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Effects of High CO_2 Molality on the Carbon Dioxide Equilibrium of Seawater

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The effects of high CO_2 molality on carbon dioxide equilibrium are important to studies related to the disposal of liquid CO_2 into the oceans. Using the Pitzer method, terms that take into account the effect of dissolved CO_2 on the solubility coefficient of CO_2 and stoichiometric dissociation constants of acid−base equilibrium have been obtained in explicit form. Using available thermodynamic data for liquid CO_2 and CO_2 gas solubility in seawater, we developed an equation for the solubility of liquid CO_2 in seawater as a function of temperature, pressure, and salinity. It was established that the effect of high CO_2 molality on carbon dioxide system constants shifts the stoichiometric carbonate equilibrium of seawater by an increased pH level of more than 0.3 pH units.

Introduction

At the end of the last century, because of the intensive development of remote methods (observations from space) and extensive application of isotopic methods in earth sciences, independent proofs of climate variability were obtained. From these results, many scientists consider that global warming is occurring now. The main cause for this is attributed to the continued increase of greenhouse gas concentrations in our atmosphere over the last century. The leading industrial countries of the world have attempted to develop practical programs (i.e., the Kyoto Protocol) to restrict and reduce the levels of greenhouse gases in our atmosphere (i.e., CO_2, CH_4, and N_2O).

Oceans have a large storage capacity for anthropogenic CO_2. The disposal and sequestration of captured anthropogenic CO_2 in the ocean is considered to be a possible way to mitigate global warming.[1] One of the disposal methods being considered is the injection of liquid CO_2 into the deep ocean (below 3500 m, where liquid CO_2 becomes denser than the surrounding water). The interaction of liquid CO_2 with seawater results in high CO_2 molalities and low pH, both of which can have detrimental effects on aquatic life.[2] The impact of liquid CO_2 on the ocean's environment cannot be considered without understanding all of the parameters of the carbon dioxide system. There are four measurable parameters of the carbon dioxide system (pH, alkalinity, dissolved inorganic carbon, and CO_2 partial pressure). A technical assessment of environmental conditions for liquid CO_2 in the oceans has to include measurements of at least two parameters of the carbon dioxide system in order to calculate the others. Activity coefficients for most species involved in acid−base equilibrium in seawater are still unknown. Therefore, the commonly accepted procedure for the calculation of the carbon dioxide system in seawater includes stoichiometric constants that are determined at different salinities, temperatures, and pressures at trace molalities of dissolved free CO_2 in seawater, where $m(CO_2) = m(CO_2)_{aq} + m(H_2CO_3)_{aq}$. Such determined stoichiometric constants are represented by empirical equations as a function of salinity, temperature, and pressure.[3] However, these equations do not contain any terms reflecting the contribution of interactions of CO_2 with acid−base species. We need to take into account these interactions at moderate and high CO_2 molality in seawater. According to recent measurements on the solubility of liquid CO_2 in seawater,[4] CO_2 molalities can exceed 1. When seawater has a CO_2 molality of 1 $mol\cdot kg^{-1}$, the solution is no longer considered to be "seawater", and the available carbon dioxide system constants[3] cannot be applied when studying this solution. Therefore, all constants must be redetermined for conditions of elevated CO_2 molalities because, at present, they have been determined at low μmol kg^{-1} levels of CO_2 in seawater. This would be a large-scale experimental task. However, there is a theoretical approach that permits us to take into account the effects of high CO_2 molality on stoichiometric acid−base equilibrium using available thermodynamic data, thus reducing the experimental task. This approach is called the Pitzer method.[5,6] Using this method, the terms that account for the effects of high CO_2 molality on stoichiometric acid−base equilibrium are evaluated. These terms, together with available stoichiometric constants,[3] allow us to calculate the parameters of the carbonate system for seawater with high CO_2 molality.

The solubility properties of liquid CO_2 and the first dissociation constants of carbonic acid are crucial for the prediction of pH values of seawater equilibrated with liquid CO_2. This paper focuses on offering accurate coefficients of the solubility of liquid CO_2 in seawater and the first dissociation constants of carbonic acid at high CO_2 molality.

Solubility of Liquid CO_2 in Seawater

The solubility of CO_2 gas in water and aqueous salt solutions has been extensively studied as a function of temperature and pressure.[7,8] However, most studies are concerned with high-temperature ranges where CO_2 exists

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as a gas.[9–12] Far fewer studies have been devoted to the solubility of liquid CO_2 in water and salt solutions.[4,13–15]

In this paper, we used a thermodynamic approach for the estimation of the solubility of liquid CO_2 in seawater. Using available thermodynamic data, we expressed the solubility as a function of temperature T (Kelvin scale), pressure P, and salinity S for the temperature range of (273 to 298) K, pressure range of (3 to 50) MPa, and salinities of 0 to 40 (expressed as mass fraction per mil). Below 283 K, liquid CO_2 and water form a solid-phase–gas hydrate.[16,17] Possible applications for the evaluated solubility of liquid CO_2 for metastable conditions (below 283 K) will be discussed.

The main feature of the interaction of liquid carbon dioxide with water is that water is not practically dissolved in liquid carbon dioxide. It is assumed that all salts will not dissolve in liquid CO_2. This feature allows us to use the following thermodynamic approach to estimate the solubility of liquid CO_2 in seawater. This approach consists of looking at the thermodynamics for two different situations. The first case considers the equilibria of three phases (CO_2–gas, CO_2–liquid, and seawater). This allows us to include the Henry's law constant (or solubility coefficient) in thermodynamic equations used to describe the equilibria of two phases (CO_2–liquid and seawater). The second situation considers the equilibria of only two phases (CO_2–liquid and seawater) and is necessary for us to analyze the effects of ocean depth on CO_2 equilibria in seawater saturated with liquid CO_2.

Situation 1. Consider the theory of mutual solubility of CO_2 (= B) in two liquid phases L_1 (= B-rich liquid) and L_2 (= water-rich liquid) under their own vapor pressure, with the sum of the partial pressures of B and water (= A) in seawater = P^s. If this system contained only B and pure water, then there would be three phases in mutual equilibrium in a two-component system, so there would be only one degree of freedom. Thus, there would be unique mutual solubility–temperature, mutual solubility–pressure, or temperature–pressure curves. In the presence of seawater, as long as all of the dissolved components of seawater (with the exception of B) are nonvolatile, salts do not dissolve in the B-rich liquid, and the seawater can be considered to have a constant composition at a given salinity (again with the exception of B). The system is pseudounivariant, and again there are unique mutual solubility–temperature, mutual solubility–pressure, or temperature–pressure curves for a given salinity.

For the equilibrium of component B (= CO_2) at temperature T and vapor pressure P^s, between the gas and B-rich liquid L_1,

$$\mu_B^{L_1}(T, P^s, x_B) = \mu_B^g(T, P^s, y_B) \tag{1}$$

where x_B and y_B are mole fractions in the liquid and gas phases, respectively. The chemical potentials are given by eq 2:

$$\mu_B^{L_1}(T, P^s, x_B) = \mu_B^{*L_1}(T, P^s) + RT \ln\{f_B(T, P^s, x_B)x_B\} \tag{2}$$

where R is the gas constant; superscript * indicates pure liquid B, f_B is the activity coefficient of B referenced to Raoult's law, and by eq 3

$$\mu_B^g(T, P^s, y_B) = \mu_B^{og}(T) + RT \ln\left(\frac{\hat{f}_B(T, P^s, y_B)}{P^o}\right) \tag{3}$$

where $\hat{f}_B$ is the fugacity of B and P° is the standard pressure. By inserting eqs 2 and 3 into eq 1, applying the resulting equation to pure B, and finally through subtraction of the two resulting equations, we obtain

$$\ln\{f_B(T, P^s, x_B)x_B\} + \int_{P_B^{S*}}^{P^S} \frac{V_{m,B}(T, P)}{RT}\,dP = \ln\left\{\frac{\hat{f}_B(T, P^s, y_B)}{\phi_B^*\, P_B^*}\right\} \tag{4}$$

where $V_{m,B}$ is the molar volume and $P_B^{S*}$and ϕ_B^* are the saturated vapor pressure and fugacity coefficient of pure B, respectively.

For the equilibrium of component B (= CO_2) at temperature T and vapor pressure P^s between the gas and A-rich liquid L_2, we use similar equations, but with the infinitely dilute standard state for B in the liquid phase. The condition for equilibrium is now

$$\mu_B^{L_2}(T, P^s, S, m_B) = \mu_B^g(T, P^s, y_B) \tag{5}$$

$$\mu_B^{L_2}(T, P^s, m_B) = \mu_{m,B}^{\infty}(T, P^o) + RT \ln\left\{\frac{\gamma_{m,B}(T, P^o, S, m_B)m_B}{m^o}\right\} + \int_{P^o}^{P^s} V_B^{L_2}(T, P, S, m_B)\,dP \tag{6}$$

where $m^\circ = 1\ \text{mol}\cdot\text{kg}^{-1}$ is the standard molality, superscript ∞ indicates infinite dilution, $\gamma_{m,B}$ is the activity coefficient of B referenced to Henry's law (molality scale), and V_B is the partial molar volume of B. The activity coefficient, $\gamma_{m,B}$, is a function of all species in the solution, but because of the specific feature of seawater (the relative composition of major ions in seawater is constant), it may be represented as a function of B and salinity only, which will be demonstrated below. Inserting eqs 3 and 6 into eq 5, applying the resulting equation to infinite dilution, and subtracting the two equations, we obtain

$$\ln\left\{\frac{\gamma_{m,B}(T, P^o, S, m_B)m_B}{m^o}\right\} + \int_{P^o}^{P^s} \frac{V_B^{L_2}(T, P, S, m_B)}{RT}\,dP - \int_{P^o}^{P_A^{s*}} \frac{V_B^{\infty}(T, P)}{RT}\,dP = \ln\left\{\frac{\hat{f}_B(T, P^s, y_B)}{k_{H,m}m^o}\right\} \tag{7}$$

where

$$\lim_{\substack{m_B \to 0\\ S \to 0}} \left[\ln\left\{\frac{\hat{f}_B m^o}{P^o \gamma_{m,B} m_B}\right\}\right] = \ln\left\{\frac{k_{H,m}m^o}{P^o}\right\} \tag{8}$$

has been used, where $k_{H,m}$ is the Henry's law constant of B (molality scale) and P_A^{s*} is the vapor pressure of water. From eqs 4, 7, and 8, we get

$$\ln\left\{\frac{\gamma_{m,B}(T, P^o, S, m_B)m_B}{m^o}\right\} = -\int_{P^o}^{P^s} \frac{V_B^{L_2}(T, P, S, m_B)}{RT}\,dP + \int_{P^o}^{P_A^{s*}} \frac{V_B^{\infty}(T, P)}{RT}\,dP + \int_{P_B^{s*}}^{P^s} \frac{V_{m,B}(T, P)}{RT}\,dP + \ln\left\{\frac{f_B(T, P^s, x_B)x_B\phi_B^*\, P_B^*}{k_{H,m}m^o}\right\} \tag{9}$$

The following approximations can be made: (a) $f_B = 1$ and (b) ignoring composition and pressure dependences of $V_B^{L_2}$ gives

$$\ln\left\{\frac{\gamma_{m,B}(T, P^o, S, m_B)m_B}{m^o}\right\} = -\frac{V_B^\infty(T)\{P^s - P_A^{s*}\}}{RT} + \int_{P_B^{s*}}^{P^s} \frac{V_{m,B}(T, P)}{RT}\,dP + \ln\left(\frac{\phi_B^* P_B^*}{k_{H,m}m^o}\right) + \ln(1 - x_A) \quad (10)$$

Equation 10 can be used to calculate the molality of CO_2 when three phases coexist in equilibrium.

Situation 2. Now we consider the two-phase equilibrium. The only condition is

$$\mu_B^{L_2}(T, P, m_B) = \mu_B^{L_1}(T, P, x_B) \quad (11)$$

In this case, eqs 2 and 6 can be rewritten as follows:

$$\mu_B^{L_1}(T, P, x_B) = \mu_B^{*L_1}(T, P^s) + RT\ln\{f_B(T, P^s, x_B)x_B\} + \int_{P^S}^{P} V_B^{L_1}(T, P, x_B)\,dP \quad (12)$$

$$\mu_B^{L_2}(T, P, m_B) = \mu_{m,B}^\infty(T, P^o) + RT\ln\left\{\frac{\gamma_{m,B}(T, P^o, S, m_B)m_B}{m^o}\right\} + \int_{P^o}^{P} V_B^{L_2}(T, P, \mathrm{S}, m_B)\,dP \quad (13)$$

From eqs 1, 2, 5, 6, and 9, we get

$$\mu_B^{*L_1}(T, P^s) - \mu_{m,B}^\infty(T, P^o) = \int_{P^o}^{P_A^{s*}} V_B^\infty(T, P)\,dP + \int_{P_B^{s*}}^{P^s} V_{m,B}(T, P)\,dP + RT\ln\left(\frac{\phi_B^* P_B^*}{k_{H,m}m^o}\right) \quad (14)$$

Inserting eqs 12 and 13 into eq 11 and taking into account eq 14, we obtain

$$\ln\left(\frac{m_B}{m^o}\right) = \int_{P_B^s}^{P} \frac{V_B^{L_1}(T, P, x_B)}{RT}\,dP + \int_{P_B^{s*}}^{P^s} \frac{V_{m,B}(T, P)}{RT}\,dP + \int_{P^o}^{P_A^{s*}} \frac{V_B^\infty(T, P)}{RT}\,dP - \int_{P^o}^{P} \frac{V_B^{L_2}(T, P, m_B)}{RT}\,dP + \ln\left\{\frac{f_B(T, P^s, x_B)x_B\phi_B^* P_B^*}{k_{H,m}m^o}\right\} - \ln\{\gamma_{m,B}(T, P^o, S, m_B)\} \quad (15)$$

Again, the following approximations can be made: (a) $f_B = 1$; (b) $V_B^{L_1} = V_{m,B}$; and (c) ignoring composition and pressure dependences of $V_B^{L_2}$ gives

$$\ln\left(\frac{m_B}{m^o}\right) = \int_{P_B^{s*}}^{P} \frac{V_{m,B}(T, P)}{RT}\,dP - \frac{V_B^\infty(T)(P - P_A^{s*})}{RT} + \ln(1 - x_A) + \ln\left(\frac{\phi_B^* P_B^*}{k_{H,m}m^o}\right) - \ln\{\gamma_{m,B}(T, P^o, S, m_B)\} \quad (16)$$

Equation 16 can be used to calculate the molality of CO_2 in seawater equilibrated with liquid CO_2. Further rearrangement of eq 16 will be made regarding the solubility coefficient of CO_2 developed by Weiss[18] and recommended by UNESCO[19] for oceanographic work.

Solubility Coefficient of CO_2 in Seawater. Weiss,[18] using his own CO_2 solubility data and those obtained at ambient total pressure by Murray and Riley,[20] developed the empirical relation for the solubility coefficient:

$$\ln(K_o/\mathrm{mol\cdot kg^{-1}\cdot bar^{-1}}) = -6.0098 \times 10^1 + 9.34517 \times 10^3\,\mathrm{K}/T + 2.33585 \times 10^1 \ln(T/100\,\mathrm{K}) - 1.001 \times 10^{-3}T/\mathrm{K} + 1.618 \times 10^{-6}T^2/\mathrm{K}^2 + S[2.4538 \times 10^{-2} - 2.3656 \times 10^{-4}T/\mathrm{K} + 4.7036 \times 10^{-7}T^2/\mathrm{K}^2] \quad (17)$$

The terms of eq 17 differ from those of the original Weiss equation because we use solubility coefficients on the molality scale. The solubility coefficient (eq 17) represents the molality of CO_2 related to the 0.1 MPa fugacity of CO_2 gas at a total standard pressure of 0.1 MPa. The small deviations from standard pressure that occurred during experiments[18,20] may be ignored. From above, the definition of the solubility coefficient and eq 7 give the relationship between the Henry's law constant and the solubility coefficient:

$$\ln(K_o k_{H,m}) = \int_{P^o}^{P_A^{s*}} \frac{V_B^\infty(T, P)}{RT}\,dP - \ln\{\gamma_{m,B}(T, P^o, \mathrm{S}, m_B)\} \quad (18)$$

Below, we will show that the solubility coefficient expressed by relation 17 cannot be inserted directly into eq 16 because it is a function of the molality of dissolved CO_2 for the experimental conditions for which relation 17 was evaluated.

The Pitzer method[5,6] gives the equation for the activity coefficient of dissolved B as follows:

$$\ln\{\gamma_{m,B}(T, P^o, S, m_B)\} = 2m_B\lambda_{B,B} + 2\sum_c m_c\lambda_{B,c} + 2\sum_a m_a\lambda_{B,a} \quad (19)$$

where $\lambda_{B,i}$ is a second virial coefficient taking into account the interaction of dissolved B with i species. Subscripts "c" and "a" mean "cation" and "anion", respectively. Because the relative composition of major ions in seawater is constant ($k_i = m_i/S$), eq 19 can be greatly simplified when applied to seawater as follows:

$$\ln\{\gamma_{m,B}(T, P^o, S, m_B)\} = 2m_B\lambda_{B,B} + 2(\sum_c m_c\lambda_{B,c} + \sum_a k_a\lambda_{B,a})S \quad (20)$$

or

$$\ln\{\gamma_{m,B}(T, P^o, S, m_B)\} = 2m_B\lambda_{B,B} + k_{set}S \quad (21)$$

where k_i is the molality/salinity ratio for the ith ion in seawater and k_{set} is the Setschenow coefficient. Taking into account eq 21, we may rewrite eq 18 as

$$\ln(K_o k_{H,m}) = \int_{P^o}^{P_A^{s*}} \frac{V_B^\infty(T, P)}{RT}\,dP - 2m_B^o\lambda_{B,B} - k_{set}S \quad (22)$$

Here, m_B^o designates the molalities of B corresponding to the experimental conditions used by Murray and Riley[20] and Weiss[18] to determine CO_2 solubility and the derivation of eq 17. From eq 22, it follows that the solubility coefficient proposed by Weiss[18] is a function of not only salinity but also the molality of CO_2. Therefore, eq 17 is applicable for the experimental conditions in which data were obtained but not for conditions where the fugacity of B is significantly less than or greater than P^o. Because eq 17 cannot be used for all conditions, we introduce a new solubility coefficient that corresponds to trace molalities of CO_2 in solution, where the term of $2m_B\lambda_{B,B}$ can be neglected:

$$\ln K_o^* = \ln K_o + 2m_B^o\lambda_{B,B} \tag{23}$$

The new solubility coefficient, K_o^*, is the molality of B related to the 0.1 MPa fugacity of B at a total pressure of 0.1 MPa, which does not depend on the molality of B and is related to the Henry's law constant by the equation

$$\ln(K_o^* k_{H,m}) = \int_{P^o}^{P_A^{s*}} \frac{V_B^\infty(T, P)}{RT}\,dP - k_{set}S \tag{24}$$

Taking into account both eqs 21 and 24 and ignoring the pressure dependence of V_B^∞, we obtained the final equation for the solubility of liquid CO_2 in seawater from eq 16.

$$\ln\left(\frac{m_B}{m^o}\right) = \int_{P_B^{s*}}^{P} \frac{V_{m,B}(T, P)}{RT}\,dP - \frac{V_B^\infty(T)(P - P^o)}{RT} + \ln(1 - x_A) + \ln\left(\frac{\phi_B^*\, P_B^*\, K_o^*}{m^o}\right) - 2m_B\lambda_{B,B} \tag{25}$$

Numerical Calculations of Equation 25. We calculated the terms of eq 25, including vapor saturation (P_B^*), fugacity coefficients (ϕ_B^*), and $V_{m,B}(T, P)$ using the data taken from Angus et al.[21] The second term of eq 25 was evaluated using measured partial molar volumes of CO_2[22] as a function of temperature. Data for the solubility of water in CO_2-rich liquid[14,23] were approximated by the relation

$$\ln(1 - x_A) = 1.2999 \times 10^{-2} - 5.2076 \times 10^{-5}T/K + (1.0424 \times 10^{-9} - 3.7787 \times 10^{-12}T/K)P/Pa + (-2.1173 \times 10^{-17} + 7.456 \times 10^{-20}T/K)P^2/Pa^2 \tag{26}$$

We used the solubility data of liquid CO_2 in water,[14] along with eq 17, to calculate the $\lambda_{B,B}$ parameter and the solubility coefficient K_o^* using an iterative procedure. The first step involved using the experimental data of King et al.,[14] along with eqs 17, 25, and 26, to obtain the $\lambda_{B,B}$ parameters, accepting that $K_o^* \equiv K_o$. Then, using eqs 17 and 23, we calculated the coefficient K_o^*, which was then used in the second cycle of the iteration. Two cycles were enough because the third iteration gave results almost identical to the second. Results of the calculations were approximated by relations given by

$$\lambda_{B,B}/\text{kg mol}^{-1} = -0.2546 + \frac{75.571}{T} - 5.428 \times 10^{-10}P/Pa \tag{27}$$

In the Pitzer method, the virial coefficient, $\lambda_{i,j}$, is expressed in kg·mol^{-1}:

$$\ln(K_o^*/\text{mol·kg}^{-1}\text{·bar}^{-1}) = -5.97508 \times 10^1 + 9.34517 \times 10^3\,K/T + 2.33585 \times 10^1 \ln(T/100\ K) - 3.2874 \times 10^{-3}T/K + 5.380 \times 10^{-6}T^2/K^2 + S[2.2843 \times 10^{-2} - 2.2534 \times 10^{-4}T/K + 4.518 \times 10^{-7}T^2/K^2] \tag{28}$$

We determined eq 25 for (273 to 298) K and for a pressure range of P_B^* to 50 MPa (depending on temperature, P_B^* varied within (3.40 to 6.4) MPa) and a salinity range of 0 to 40 using an iterative procedure. An iterative procedure was necessary because there is a molality term of B on the right-hand side of the equation. Numerical calculations of the equation were approximated by the following expression with a 0.004 mol·kg^{-1} standard deviation:

$$\ln(m_B/\text{mol·kg}^{-1}) = -3.29489 \times 10^1 - 3.41348 \times 10^{-2}T/K + 5.380 \times 10^{-6}T^2K^2 + 5.180547 \times 10^3\,K/T + 2.33585 \times 10^1 \ln(T/100\ K) + S[-1.1694 \times 10^{-2} - 1.71518 \times 10^{-4}T/K + 4.518 \times 10^{-7}T^2/K^2 + 5.5246\ K/T + (-1.7667 \times 10^{-10} + 2.93886 \times 10^{-13}T/K + 2.36595 \times 10^{-8}K/T)P/Pa] + (-2.78153 \times 10^{-7} + 5.532929 \times 10^{-10}T/K + 3.70381 \times 10^{-5}K/T)P/Pa + (3.00159 \times 10^{-15} - 5.8187 \times 10^{-18}T/K - 3.9493 \times 10^{-13}K/T)P^2/Pa^2 \tag{29}$$

Figure 1a compares the calculated solubility of liquid CO_2, using eq 29, with previously measured data for water.[13,14] Predicted values agree with King et al.'s data[14] to within 0.4% of the standard deviation. Differences between Weibe and Gaddy's experimental data[13] and calculations are mostly about 2%, with the exception of four points (298 K, 5.06 MPa; 298 K, 40.5 MPa; 298 K, 40.5 MPa; 285 K, 30.4 MPa). However, the comparison of calculations and experiments for seawater[4] (Figure 1b) demonstrates reasonable agreement (within 3%) for 293 K only. For lower temperatures, the disagreement increases as temperature decreases and reaches 8 to 13% at 278 K. This disagreement will be discussed later.

Using eq 29, we calculated a profile of CO_2 concentration in seawater for a column equilibrated with liquid CO_2 (Figure 2). From this Figure, we see that the molality of CO_2 varied from 1.46 mol·kg^{-1} (400 m) to 1.97 mol·kg^{-1} (4282 m). Such a high CO_2 content should change the constants of the acid−base equilibrium, which is discussed below.

Evaluation of Stoichiometric Constants of the Carbon Dioxide System at High CO_2 Molalities

The generally accepted approach for the evaluation of constants of chemical equilibrium in seawater uses stoichiometric constants, as a function of salinity, because the relative composition of seawater is constant, rather than thermodynamic constants, and activity coefficients ex-

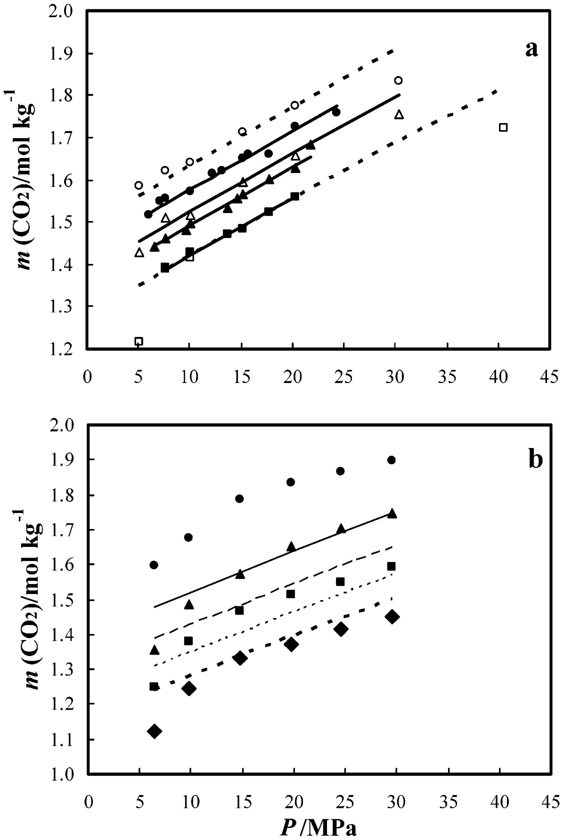

Figure 1. Comparison of the calculated solubility of liquid CO_2 (lines) using eq 29 with previously measured data in (a) water (solid symbols, King et al.[14] at the following temperatures: −●−, 288 K; −▲−, 293 K; −■−, 298 K; open symbols, Weibe and Gaddy[13] at the following temperatures: - -○- -, 285 K; −△−, 291 K; - -□- -, 298 K) and in (b) seawater (filled symbols, Teng and Yamasaki[4] at the following temperatures: ● and −, 278 K; ▲ and − −, 283 K; ■ and ···, 288 K; ◆ and - -, 293 K).

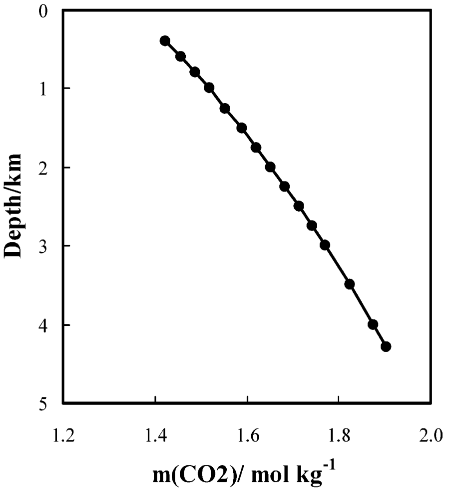

Figure 2. CO_2 concentration of a seawater column hypothetically equilibrated with liquid CO_2. Calculations were carried out using eq 29 and conductivity, temperature, and depth (CTD) data from Ocean Station Papa (50° N, 145° W, Cruise 9910).

pressed as a function of molality for each constituent. An alternative approach (Pitzer's method[6]) can also be used that takes into account the nonideal portions of the constants in terms of ionic interaction parameters and molalities of each species. Below, we will use a combined approach that is based on the assumption that the major ionic composition of seawater does not change during the interaction of liquid CO_2 with seawater. The stoichiometric constants are divided into two parts. One part takes into account the effect of the ionic medium on the dissociation equilibrium using empirical relations from salinity and temperature (commonly used stoichiometric constants); the other takes into account the effects of high CO_2 molality on the acid−base equilibrium using the Pitzer method.

The logarithm of the stoichiometric constants of carbonic acid dissociation on the molality scale can be represented by the following equations:

$$\ln k_{1C} = \ln\left[\frac{m_H m_{HCO_3}}{m_{CO_2} m^o}\right] = \ln K^o_{1C} + \ln \gamma_{CO_2} - \ln \gamma_H - \ln \gamma_{HCO_3} \quad (30)$$

$$\ln k_{2C} = \ln\left[\frac{m_H m_{CO_3}}{m_{HCO_3} m^o}\right] = \ln K^o_{2C} + \ln \gamma_{HCO_3} - \ln \gamma_H - \ln \gamma_{CO_3} \quad (31)$$

where K^o_{1C} and K^o_{2C} are thermodynamic constants of carbonic acid dissociation for the standard state (infinite dilution); k_{1C} and k_{2C} are the first and second stoichiometric carbonic acid constants at high CO_2 molalities in seawater. Pitzer's method gives an equation for the activity coefficient of any species dissolved via ion−ion, ion−molecule, and molecule−molecule interaction parameters

$$\ln \gamma_M = z_M^2 F + \Sigma m_a(2B_{Ma} + ZC_{Ma}) + \Sigma m_c(2\Phi_{Mc} + \Sigma\, m_a \psi_{Mca}) + \frac{1}{2}\Sigma m_a m_{a'} \psi_{Maa'} + z_M \Sigma\Sigma m_c m_a C_{ca} + 2\Sigma m_n \lambda_{nM} \quad (32)$$

The quantities in eq 32 are defined as follows:

$$F = f^{\gamma} + \Sigma\Sigma m_c m_a B_{ca'} + \Sigma\Sigma m_c m_{c'} \Phi_{cc''} + \Sigma\Sigma m_a m_{a'} \Phi_{aa''} \quad (33)$$

$$f^{\gamma} = -A^{\phi}\left[\frac{I^{1/2}}{1 + 1.2 I^{1/2}} + \frac{2}{1.2}\ln(1 + 1.2 I^{1/2})\right] \quad (34)$$

$$B_{MX} = \beta^0_{MX} + \beta^1_{MX} g(\alpha_1 I^{1/2}) + \beta^2_{MX} g(\alpha_2 I^{1/2}) \quad (35)$$

$$g = \frac{2[1 - (1 + x)\exp(-x)]}{x^2} \quad (36)$$

$$Z = \Sigma m_i |z_i| \quad (37)$$

$$\Phi^{\phi}_{cc'} = \Phi_{cc'} + I\Phi_{cc''} \quad (38)$$

Here, A^{ϕ} is the Debye−Huckel limiting slope, and $\alpha_1 = 2$, $\alpha_2 = 0$ for nonassociated electrolytes. For 2−2 electrolytes, the optimized values of α_1 and α_2 are 1.4 and 12 $kg^{1/2}\ mol^{-1/2}$, respectively; I is the ionic strength and Φ' represents the ionic strength derivatives of B and Φ; and β^0_{MX}, β^1_{MX}, β^2_{MX}, Φ_{ij}, ψ_{ijk}, and λ_{ni} are empirical constants (Pitzer parameters). In accordance with eq 32, we may group terms containing CO_2 molalities and rewrite eqs 30 and 31 as follows:

$$\ln k_{1C} = \ln K^o_{1C} + \ln \gamma^*_{CO_2} - \ln \gamma^*_H - \ln \gamma^*_{HCO_3} + 2m_{CO_2}(\lambda_{CO_2,CO_2} - \lambda_{CO_2,H} - \lambda_{CO_2,HCO_3}) \quad (39)$$

$$\ln k_{2C} = \ln K^{o}_{2C} + \ln \gamma^{*}_{CO_3} - \ln \gamma^{*}_{H} - \ln \gamma^{*}_{CO_3} + 2m_{CO_2}(\lambda_{CO_2,CO_3} - \lambda_{CO_2,H} - \lambda_{CO_2,CO_3}) \quad (40)$$

Reduced activity coefficients, denoted by *, are determined by eq 32 without the last term. These activity coefficients reflect the nonideal behavior of carbon dioxide system constituents when seawater has trace molalities of CO_2 (the normal state of seawater). Therefore, these terms can be described by the available stoichiometric constants as follows:

$$\ln k_{1C} = \ln K_{1C} + 2m_{CO_2}(\lambda_{CO_2,CO_2} - \lambda_{CO_2,H} - \lambda_{CO_2,HCO_3}) \quad (41)$$

$$\ln k_{2C} = \ln K_{2C} + 2m_{CO_2}(\lambda_{CO_2,HCO_3} - \lambda_{CO_2,H} - \lambda_{CO_2,CO_3}) \quad (42)$$

where K_{1C} and K_{2C} are the stoichiometric constants of carbonic acid in normal seawater and are available in the current literature.[3] When liquid CO_2 is injected into seawater, it will acidify seawater; therefore, dissociation constants of HSO_4^- and HF should be involved in the general description of the carbon dioxide system. Analogous to eqs 41 and 42, we can write

$$\ln k_{S} = \ln K_{S} + 2m_{CO_2}(\lambda_{CO_2,HSO_4} - \lambda_{CO_2,H} - \lambda_{CO_2,SO_4}) \quad (43)$$

$$\ln k_{F} = \ln K_{F} + 2m_{CO_2}(\lambda_{CO_2,HF} - \lambda_{CO_2,H} - \lambda_{CO_2,F}) \quad (44)$$

A second virial coefficient is included in eqs 41 to 44, but this parameter is immeasurable when the *i*th species is ionic. Measurements can be made only in neutral solutions, so only electroneutral combinations of these parameters, for example, are measurable.[24] Therefore, one of the CO_2-ion interaction parameters must be assigned arbitrarily. Presently, there is no generally accepted convention for the description of molecule−ion interaction. Harvie et al.[25] treated CO_2 solubility data and found using the convention. Their results are listed in Table 1. Which convention is used does not affect the final results of these calculations because they are all carried out within the electroneutral combinations. For example, in our case

$$(\lambda_{CO_2,H} + \lambda_{CO_2,HCO_3}) = \lambda_{CO_2,HCl} + \lambda_{CO_2,NaHCO_3} - \lambda_{CO_2NaCl} \quad (45)$$

In addition to data listed in Table 1, we carried out experiments on the solubility of CO_2 in HCl and $NaHCO_3$ aqueous solutions at different temperatures and obtained values for $(\lambda_{CO_2,H} + \lambda_{CO_2,Cl})$ and $(\lambda_{CO_2,Na} + \lambda_{CO_2,HCO_3})$ as a function of temperature[24]

$$(\lambda_{CO_2,H} + \lambda_{CO_2,Cl})/\mathrm{kg{\cdot}mol^{-1}} = 1.2674 - 273.414\ \mathrm{K}/T \quad (46)$$

$$(\lambda_{CO_2,H} + \lambda_{CO_2,Cl})/\mathrm{kg{\cdot}mol^{-1}} = -0.1926 + 59.669\ \mathrm{K}/T \quad (47)$$

The Pitzer parameter, $(\lambda_{CO_2,Na} + \lambda_{CO_2,Cl})$, was also required to use eqs 41 and 42. This parameter can be derived from previously published CO_2 solubility data[26] for NaCl−H_2O solutions. We treated these data by Pitzer's method using the least-squares evaluation and obtained $(\lambda_{CO_2,Na} + \lambda_{CO_2,Cl})$ parameters, expressed by the equation with a standard deviation of 0.001.

$$(\lambda_{CO_2,Na} + \lambda_{CO_2,Cl})/\mathrm{kg{\cdot}mol^{-1}} = 2.1246 + 355.666\ \mathrm{K}/T + 3.475 \times 10^{-3} T/\mathrm{K} \quad (48)$$

For further calculations, we make three assumptions. (i) Parameters of Table 1 may be used for any temperature, although they were obtained at 298.15 K. (ii) Since it is impossible to derive the λ_{CO_2,CO_3} parameter because there is no coexistence between CO_2 and CO_3 species in solution at moderate concentrations, we assumed that $\lambda_{CO_2,CO_3} \equiv \lambda_{CO_2,SO_4}$. (iii) We could not find any published data relating to CO_2(aq)−F(aq) and CO_2(aq)−HF(aq) and therefore used the approximations of $\lambda_{CO_2,HF} \equiv \lambda_{CO_2,CO_2}$ and $\lambda_{CO_2,F} \equiv \lambda_{CO_2,Cl}$. Using eqs 46 to 48, the data in Table 1, and the above-noted assumptions, we can rewrite eqs 41 to 44 as follows:

$$\ln(k_{1C}/\mathrm{mol{\cdot}kg^{-1}}) = \ln K_{1C} + \frac{m_{CO_2}(-6.908 + 1.289964\times10^{3}\mathrm{K}/T + 6.95\times10^{-3}T/\mathrm{K} - 1.0856\times10^{-9}P/\mathrm{Pa})}{m^{o}} \quad (49)$$

$$\ln(k_{2C}/\mathrm{mol{\cdot}kg^{-1}}) = \ln K_{2C} + \frac{m_{CO_2}(6.2048 - 1.13882 \times 10^{3}\ \mathrm{K}/T - 6.95 \times 10^{3}T/\mathrm{K})}{m^{o}} \quad (50)$$

$$\ln(k_{S}/\mathrm{mol{\cdot}kg^{-1}}) = \ln(K_{S}/\mathrm{mol{\cdot}kg^{-1}}) - \frac{0.2m_{CO_2}}{m^{o}} \quad (51)$$

$$\ln(k_{F}/\mathrm{mol{\cdot}kg^{-1}}) = \ln(K_{F}/\mathrm{mol{\cdot}kg^{-1}}) + \frac{m_{CO_2}(-0.124 + 31.804\ \mathrm{K}/T - 1.0856 \times 10^{-9}P/\mathrm{Pa})}{m^{o}} \quad (52)$$

Equations 49 to 52 allow us to calculate the carbon dioxide system of seawater for high CO_2 molalities.

Discussion

Theoretical aspects of the solubility of liquid CO_2 in seawater were considered earlier by Teng et al.[15] They derived the thermodynamic equation for this solubility. Using notations from our paper, this equation can be written as

$$\ln\left(\frac{m_B}{m^{o}}\right) = \ln\left(\frac{\phi^{*}_{B}\, P^{*}_{B}\, K^{*}_{o}}{m^{o}}\right) - \frac{V^{\infty}_{B}(P^{s*}_{B} - P^{o})}{RT} \quad (53)$$

Teng et al.,[15] using seawater with a salinity of 35, calculated the concentration of CO_2 (their values have been converted into molality for this publication) in seawater equilibrated with liquid CO_2 for a temperature profile (Figure 3a). Our calculations (eq 29) and the predictions from their paper[15] are compared in Figure 3b. There are two important points to note: (i) our predicted values are significantly lower than the results of their calculations, using eq 53 and (ii) our values are a function of hydrostatic pressure, but their results, from eq 53, are independent of hydrostatic pressure because when $P > P^{s*}_{B}$ (i.e. when the

Table 1. CO_2-Ion Parameter Values Obtained by Harvie et al.[25]

ion	H	Na	K	Ca	Mg	Cl	SO_4	HSO_4
$\lambda_{CO_2,i}/\mathrm{kg{\cdot}mol^{-1}}$	0.000	0.100	0.051	0.183	0.183	−0.005	0.097	−0.003

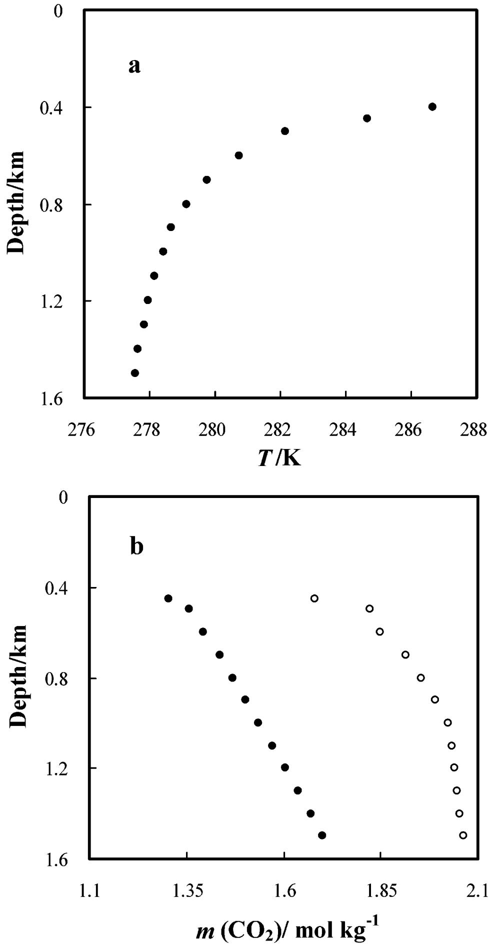

Figure 3. Comparison of the solubility of liquid CO_2 profiles calculated by Teng et al.[15] and eq 29. (a) Temperature profile of seawater at $S = 35$; (b) solubility profiles of ○, Teng et al.[15] and ●, eq 29.

depth is greater than 450 m at the temperature considered) the second term of eq 53 is constant at constant temperature. This independence of liquid CO_2 solubility from pressure in water and/or seawater is not supported by previously published experimental data[4,13,14] (Figure 1). The pressure dependence of the solubility of liquid CO_2 is determined mainly by the first and second terms of our eq 25. Interaction between dissolved CO_2 molecules causes a decrease in CO_2 solubility. The fifth term of our eq 25 takes this effect into account, but it is omitted in their eq 53.

The Pitzer method gives clear expressions reflecting the effects of each species, including dissolved CO_2 molalities (eq 19) with respect to CO_2 solubility. Irrespective of the phase state of CO_2 (gas or liquid), the equation of CO_2 solubility contains the term $\lambda_{CO_2,CO_2}m_{CO_2}$. This indicates that there is nonlinearity between CO_2 fugacity above the solution and the dissolved CO_2 contents in the solution. In other words, a deviation from Henry's law has occurred because of the nonideal behavior of dissolved CO_2 in solution. This deviation is magnified at high CO_2 molality and is taken into account by the $\lambda_{CO_2,CO_2}m_{CO_2}$ term in combination with the solubility coefficient, K_0^* (eq 14). Edwards et al.[10] obtained an empirical expression for the virial coefficient λ_{CO_2,CO_2}

$$\lambda_{CO_2,CO_2}/\text{kg}\cdot\text{mol}^{-1} = -0.4922 + 149.20\ \text{K}/T \qquad (54)$$

They considered eq 54 to be valid for a temperature range of (273 to 523) K. Figure 4 compares λ_{CO_2,CO_2} calculated by eqs 27 and 54 and extrapolated data obtained by Corti et al.[12] Reasonable agreement between eqs 27 and 54 and Corti et al.'s data[12] is found for temperatures from (293 to 309) K. For an evaluation of the λ_{CO_2,CO_2} parameter, Edwards et al.[10] and Corti et al.[12] used previously published experimental data that were originally obtained at high temperatures. Nevertheless, eq 27 gives λ_{CO_2,CO_2} parameters that are between the predictions of Edwards et al. and Corti et al. We suggest that eq 54 is preferable for the temperature range of (298 to 523) K but eq 27 is preferable for (273 to 298) K.

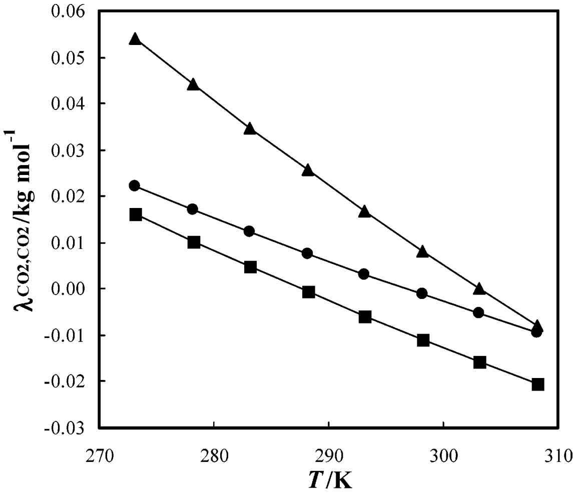

Figure 4. Comparison of λ_{CO_2,CO_2} parameters calculated by ●, eq 27 and ▲, eq 54 and from ■, extrapolated data.[12] In this paper, eq 24 was derived from the solubility of liquid CO_2 data,[14] but eq 57 and data[12] were evaluated from the solubility of CO_2 gas in water.

As noted above, Figure 1b shows agreement within 3% (except for the first point, $P = 6.44$ MPa) between the measured and calculated solubility of liquid CO_2 in seawater for a temperature of 293 K. However, at 278 K the differences between experiment[4] and calculations (eq 29) differ by up to (8 to 13)%. One potential source of error in the calculations by means of eq 29 may be the simplified expression for the activity coefficient of CO_2 (eq 19). The terms, taking into account the triplet interactions of the species in the solution ($3m_B^2\mu_{B,B,B}$, $\sum_c\sum_a m_c m_a \xi_{B,c,a}$, $\sum\sum_{c<c'} m_c m_{c'} \eta_{B,c,c'}$, $\sum\sum_{a<a'} m_a m_{a'} \eta_{B,a,a'}$) were omitted when writing eq 19 because it was found in previous studies[10,12] that $\ln(\gamma_B)$ is a linear function of m_B within experimental uncertainties. We therefore set $\mu_{B,B,B}$ equal to zero. When the molality of the salts exceeds 1, the term $\sum_c\sum_a m_c m_a \xi_{B,c,a}$-becomes important.[11,12] In our case, at maximum salinity (40) all ionic species have a molality of less than 1. At the present time, the commonly used formula in chemical oceanography (eq 17) for the logarithmic solubility coefficient of CO_2 in seawater has only a linear term in relation to the salinity function. This means that the triplet interaction should be insignificant. Therefore, the simplified form of eq 19 for the activity coefficient of CO_2 should not contribute significant errors to the calculations of the solubility of liquid CO_2 in seawater. The effect of pressure on the partial molar volume of dissolved carbon dioxide had to be ignored because the required data were not available. Because the partial molar compressibility of most dissolved species is on the order of 10^{-3} $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{bar}^{-1}$ (see ref 27), the maximum error caused by this approximation is an underestimation of the solubility by 0.01 $\text{mol}\cdot\text{kg}^{-1}$ for 50 MPa, calculated by eq 29. This error is less than 1%. We assume that salt contained in the solution decreases the partial molar volume of about 1 $\text{cm}^3\cdot\text{mol}^{-1}$ in $V_B^{L_2}$. Thus,

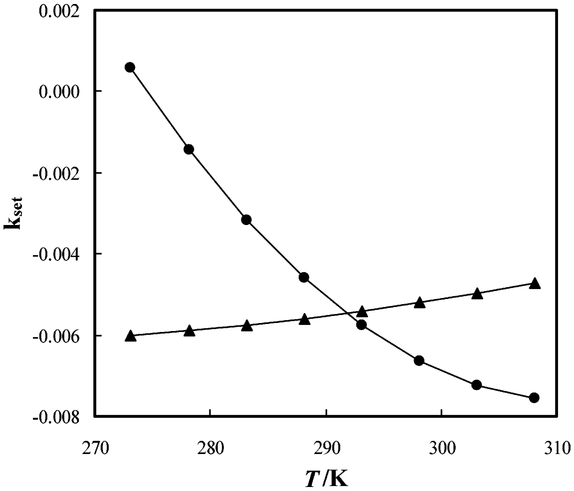

Figure 5. Comparison of Setschenow coefficients (k_{set}) calculated by equations suggested by ●, Teng and Yamasaki[4] and ▲, Weiss.[18]

an underestimation of the solubility would be expected to be about 2% at the highest considered salinity and pressure, but values predicted by eq 29 are systematically higher than the experimental data[4] for 293 K (Figure 1b). However, there are opposing strong systematic differences at low temperature that are unexpected when neglecting the salt effect on the partial molar volume of CO_2. The experimental slopes of the dependence of solubility versus pressure (Figure 1b) are close to those calculated for the pressure range of (15 to 30) MPa. However, at low pressures the experimental slopes sharply increase. We have not found any theoretical argument in the published literature for such a change in the experimental slope. Figure 5 compares the Setschenow coefficient calculated by equations suggested in the publications of Teng and Yamasaki[4] and Weiss.[18] There is satisfactory agreement between the two sets of Setschenow coefficients for 293 K only, where the experimental and calculated solubilities of liquid CO_2 in seawater are in good agreement. According to the equation suggested by Teng and Yamasaki,[4] the Setschenow coefficient increases as temperature decreases and becomes positive close to 273 K. Positive values of the Setschenow coefficient would result in increasing values for the solubility of CO_2 gas in seawater as salinity increases, but this contradicts all experimental data for the solubility of CO_2 gas in seawater. Because our calculated solubility of liquid CO_2 in pure water agrees well with experimental data[13,14] (Figure 1a) and because we used well-established Setschenow coefficients,[18] we believe that eq 29 gives more reasonable values than the experimental data obtained by Teng and Yamasaki.[4]

The Pitzer method gives clear terms for taking into account the effects of high CO_2 molalities on the stoichiometric constants of the carbon dioxide system (eqs 41 to 44). For an accurate determination of the first dissociation constant at high CO_2 concentration, an extended experimental study of CO_2 gas solubility in HCl and $NaHCO_3$ aqueous solutions was carried out.[24] These data were combined with available CO_2 solubility in NaCl solutions,[17] which permitted an accurate account of the nonideal effects of dissolved CO_2 on the first dissociation of carbonic acid. The experimental uncertainties of the $\lambda_{CO_2,NaHCO_3}$ parameter[24] limit the accuracy of our prediction of $\log(k_{1C})$, which we estimate to be ±0.015 for $\log(k)$. Alkalinity and pH are the most important parameters of the carbon dioxide system for technological control during the disposal of liquid CO_2 into the ocean because these parameters are easiest to measure at high CO_2 concentrations. Alkalinity does not depend on CO_2 concentration; therefore, it can be accurately measured by generally accepted methods, and pH may be measured by an in situ probe, as was demonstrated in the pioneering experiments conducted by Brewer et al.[28,29]

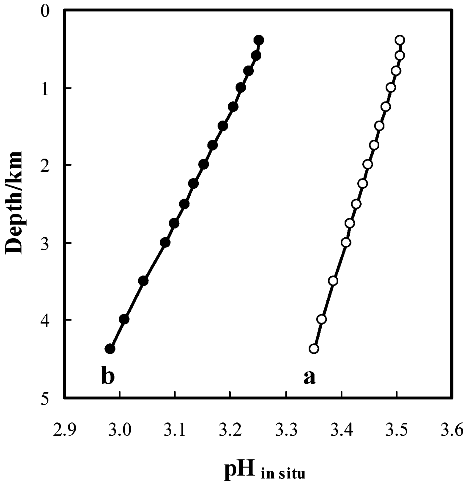

Figure 6. Theoretical CO_2-saturated seawater pH profiles of Station Papa calculated (a) with and (b) without taking into account the effects of CO_2 concentration on the equilibrium constants.

As an aid to a better understanding of the main features of the carbon dioxide system during the disposal of liquid CO_2, we carried out modeling calculations of the carbonate parameters for Ocean Station Papa (50° N, 145° W). In these calculations, we used real *T*, *S*, and TA profiles obtained for Ocean Station Papa and an additional assumption that the seawater was equilibrated with liquid CO_2. To estimate the effects of high CO_2 molality on calculated $pH_{in\ situ}$ and molalities of HCO_3, HSO_4, and HF, we carried out these calculations with two sets of constants: (1) those that include the effect of CO_2 molality (eqs 49 to 52) (taking into account the effects of CO_2 molality on equilibrium constants) and (2) K_i constants that have no term containing CO_2 molality (without taking into account the effects of CO_2 molality on equilibrium constants). Figure 6 demonstrates theoretical pH profiles calculated with and without taking into account the effects of CO_2 concentrations on equilibrium constants. The behavior of the carbon dioxide system at high CO_2 concentration has the distinct feature of higher molalities of the HCO_3^- species compared to alkalinity, as seen in Figure 7. An exact definition of the total alkalinity (TA) is as follows:[30]

$$\mathrm{TA} = m_{\mathrm{HCO_3^-}} + 2m_{\mathrm{CO_3^{2-}}} + m_{\mathrm{B(OH)_4^-}} + m_{\mathrm{OH^-}} + m_{\mathrm{HPO_4^{2-}}} + 2m_{\mathrm{PO_4^{3-}}} + m_{\mathrm{SiO(OH)_3^-}} + m_{\mathrm{HS^-}} + 2m_{\mathrm{S^{2-}}} + m_{\mathrm{NH_3}} + \ldots - m_{\mathrm{H^+}} - m_{\mathrm{HF}} - m_{\mathrm{H_3PO_4}} - m_{\mathrm{HSO_4^-}} \quad (55)$$

However, the simplified form of eq 55 may be used for normal oceanic conditions:

$$\mathrm{TA} = m_{\mathrm{HCO_3^-}} + 2m_{\mathrm{CO_3^{2-}}} + m_{\mathrm{B(OH)_4^-}} + m_{\mathrm{OH^-}} + \ldots - m_{\mathrm{H^+}} - m_{\mathrm{HF}} - m_{\mathrm{HSO_4^-}} \quad (56)$$

Total alkalinity is independent of CO_2 content, but constituents included in eq 55 are not. At low pH values

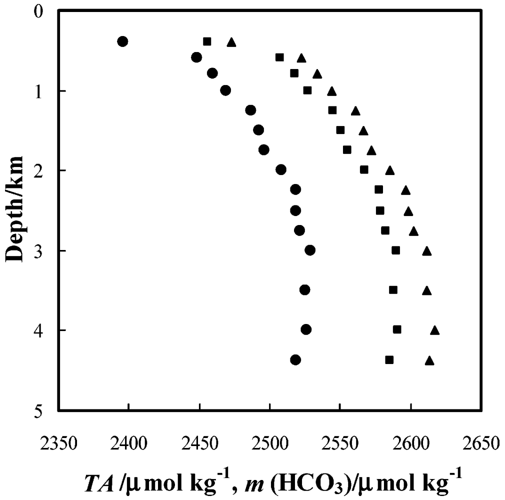

Figure 7. TA measured (●) at Station Papa (Cruise 9910) and theoretical molality of HCO_3 profiles calculated for CO_2 saturated seawater with (■) and without (▲) taking into account the effects of CO_2 concentration on equilibrium constants.

(3.3 to 3.5), carbonic acid titrates SO_4^{2-} and F^- anions according to the reactions

$$CO_2 + H_2O + SO_4^{2-} \leftrightarrow HCO_3^- + HSO_4^-$$

and

$$CO_2 + H_2O + F^- \leftrightarrow HCO_3^- + HF$$

According to these reactions, high CO_2 content will increase the molality of the HCO_3^-, HSO_4^-, and HF species. Expected concentrations of HSO_4^- and HF are shown in Figure 8. It is clearly seen from Figures 6 to 8 that the effect of dissolved CO_2 on calculated parameters is appreciable. The difference between the two pH profiles is as high as 0.35 pH units (Figure 6).

Direct pH measurements of the interaction of liquid CO_2 and seawater were carried out by Brewer et al.[29] at 619 m depth for $T = 277.92$ K and pH 4.5 on the NBS scale. This pH value converts to 4.35 pH units on the total concentration scale.[19] For similar conditions, our predicted pH value is about 3.51. The main difference between Brewer's[29] measured pH value and our predicted values can be explained as follows.

First, full equilibrium between liquid CO_2 and seawater was probably not reached because of kinetic limitations of the dissolution process. This would result in a higher detected pH value. Second, the experimental conditions were considered to be metastable for liquid CO_2—seawater equilibrium because of hydrate formation.[16,17] This would also result in higher detected pH values. Equation 29 was evaluated for a temperature range of (273 to 298) K, a pressure range of (3 to 50) MPa, and salinities of 0 to 40, but its application may be limited by T, P, S conditions. Liquid CO_2 is metastable in relation to CO_2 hydrates at temperatures below 283.2 K in pure water[16] and below 280.8 K in seawater (our estimation) for the considered pressure range. In hydrate-forming regions, the solubility of CO_2 has a temperature dependence (i.e., positive slope rather than negative slope with increasing temperature) opposite to that of liquid CO_2 in seawater, as has been recently shown.[17] However, recent experiments on CO_2 dissolution in hydrate-forming regions[31] demonstrated that CO_2 droplets were not often covered with a hydrate membrane. The dissolution rate of droplets not covered with hydrate was higher than that of droplets with a hydrate membrane. The temperature dependence of the dissolution rates of these two types of CO_2 droplets also had opposite slopes. The dissolution rate is strongly dependent on solubility.[15,31] Thus, eq 29 may be useful for describing the dissolution of liquid CO_2 even in the hydrate-forming region for some situations. Obviously, the kinetic aspects of liquid CO_2 dissolution, the thermodynamics of gas hydrate formation, and the solubility of gas hydrates should also be considered when describing the scenario for the disposal of liquid CO_2 into the ocean.

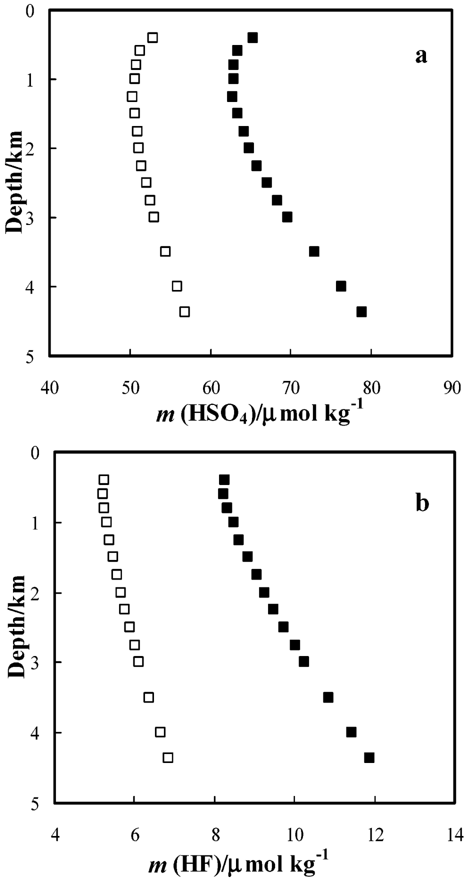

Figure 8. Theoretical molality of (a) HSO_4^- and (b) HF profiles calculated for CO_2-saturated seawater with (□) and without (■) taking into account the effects of CO_2 concentration on equilibrium constants from Station Papa.

Conclusions

A thermodynamic consideration of the equilibrium between three phases (CO_2—gas, liquid CO_2, and seawater) permits us to include the Henry's law constant in an equation for the solubility of liquid CO_2 in seawater (eq 16). This equation was parametrized as a function of temperature, pressure, and salinity using available thermodynamic data, and eq 29 was obtained for calculating the solubility of liquid CO_2 in seawater. Equation 29 is applicable for the temperature range of (273 to 298) K, pressure range of (3 to 50) MPa, and salinities of 0 to 40 when two phases coexist (liquid CO_2 and seawater).

Very high CO_2 concentration results in the low pH of seawater (less than 4 pH units). Under these conditions, CO_2 partially converts SO_4^{2-} and F^- ions to HSO_4^- and HF. Therefore, concentrations of HCO_3^- will exceed the total alkalinity.

The effects of high CO_2 concentration on the constants of the carbon dioxide system were taken into account using combined approaches: the Pitzer method and the method of stoichiometric constants. The effect of high CO_2 concentration on the constants of the carbon dioxide system shifts the carbonate equilibrium toward that of increasing pH of seawater. Results indicated this shift is greater than 0.3 pH units.

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Page 827. Equations 46 and 48 contain errors. The correct equations are as follows:

$$(\lambda_{CO_2,Na} + \lambda_{CO_2,HCO_3})/\text{kg}\cdot\text{mol}^{-1} = 1.2674 - 273.414\ \text{K}/T \quad (46)$$

and

$$(\lambda_{CO_2,Na} + \lambda_{CO_2,Cl})/\text{kg}\cdot\text{mol}^{-1} = -2.1246 + 355.666\ \text{K}/T + 3.475 \times 10^{-3} T/\text{K} \quad (48)$$

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