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Solubility of Carbon Dioxide in Water under Incipient Clathrate Formation Conditions

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The solubility of carbon dioxide in water was measured at temperatures from 1 °C to 15 °C, at pressures approaching the clathrate-forming pressure. The goal was to fill gaps in the literature as well as to look for evidence of structural changes in liquid water near the onset of clathrate formation. The data were analyzed according to the Krichevsky−Kasarnovsky (KK) equation. The Henry's law constant K_H and the partial molar volume at infinite dilution $\bar{V}^{\infty}_{CO_2}$ were determined at each temperature. Contrary to claims based on older data in the literature, the KK equation was found to be an adequate representation of the solubility. The Henry's law constants are in excellent agreement with accepted literature values. No evidence was found for dramatic changes in water structure as the clathrate-forming pressure is approached.

Introduction

The ubiquity of carbon dioxide/water mixtures in natural and artificial settings has given rise to many studies of the solubility of carbon dioxide. When the pressure of carbon dioxide in a system of gaseous CO_2 and liquid water is high enough and the temperature is low enough, a new phase forms; it is the solid clathrate hydrate compound, with the approximate formula $CO_2 \cdot 6H_2O$.[1] A clathrate is a cage structure in which a guest molecule (in this case CO_2) is held in a cage of water molecules that is formed by a modification of the crystal structure of ice. Water, clathrate, and gaseous CO_2 can coexist at temperatures in the range from about −1 °C to about 10 °C.[2] At 0.78 °C the clathrate-forming pressure is 13.7 bar; at 9.76 °C it is 44.6 bar.[2] Below the clathrate-forming pressure, the mole fraction of carbon dioxide dissolved in water is generally on the order of 0.02 or less. In a clathrate having the formula $CO_2 \cdot 6H_2O$, however, the mole fraction of CO_2 is $^1/_7 = 0.143$. It is reasonable to ask whether some of this large change occurs while the water is still liquid or only when a solid phase forms. Only sparse data exist in the pressure and temperature regime near the onset of clathrate hydrate formation. Once the clathrate begins to form, it becomes nearly impossible to assess the partitioning of CO_2 between the liquid and solid phases. This fact invalidates some of the older solubility data in the literature, since the possibility of the existence of a solid phase was not acknowledged by and probably not known to the investigators.

This work extends the study of CO_2 solubility in water to a temperature and pressure regime where incomplete or invalid data had existed previously. We are able to model the solubility using the well-known Krichevsky−Kasarnovsky[3] (KK) equation using physically reasonable parameters.

Experimental Section

Materials. Carbon dioxide with a stated purity of 99.995% was obtained from Matheson Tri Gas. Laboratory tap water was purified with a Barnstead Nanopure model 4751 deionizer which was also equipped with an organic removal filter.

Apparatus. Solubility measurements were made in an Autoclave Engineers "Zipperclave" pressure vessel. The vessel has a nominal capacity of 1 L. An accurate measurement of the autoclave and associated connections determined the system volume to be (1.119 ± 0.011) L. The autoclave was jacketed by an aluminum vessel through which coolant (50% aqueous propylene glycol solution) was circulated, using a VWR model 1172 chiller to control the temperature of the coolant. A separate small chiller was used to circulate coolant through the top cover of the autoclave. The autoclave was stirred by a gas-entraining stirrer via a magnetically coupled, air-driven motor. The temperature in the autoclave was measured to ±0.1 °C by means of a type K thermocouple read by a Stanford Research Systems model SR630 thermocouple readout. Pressure was measured either with a Baratron electronic manometer (for pressures near 1 bar) or with Heise (Bourdon tube) dial pressure gauges. The Heise gauge range was selected to give the greatest possible accuracy for each experiment. The estimated accuracy of the pressure measurements was as follows:

0 to 1.5 bar,	±0.002 bar
1.5 to 7.0 bar,	±0.010 bar
7.0 to 15 bar,	±0.02 bar
15 to 30 bar,	±0.10 bar

Carbon dioxide and water were admitted to the system via separate ports. Deionized water was injected into the autoclave through a valve by means of an Isco model 260D positive displacement pump which recorded the volume delivery with a precision of 0.01 mL.

Procedure. An experiment consisted of the following steps: (i) repeatedly flush and vent the system with CO_2 to remove all air; (ii) admit CO_2 gas at a known temperature and pressure; (iii) inject a known volume of water (nominally 500 mL) into the autoclave at room temperature; (iv) while stirring, chill the autoclave to approximately 0 °C (or to the lowest possible temperature before clathrates

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start to form) and wait (1 to 2) h for equilibration; (v) turn off the refrigeration in the chiller, allowing the autoclave to warm slowly; (vi) record the pressure at 2 °C increments in temperature, from 1 °C to 15 °C.

Analysis and Results. The analysis is based on two reasonable assumptions: (i) the liquid phase has nearly constant volume, and (ii) the gas phase is nearly all CO_2 and is therefore described well by the pure CO_2 equation of state.

We examine each assumption in turn. Pure water is all but incompressible and has only a small amount of thermal expansion over the range of temperature from 0 to 15 °C. Dissolved carbon dioxide amounts at most to about 3 mole %, which is not enough to appreciably change the volume. The vapor pressure of pure water is less than or equal to 0.025 bar over the range of temperatures in this experiment. This is negligible with respect to the pressures of carbon dioxide employed, except perhaps at the lowest pressure (approximately 1 bar). Thus, the contribution of water vapor to the gas phase can be neglected in most of the data and simply corrected for in the low-pressure runs.

The determination of the mole fraction of CO_2 dissolved in the water phase proceeds simply from the data. The starting temperature and pressure are used to find the initial CO_2 density using an equation of state (EOS). This yields the total number of moles, since the volume is known. After the water is injected, the density of CO_2 remaining in the gas phase is determined at each temperature and pressure from the EOS. Now the number of moles in the gas phase is found using the new gas volume, which is the autoclave volume (1.119 L) minus the volume of water (nominally 0.5 L) injected. The number of moles of CO_2 dissolved in the water is found by difference. The relative volumes of liquid and gas phases were chosen to give a roughly equal partitioning of the CO_2, resulting in the greatest possible accuracy. Each experiment yields a table of temperature (T), pressure (p), and dissolved mole fraction (x), at 2 °C temperature increments. By repeating the experiment at several initial pressures, sets of data for x versus p were generated at each temperature. These rearranged data sets were then used to model the results.

The equation of state data for CO_2 came from the *NIST Chemistry WebBook*.[4] CO_2 is one of a small group of gases for which highly accurate EOS data are available from this source.

To make a rough estimate of the uncertainty in the determination of dissolved mole fraction x, we note that the greatest source of random error would appear to be in the pressure measurements. Since x is determined (approximately) by the *difference* between two pressure measurements of similar precision, a reasonable estimate of the fractional uncertainty in x is $\sqrt{2}$ times the fractional uncertainty in p. This varies depending on the pressure range of a given experiment (i.e., which of several gauges was used), so no single number can be given. The uncertainty in each pressure range was given in the Experimental Section. The "best case" fractional uncertainties in x are on the order of ±0.20%, while the "worst case" uncertainties approach ±1.0%. Another (but more qualitative) way to assess random error is to examine the scatter in the data from individual experiments; the results of this examination are consistent with the above random error estimates.

The data analysis requires the fugacity of CO_2 in the vapor phase, which by assumption we take to be the fugacity of pure CO_2 at the same pressure. The fugacity of CO_2 is found from the EOS by the use of the rigorous expression given by Prausnitz, et al.[5]

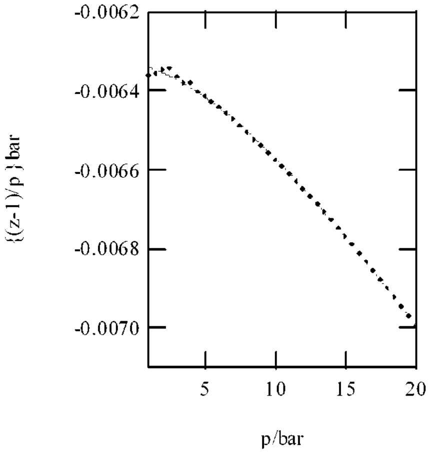

Figure 1. Fourth-order polynomial fit to the integrand of eq 1, for carbon dioxide at t = 5 °C.

$$\ln(f/p) = \int_0^p \frac{z-1}{p}\,\mathrm{d}p \tag{1}$$

where $z \equiv pV/RT$ is the compressibility factor of the gas. We wish to know how the fugacity varies with pressure in the temperature range 1 to 15 °C, at intervals of 2 °C. Therefore, for each temperature we perform a numerical integration of eq 1 by fitting the integrand to a third-order polynomial in p. Figure 1 shows the EOS data for the integrand at t = 5 °C, with the third-order fit superimposed.

A minor problem occurs in that some nonphysical values of the integrand are generated at low pressure, due to small inaccuracies in the EOS data. These data points are merely eliminated before fitting takes place. Given

$$\left\{\frac{z-1}{p}\right\}\text{bar} = a_0 + a_1(p/\text{bar}) + a_2(p/\text{bar})^2 + a_3(p/\text{bar})^3 \tag{2}$$

integration of eq 1 leads directly to

$$f/p = \exp[a_0(p/\text{bar}) + a_1(p/\text{bar})^2/2 + a_2(p/\text{bar})^3/3 + a_3(p/\text{bar})^4/4] \tag{3}$$

When f/p has been found by this rigorous and highly accurate technique, it is found to deviate only slightly from unity over the modest pressure range in these experiments. Therefore, f/p can be expressed adequately by a much simpler expression than eq 3. In Figure 2 we plot (f/p − 1) versus p (again at 5 °C).

A straight line fit is found to be perfectly adequate. This conclusion is valid for all temperatures in the range of the present results, at all pressures up to 20 bar. Thus, we have the simple parametrization

$$f/p = 1 + k_0 + k_1(p/\text{bar}), \tag{4}$$

where the coefficients k_0 and k_1 are given in Table 1.

The starting point for modeling the results is the rigorous thermodynamic statement that, at equilibrium, the fugacity of a given component is the same in each of the phases. For CO_2

$$\hat{f}^{\,l}_{CO_2} = \hat{f}^{\,v}_{CO_2} \tag{5}$$

At low pressures both the liquid and vapor are ideal, in which case the liquid fugacity is proportional to the mole

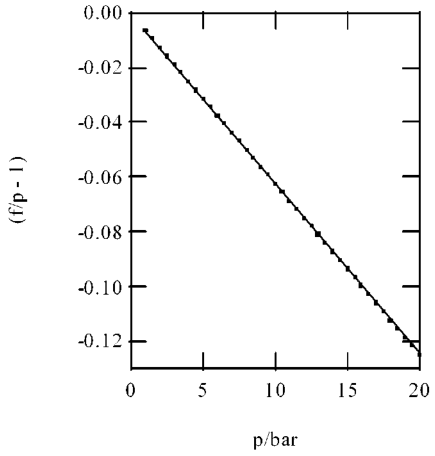

Figure 2. ($f/p - 1$) versus p for carbon dioxide at 5 °C.

Table 1. Coefficients for Determination of CO_2 Fugacity via Eq 4

t/°C	10^4k_0	10^3k_1/bar
1	−1.158	−6.4786
3	−1.362	−6.3240
5	−2.112	−6.1623
7	−2.872	−6.0073
9	−3.170	−5.8656
11	−2.8982	−5.7286
13	−3.1292	−5.5960
15	−2.9783	−5.4673

fraction and the vapor fugacity is equal to the gas partial pressure. This gives rise to the simplest form of Henry's law

$$x_{CO_2}K_H = y_{CO_2}p \quad \text{(Henry's law, ideal gas)} \tag{6}$$

x_{CO_2} and y_{CO_2} are the mole fractions of CO_2 in the liquid and vapor phases, respectively, K_H is Henry's constant, and p is the total pressure. At intermediate pressures the vapor phase must be treated as a real gas while the liquid-phase remains ideal, and the pressure dependence of the fugacity in the liquid phase can be neglected.

$$x_{CO_2}K_H = \hat{f}^{\,v}_{CO_2} = y_{CO_2}\phi_{CO_2}p \quad \text{(Henry's law, real gas)} \tag{7}$$

where ϕ_{CO_2} is the fugacity coefficient. When the pressure is large, the dependence of $\hat{f}^{\,l}_{CO_2}$ on pressure must be explicitly included. This results in the Krichevsky−Kasarnovsky[3] equation

$$x_{CO_2}K_H \exp\left\{\frac{\bar{V}^{\infty}_{CO_2}(p - p^0)}{RT}\right\} = \hat{f}^{\,v}_{CO_2} \quad \text{(KK equation)} \tag{8}$$

where $\bar{V}^{\infty}_{CO_2}$ is the partial molar volume of CO_2 in water at infinite dilution and p^0 is the vapor pressure of water (the pressure at which the reference fugacity is defined). The term in eq 8 involving $\bar{V}^{\infty}_{CO_2}$ is called the Poynting correction term to Henry's law. Dropping superfluous symbols and rearranging,

$$\ln(f/x) = \ln K_H + \frac{\bar{V}^{\infty}(p - p°)}{RT} \tag{9}$$

The KK equation states that a plot of ln(f/x) versus ($p - p°$) for a given T will be a straight line with intercept ln K_H and slope $\bar{V}^{\infty}/RT$.

Figure 3 shows our data for f/x versus ($p - p°$) for odd integral temperatures between 1 °C and 15 °C. Also shown are the straight lines that were least-squares fitted to the data.

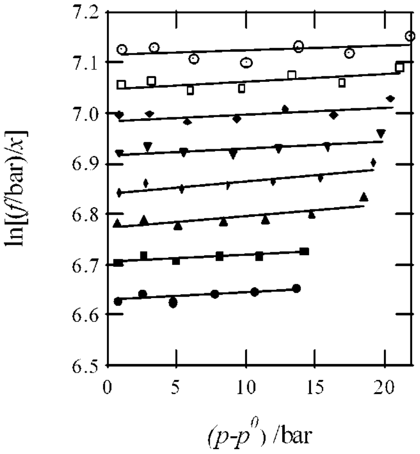

Figure 3. KK plots for CO_2 solubility in H_2O: ●, 1 °C; ■, 3 °C; ▲, 5 °C; ♦, 7 °C; ▼, 9 °C; ◆, 11 °C; □, 13 °C; ⊙, 15 °C.

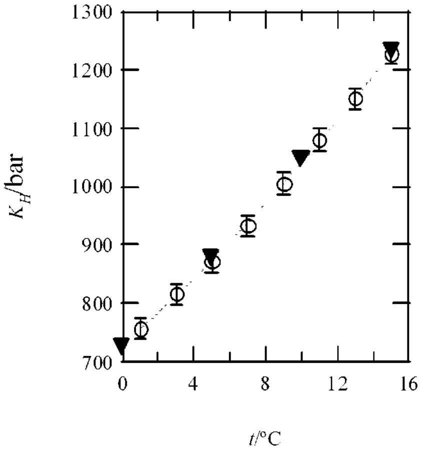

Figure 4. Henry's law constants measured in this work, compared with the recommended values from ref 6: ○, this work; ▼, Crovetto.

Table 2. Results of KK Analysis of CO_2 Solubility in H_2O

t/°C	ln(K_H/bar)	K_H/bar	$\bar{V}^{\infty}_{CO_2}$/(cm^3 mol^{-1})
1	6.629 ± 0.001	756 ± 1	39 ± 31
3	6.705 ± 0.008	817 ± 6	31 ± 22
5	6.771 ± 0.016	872 ± 14	57 ± 32
7	6.840 ± 0.013	934 ± 12	58 ± 26
9	6.914 ± 0.013	1006 ±13	36 ± 28
11	6.986 ± 0.017	1081 ± 18	31 ± 33
13	7.049 ± 0.017	1152 ± 19	31 ± 33
15	7.114 ± 0.023	1229 ± 29	24 ± 43

In Table 2 we give the values of K_H and $\bar{V}^{\infty}_{CO_2}$ that were determined by the fitting procedure. The stated uncertainties are two times the estimated standard deviations found in the least-squares fitting procedure.

In Figure 4 we plot the Henry's law constants derived from the KK analysis, along with the recommended values given by Crovetto[6] based on an exhaustive analysis of data taken at low pressures. The near-perfect agreement of our results with those in ref 6 lends confidence in the validity of our technique and the quality of our data.

Discussion

The $CO_2 + H_2O$ system has been studied extensively over the past 150 years. Comprehensive reviews have been written by Crovetto[6] and Carroll and Mather.[7] Crovetto[6] mentions the KK equation and the techniques required to find Henry's law constants from pressure-dependent solubility data. However, the focus of her work is to parametrize the temperature dependence of the Henry constant, which is the zero-pressure intercept of the KK equation. She makes no use of the available data for pressure dependence at low temperatures, which is the focus of the present work. In contrast to Crovetto,[6] Carroll and Mather[7] are primarily interested in the pressure dependence of CO_2 solubility, specifically examining whether the KK equation is obeyed. With respect to data at temperatures close to 0 °C, however, they find many problems in the literature. In particular, many authors have made use of the "data" of Houghton et al.,[8] who in turn used the solubility data of Zelvensky.[9] Zelvensky measured solubility as a function of pressure at (0, 12.43, 25, 50, and 75) °C. Houghton et al.[8] then interpolated that data to get solubility at other temperatures. The arbitrary nature of the choice of an interpolation technique is a serious weakness. A bigger problem is that much of Zelvensky's data at 0 °C were taken at pressures where a clathrate phase could have formed. Thus, the data at 0 °C are suspect, and any interpolation between 0 and 12.43 °C is suspect also. No other pressure-dependent solubility data have been found in the literature for temperatures in the clathrate-forming range.

The data of Houghton et al.[8] have been used by some investigators to infer that the KK equation is not valid for the $CO_2 + H_2O$ system. Parkinson and de Nevers[10] used a direct technique to measure the partial molar volume of CO_2 in water and then extrapolated to zero pressure to find the infinite dilution value, which they report as $\bar{V}^{\infty}_{CO_2} =$ 37.6 cm^3/mol. However, they used the Houghton et al.[8] solubility results to reduce their data. While their infinite dilution value seems quite reasonable, they find anomalously large values of $\bar{V}_{CO_2}$ at high pressures for temperatures below 16.65 °C, which is exactly the range in which the solubility data are suspect. They themselves acknowledged the possibility of false conclusions from errors in the data. There is simply no physical reason to believe that the partial molar volume of CO_2 in water increases from 37.6 cm^3/mol to 65.8 cm^3/mol as the pressure is increased in the clathrate-forming vicinity, as their results imply. If anything, $\bar{V}_{CO_2}$ should decrease as the conditions for clathrate formation become more favorable. Gibbs and van Ness[11] also inferred that the KK equation is invalid because they could not fit the KK equation using the Houghton et al.[8] data and Parkinson and de Nevers'[10] value for $\bar{V}^{\infty}_{CO_2}$. They invoked the need to add a further term correcting for nonideality of the solute, resulting in the so-called Krichevsky−Ilinskaya[12] equation. However, the additional term (supposedly independent of temperature) used in the KI equation showed a large and completely nonphysical variation with temperature, even changing sign at 25 °C.

Carroll and Mather[7] pointed out the abovementioned problems with the low-temperature data but were able to test the KK equation at temperatures above 50 °C, where data are more plentiful and presumably more accurate. Even here, though, all is not well. While the (50, 75, and 150) °C data fit the KK equation very well with reasonable values of 30 to 35 cm^3/mol for $\bar{V}^{\infty}_{CO_2}$, the intermediate and higher temperature data do not. Many of the data sets have anomalous points which have a large effect on the apparent $\bar{V}^{\infty}_{CO_2}$ when they are left out of the analysis. Carroll and Mather[7] concluded that the KK equation is valid below 100 °C and invalid above 100 °C, though they offered no further explanation. Our results are consistent with theirs and show that the range of validity of the KK equation extends at least from 100 °C down to 0 °C.

Conclusion

In conclusion, the low-temperature solubility of carbon dioxide in water appears to be very well modeled by the Krichevsky−Kasarnovsky equation. The apparent CO_2 partial molar volume at infinite dilution, while exhibiting considerable uncertainty and scatter, has an average value of 38.4 cm^3/mol over the temperature range from 1 °C to 15 °C. This is very reasonable and is close to the value of 37.6 cm^3/mol measured by Parkinson and de Nevers.[10] There is no evidence for significant changes in the structure of water near the onset of clathrate formation. These experiments demonstrate that very accurate solubility data are required to test the KK equation, due to the smallness of the Poynting correction term.

Supporting Information Available:

Tables listing pressure, fugacity, and dissolved mole fraction for the CO_2 + water system at various temperatures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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