* in real seawater, however, do not agree with the measurement made in artificial seawater at temperatures above 5 °C. Calculations of pK_1^* and pK_2^* near 25 °C using an ionic interaction model (Millero and Roy, 1997) suggest that the pK_2^* results in SW are more reliable than in ASW.

The equations from this study should be valid from $S=0$ to 50 and $t=0$ to 50 °C for most estuarine and marine waters (check values at $S=35$ and $t=25$ °C are p$K_1^*=5.8401$ and p$K_2^*=8.9636$).

Keywords: Seawater; Carbonic acid; Dissociation constants; pK_1; pK_2; Titration; Modeling

---

1. Introduction

To examine the thermodynamics of the carbonic acid system in seawater from measurements of pH, total alkalinity (TA), total carbon dioxide (TCO_2) and the partial pressure of carbon dioxide (pCO$_2$) one needs reliable constants for the dissociation of carbonic acid.

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{1}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}. \tag{2}$$

The stoichiometric constants are given by

$$K_1^* = [H^+]\left[HCO_3^-\right]/[CO_2] \tag{3}$$

$$K_2^* = [H^+]\left[CO_3^{2-}\right]/\left[HCO_3^-\right]. \tag{4}$$

The concentrations (mol kg SW^{-1}) are the total stoichiometric values, $[H^+]=[H^+]_F+[HSO_4^-]+[HF]$ (where the subscript F is used to designate the free proton concentration). Theoretically the measured stoichiometric constants (K_1^* and K_2^*) for carbonic acid in seawater are related to the thermodynamic constants (K_i^0) by

$$K_1^* = K_1^0 a_{H_2O}\gamma_{CO_2}/\gamma_H\gamma_{HCO_3} \tag{5}$$

$$K_2^* = K_2^0 \gamma_{HCO_3}/\gamma_H\gamma_{CO_3} \tag{6}$$

where a_i is the activity and γ_i is the activity coefficient of species i.

A number of workers have made measurements of the stoichiometric constants for the dissociation of carbonic acid in real seawater (SW) (Mehrbach et al., 1973; Mojica-Prieto and Millero, 2002) and artificial seawater (ASW) (Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993). A summary of these studies is given in Table 1 along with the standard errors of the individual measurements being fit to the same equation (Eqs. (11)–(14)). All of the individual studies have similar standard deviations, $\sigma=0.004$ to 0.007 for pK_1^* and $\sigma=0.002$ to 0.010 for pK_2^*. The measurements by Mehrbach et al. (1973) and Mojica-Prieto and Millero (2002) were made on real seawater (SW) while the measurements made by Hansson (1973), Goyet and Poisson (1989) and Roy et al. (1993) were made on artificial seawater

Table 1
A summary of the measurement made on the dissociation constants of carbonic acid in real (SW) and artificial (ASW) seawater by various workers

Reference	Media	Salinity range	Temperature range (°C)	σ(pK_1^*)[a]	σ(pK_2^*)[a]
Hansson	ASW	5–40	5–35	0.0070 (62)	0.010 (62)
Mehrbach et al.	SW	19–43	2–35	0.0043 (30)	0.010 (33)
Goyet and Poisson	ASW	10–50	− 1–40	0.0057 (84)	0.010 (90)
Roy et al.	ASW	5–45	0–45	0.0044 (80)	0.002 (80)
Mojica-Prieto and Millero	SW	12–45	5–45	0.0040 (80)	0.008 (80)
This study	SW	1–50	0–50	0.0054 (466)	0.011 (458)

[a] The values in parentheses are the number of measurements made and the standard errors are based upon fitting the measurements to the same functional form (Eqs. (11)–(14)).