

Parameterization of drag and dissolution of rising CO₂ drops in seawater

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[1] In this work the dynamics and dissolution of a hydrate-covered CO₂ drop were studied, using a numeric model and data from one of very few CO₂ experiments performed in the real ocean. A theory including the standard drag curve of rigid spheres was shown not to fit the observed drop rise velocity. However, a drag parameterization supported by numerous laboratory experiments with gas bubbles provides a good match of the observed rise velocity of a liquid CO₂ drop covered with hydrate. The results confirm laboratory results showing that shape is a key factor determining the CO₂ drop dynamics. We also found that hydrate reduces the mass transfer of the observed drop by a factor of 2, which is compatible with laboratory experiments. Numerical experiments with different drop sizes showed that the choice of drag parameterization has a significant impact on the estimated vertical distribution of dissolved CO₂.

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1. Introduction

[2] To mitigate the increasing atmospheric CO₂ level and reduce the subsequent impacts, sequestration of CO₂ is one option that might become needed in a conversion period to newer energy forms. Ocean storage and storage of CO₂ under the sea bottom with potential leakage into the ocean both require knowledge of the behavior of CO₂ drops in seawater. To achieve such knowledge, several model calculations [Sato *et al.*, 2000; Chen *et al.*, 2003; Alendal and Drange, 2001] and laboratory experiments [Aya *et al.*, 1997; Hirai *et al.*, 1996] have been performed. Only a few ocean experiments have been made so far. Brewer *et al.* [1999] did deep-sea experiments with injection of liquid and gaseous CO₂, Rehder *et al.* [2002] studied methane bubbles released into the ocean and Tsouris *et al.* [2004] injected a mix of CO₂, seawater and hydrate into the sea.

[3] Brewer *et al.* [2002] released single CO₂ drops into the ocean in Monterey Bay, California. Fixed to an ROV was a transparent imaging box, open in top and bottom so

that the drops could move freely in the vertical direction when released inside. A meter scale was attached to the box, and a high-definition television camera was positioned at the ROV. This way Brewer *et al.* [2002] impressively managed to follow and measure the drops while rising several hundred meters. A drop with initial diameter of 8.9 mm was followed for about 45 min, rising from 800 m to about 500 m. A second larger drop was attached to this drop after a while; however it was possible to measure the properties of each drop individually and no change in rise velocity was observed due to the attachment [Brewer *et al.*, 2002]. Only the first drop is included in this study. Data from five observational points were given by Brewer *et al.* [2002]. At 800 m the seawater temperature was 4.4°C and it increased to 5.4°C at 500 m. CO₂ hydrate is expected to form at depths greater than 200–400 m and at temperatures below 10°C. A thin hydrate layer was observed to surround the drop.

[4] In the present study a numerical model is used to simulate the observed drop [Brewer *et al.*, 2002]. The seawater and CO₂ drop characteristics from the ocean experiment are implemented in the numerical model.

2. Theoretical Approaches

2.1. Rise Velocity

[5] The drop terminal rise velocity, U_T [m/s], can be calculated from the equation:

$$U_T = \left(\frac{8gr_e(\rho - \rho_{CO_2})}{3C_d\rho} \right)^{0.5} \quad (1)$$

Here g [m/s²] is the gravitational acceleration, r_e [m] is the equivalent radius, ρ [kg/m³] is the seawater density, ρ_{CO_2} [kg/m³] is the density of CO₂ and C_d [1] is the drag coefficient. All parameters in equation (1), apart from the drag coefficient, can be taken from Brewer *et al.* [2002]. Two different drag parameterizations will be used to match results from Brewer *et al.* [2002].

[6] Some laboratory experiments have shown that hydrate-covered CO₂ drops get spherical shapes [Radhakrishnan *et al.*, 2003, and references therein]. It has been suggested that these drops behave as rigid spheres

Table 1. The Dimensionless Numbers of the Observed Drop [Brewer *et al.*, 2002], at Five Stages^a

Depth [m]	Re [1]	Eo [1]	Mo [1]
804.5	871.02	3.12	$9.34 \cdot 10^{-11}$
706.3	656.73	1.59	$1.03 \cdot 10^{-10}$
649.1	558.00	1.08	$1.09 \cdot 10^{-10}$
602.1	436.14	0.64	$1.14 \cdot 10^{-10}$
496.8	209.53	0.14	$1.27 \cdot 10^{-10}$

^a $Re = 2r_e \rho U / \mu$, $Eo = [gd_e^2(\rho - \rho_{CO_2})] / \sigma$ and $Mo = [g\mu^4(\rho - \rho_{CO_2})] / (\rho^2 \sigma^3)$, where U is the relative velocity between the CO₂ drop (U_T) and the seawater. The seawater velocity is set equal to 0 m/s as the natural background velocities in seawater are orders of magnitude smaller than the velocities studied here, and the drag produced by the walls of the imaging box has a negligible effect on the rise velocity [Rehder *et al.*, 2002]. The interfacial tension σ is set to 0.023 N/m.

[e.g., Mori and Mochizuki, 1998]. For the Reynolds numbers, Re , of our drop (Table 1) the standard drag curve of a rigid non-rotating sphere can be approximated [Schiller and Naumann, 1933] by:

$$C_d = \frac{24}{Re} (1 + 0.15Re^{0.687}). \quad (2)$$

[7] According to Chen *et al.* [2003], laboratory observations by Ozaki [1999] have shown deformation of hydrate-covered drops and these drops can be described as rigid irregular-ellipse particles. Calculations made by Chen *et al.* [2003] where deformation was taken into account matched observations of Ozaki [1999] for three different seawater conditions, while the use of theory for rigid spheres did not match the experimental data.

[8] Bozzano and Dente [2001] also developed a theory that takes deformation into account by using a drag coefficient C_d that includes the dimensionless Reynolds, Eötvös and Morton numbers, Re , Eo and Mo , respectively (Table 1). Based on a number of experiments with gas bubbles in different viscous environments they expressed the drag coefficient as a function of the generalized friction factor f [1], the drop major semi-axis a [m], and the equivalent radius r_e [m]:

$$C_d = f \left(\frac{a}{r_e} \right)^2. \quad (3)$$

The friction factor f was found to be:

$$f = \frac{48}{Re} \left(\frac{1 + 12Mo^{1/3}}{1 + 36Mo^{1/3}} \right) + 0.9 \frac{Eo^{3/2}}{1.4(1 + 30Mo^{1/6}) + Eo^{3/2}}. \quad (4)$$

They also found an expression for the last part of equation (3):

$$\left(\frac{a}{r_e} \right)^2 \cong \frac{10(1 + 1.3Mo^{1/6}) + 3.1Eo}{10(1 + 1.3Mo^{1/6}) + Eo}. \quad (5)$$

The dimensionless numbers for the 5 measurement depths, taken from Brewer *et al.* [2002] are given in Table 1.

2.2. Mass Transfer

[9] Brewer *et al.* [2002] found that the mass transfer from the observed drop could be matched by using the equation

$$\frac{dm}{dt} = -4\pi r_e^2 \rho_{CO_2} V_m \Gamma \quad (6)$$

with a constant dissolution rate of $\Gamma = 3.0 \mu\text{mol}/(\text{cm}^2\text{s})$. Here m [kg] is the mass of the drop and V_m [m^3/mol] is the molar volume of CO₂.

[10] Hydrate formation is expected to reduce the dissolution of CO₂ into seawater. To find this reduction a commonly used theory to calculate dissolution rate is also tried. The mass transfer equation [Crowe *et al.*, 1998; Alendal and Drange, 2001] is here defined by:

$$\frac{dm}{dt} = -Sh\pi d_e D_v M_{CO_2} (C_s - C) \quad (7)$$

where Sh is the Sherwood number, D_v [m^2/s] = $[7.1141 \cdot 10^{-15} \cdot (273.15 + T)] / \mu$ is the diffusion coefficient and M_{CO_2} is the molar CO₂ equal to $44.01 \cdot 10^{-3} \text{ kgmol}^{-1}$. $C \approx 0$ and $C_s = 1363.33 \text{ mol C m}^{-3}$ are the concentrations of CO₂ in the ocean far from the drop and at the drop surface, respectively. C_s is obtained from the equation of state for liquid CO₂ [Ely *et al.*, 1989]. T [°C] is the seawater temperature; here we have used a temperature profile based on the data given by Brewer *et al.* [2002] and the seawater viscosity μ is set equal to $1.075 \cdot 10^{-3} \text{ kg}/(\text{ms})$. The Sherwood number is found from the Ranz-Marshall correlation [Ranz and Marshall, 1952]: $Sh = 2 + 0.69Re^{0.5}Sc^{0.33}$, with the non-dimensional Schmidt number $Sc = \nu/D_v$ and $\nu = 1.049 \cdot 10^{-6} \text{ m}^2/\text{s}$ being the kinematical viscosity of seawater. The decrease in mass transfer due to hydrate is expressed by dividing the Sherwood number by different values of a reduction factor RF .

2.3. Vertical Distributions of Dissolved CO₂

[11] A CO₂ drop rising and dissolving in the ocean will provide a spread of dissolved CO₂ in the water column. To present this vertical distribution, resulting from a single drop, the mass that dissolves at each depth is divided by the initial drop mass. Thus the depth integral of each distribution curve is equal to one, and these normalized vertical distributions of dissolved CO₂ from drops of different sizes can be compared. The numerical solution is obtained by time-stepping the vertical position, velocity, radius and mass of each drop using a discretized version of equation (1) coupled to either equation (6) or (7).

3. Results

[12] The result of using the two drag parameterizations are shown and compared to the observations by Brewer *et al.* [2002], in Figure 1. The theory with the standard drag curve (dashed line) deviates strongly from the measurement points (circles). The result of using the theory by Bozzano and Dente [2001] (solid line) however matches the observations quite well, except for the smallest radius.

[13] The mass transfer results are shown in Figure 2 for the reduction factor RF having the values 1, 2 and 3. Of these values, using a reduction factor of 2 (stippled line)

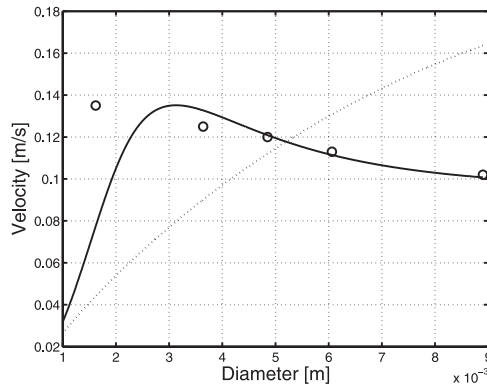


Figure 1. Drop diameter and corresponding terminal velocity. The circles represent the observations made by *Brewer et al.* [2002], the solid line use of the theory by *Bozzano and Dente* [2001] and the dashed line the theory with standard drag.

evidently fits the observed dissolution rate best. This is compatible with laboratory results [*Aya et al.*, 1992, 1997; *Nishikawa et al.*, 1995]. Thus the matching Sherwood number becomes: $Sh \approx 2 + 0.35Re^{0.5}Sc^{0.33}$. Nevertheless, the constant dissolution rate of $\Gamma = 3.0 \mu\text{mol}/(\text{cm}^2\text{s})$ by *Brewer et al.* [2002] (dashed line) matches the dissolution rate of this drop better than any reduction factor in the Ranz-Marshall equation.

[14] The two drag parameterizations are also compared for different initial drop diameters of 4, 6, 8 and 10 mm (Figure 3). Using the theory with standard drag (dashed lines) provides a much larger spread in the terminal velocities than using the theory [*Bozzano and Dente*, 2001] that takes deformation into account (solid lines).

[15] The normalized vertical distributions of dissolved CO₂ for the four different drop sizes in Figure 3 are presented in Figure 4. The results show that for the smallest drop the modeled dissolved CO₂ is spread over a larger depth interval when the theory by *Bozzano and Dente* [2001] is used, while for the largest drop the modeled dissolved CO₂ reaches highest when the theory with standard drag is used. For the two sizes in between this difference is smaller.

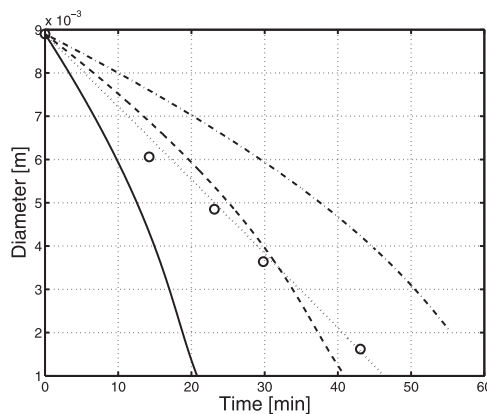


Figure 2. Time versus drop diameter for calculated and observed mass transfer. Dashed line represents the use of equation (6), solid line the use of no reduction factor, and stippled and stippled-dashed line the use of $RF = 2$ and 3, respectively.

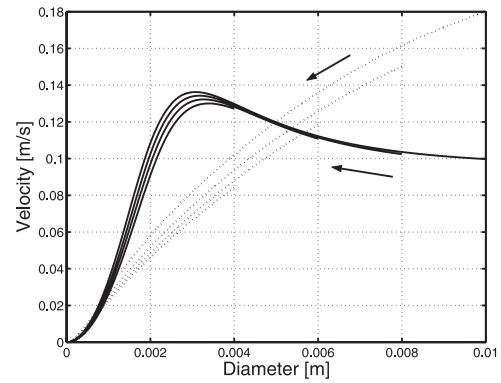


Figure 3. Modeled diameters and rise velocities for four drops with initial diameters of 4, 6, 8 and 10 mm released at 800 m. Solid lines represent the theory by *Bozzano and Dente* [2001], dashed lines the theory with standard drag. Time elapses in the direction of the arrows.

[16] *Chen et al.* [2003] suggested that the vertical spread of dissolved CO₂ could be overestimated if the theory of rigid spheres were used to simulate the release of CO₂ drops in seawater. Figure 4 confirms that this happens if there are drops larger than 10 mm in the distribution.

4. Discussion and Conclusions

[17] By comparing two drag parameterizations it has been shown that the terminal velocity of the observed drop [*Brewer et al.*, 2002] was best matched with the theory by *Bozzano and Dente* [2001]. The exception is the last observational point where the calculated velocity decreases while the observed velocity increases. At this point the drop is very small and the measurement errors would be largest. This deviation might also be due to the fact that trapping of the very smallest drops was observed in a corner of the observing box. This seemed to promote some form of boundary layer attachment and thus the rise rate of the vehicle perhaps exerted control over the drops rather than the other way around (P. G. Brewer, personal communication).

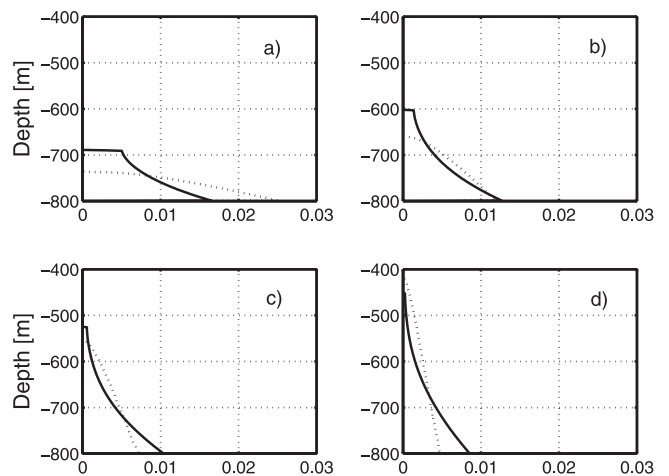


Figure 4. Vertical distributions of dissolved CO₂ for the drop of (a) 4 mm, (b) 6 mm, (c) 8 mm and (d) 10 mm. Solid lines represent the theory by *Bozzano and Dente* [2001], dashed lines the theory with standard drag.

tion, 2005). Thus this theory seems to work for liquid, hydrate-covered drops. That a theory accounting for change of shape can describe the behavior of a rising CO₂ drop in the real ocean verifies the laboratory results by *Chen et al.* [2003] and *Ozaki* [1999], and acts in contrast to the earlier theory that a hydrate film makes the drop spherical.

[18] That hydrate formation reduces the mass transfer by a factor of two [e.g., *Aya et al.*, 1997] is confirmed in this study by comparing theory to a rising CO₂ drop in the real ocean. This suggests that the dissolution rate found in laboratory experiments equals the dissolution rate of a drop in the real ocean. The dissolution of a CO₂ drop is however dependent on various factors like turbulence and relative velocity between the drop and the surrounding medium. When the drop is covered with hydrate, the mass transfer also decreases with decreasing temperature. In the experiment by *Aya et al.* [1997] the reduction factor of 2 matched well for the temperatures in the present study, but for lower temperatures a greater value of the reduction factor might be required.

[19] We found a clear difference in vertical dissolution of the dissolved CO₂ depending on drag parameterization. Using the theory that best fits the behavior of the drop observed by *Brewer et al.* [2002] suggests a higher concentration of dissolved CO₂ than using the rigid sphere theory. Seawater density increases with approximately $8 \cdot 10^{-3} \text{ kg m}^{-3}$ per mol m^{-3} of total dissolved inorganic carbon [*Haugan and Drange*, 1992]. A high concentration of dissolved CO₂ may lead to sinking of the CO₂ enriched seawater, giving a longer residence time. The lower value of pH related to a high concentration of dissolved CO₂ may on the other hand have a negative effect on the marine life. The high sensitivity of vertical distribution of dissolved CO₂ to drag parameterization implies that more experiments similar to the ocean experiment by *Brewer et al.* [2002] are needed to put this result on a firm basis.

[20] If it can be shown (see *Batchelor* [1987] for the bubble case), that Rayleigh-Taylor instabilities maintain CO₂ drops at the cm scale observed [*Brewer et al.*, 2002] and modeled here, then drops of this size class are indeed the important objects of study.

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