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## Mass Transfer of CO<sub>2</sub> Into Water and Surfactant Solutions

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**Abstract:** The mass transfer of CO<sub>2</sub> into water and aqueous solutions of sodium dodecyl sulphate (SDS) is experimentally studied using a pressure, volume, temperature (PVT) cell at different initial pressures and a constant temperature ( $T = 25^{\circ}\text{C}$ ). It is observed that the transfer rate is initially much larger than expected from a diffusion process alone. The model equations describing the experiments are based on Fick's Law and Henry's Law. The experiments are interpreted in terms of two effective diffusion coefficients—one for the early-stages of the experiments and the other one for the later stages. The results show that at the early stages, the effective diffusion coefficients are one order of magnitude larger than the molecular diffusivity of CO<sub>2</sub> in water. Nevertheless, in the later stages the extracted diffusion coefficients are close to literature values. It is asserted that at the early stages, density-driven natural convection enhances the mass transfer. A similar mass transfer enhancement was observed for the mass transfer between a gaseous CO<sub>2</sub> rich phase with an oil (n-decane) phase. It is also found that at the experimental conditions studied addition of pure SDS does not have a significant effect on the mass transfer rate of CO<sub>2</sub> in water.

**Keywords:** CO<sub>2</sub>, effective diffusion coefficient, mass transfer, natural convection, surfactant

### 1. INTRODUCTION

The mass transfer of a gas through a gas-liquid interface (with and without monolayers of surfactant) is of great importance in many fields of science and engineering. Examples include CO<sub>2</sub> sequestration to reduce global heating effects (Holt, Jensen, and Leindeberg, 1994; Lindeberg and Wessel-Berg, 1997; Bachu and Adams, 2003; Yang and Gu, 2006), oil recovery (Zhang,

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Hyndman, and Maini, 2000; Nguyen, Zitha, and Currie, 2002), and gas absorption (Vazquez, Antorrena, and Navaza, 2000). There is a vast literature on the mass transfer between gas and liquids. We confine our interest to the experimental determination of the mass transfer rate of CO<sub>2</sub> into water in a PVT cell. It has been suggested in the literature that natural convection enhances the mass transfer (Lindeberg and Wessel-Berg, 1997; Yang and Gu, 2006).

Lindeberg and Wessel-Berg (1997) studied the conditions under which natural convection occurs as a result of CO<sub>2</sub> injection in saline aquifers. They found the following sequence of events: initially the injected CO<sub>2</sub> accumulates under the cap rock. Then CO<sub>2</sub> dissolves into the reservoir brine by molecular diffusion. As a result, the density of brine increases, and therefore, natural convection occurs. Nevertheless, Lindeberg and Wessel-Berg (1997) did not quantify the effects of the natural convection in terms of enhanced mass transfer of CO<sub>2</sub> into the reservoir brine. Yang and Gu (2006) studied the mass transfer of CO<sub>2</sub> into water at high pressures and temperatures. They interpreted the experimental results in terms of a modified diffusion equation and found an effective diffusion coefficient for each experiment. The effective diffusion coefficients were two orders of magnitude larger than the molecular diffusion coefficient. The duration of their experiments, however, were short (3–4 hr) and they did not study the long time behavior of the CO<sub>2</sub> mass transfer into water.

When surfactants are added to a quiescent liquid, the total resistance to the transfer of gas molecules is the sum of the liquid-phase resistance, the gas resistance, and the interfacial resistance which arises from the adsorption of surfactant molecules to the interface. It has been shown that the presence of soluble surfactants has no measurable effect on the passage of gas molecules through the gas-liquid interface (Springer and Pigford, 1979; Caskey and Barlage, 1972; Hanwright et. al., 2005); insoluble surfactants, however, can offer resistance to mass transfer (Koide, Orito, and Hara, 1974; La Mer, Aylmore, and Healy, 1963; Blank, 1962; Barnes and Hunter, 1989; Barnes, 1997). To our knowledge, the reported experiments in this area are conducted under atmospheric pressure and the effect of surfactants on mass transfer at higher pressures apparently has not been reported in the literature.

In this report we study the mass transfer of CO<sub>2</sub> into bulk water and surfactant solutions experimentally to avoid the complex adsorption mechanism between surfactants and the porous medium. The emphasis of this article is on the experimental results and procedure. In order to quantify the results, we interpret the results in terms of two effective diffusion coefficients using a modified diffusion equation and leave a more complicated interpretation including natural convection for future work. This article adds three contributions to the experimental knowledge base: Firstly, by extending the duration of the experiments we investigate the long-term behavior of CO<sub>2</sub> mass transfer and investigate whether enhanced transfer persists over time or whether it dies out. Secondly, we perform the experiments with oil phase (in

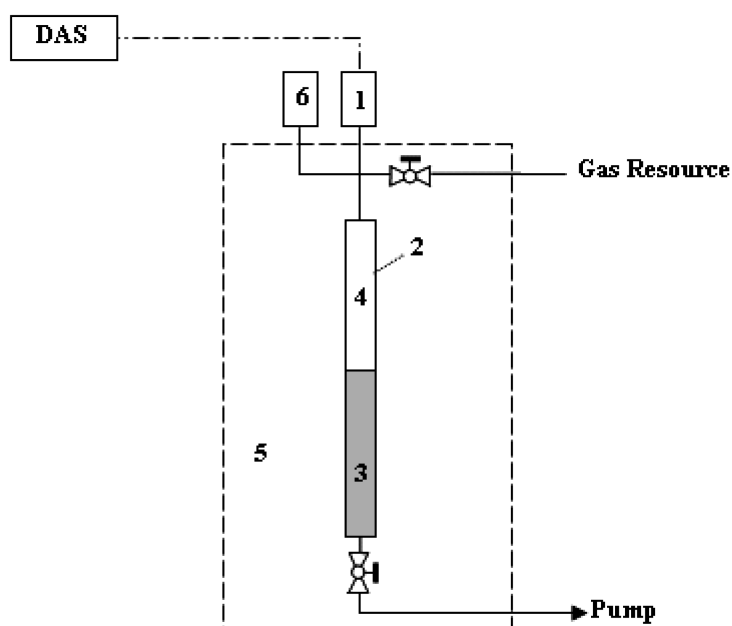
this article n-decane) and show experimentally the enhancement of CO<sub>2</sub> mass transfer to the oil phase. Thirdly, this article reports the effect of surfactants at high pressures. In section 2 we describe the experimental set-up, materials, and experimental procedure. In section 3 we define a model to interpret the experiments, and in section 4 the obtained experimental data are incorporated into a physical model.

This allows us to obtain two diffusion coefficients for the mass transfer process of CO<sub>2</sub> through a air-liquid interface—one for the early stages of the experiments and one for the late stages of the experiments. The possible mechanisms for the observed phenomena are discussed in section 5.

## 2. EXPERIMENTS

### 2.1. Experimental Set-Up

The experimental apparatus is shown in Figure 1. It consists of a transparent, scaled glass tube with an inner diameter of 7.0 mm, an outer diameter of 11.0 mm, and a length of 45.0 cm. The tube was embedded in Teflon at



**Figure 1.** Schematic of the set-up: The set-up consists of a long tube in which the liquid phase and gas phase are brought in contact with each other at a certain pressure. The set-up is held in a liquid bath with a constant temperature. The pressure of the gas in the top part is monitored by a pressure transducer.

the top and bottom and was sealed with o-rings and fitted inside a stainless-steel cylinder. The glass tube has the capability of withstanding pressures up to 50 bar. To assure that the liquid is stagnant, the stainless-steel cylinder was mounted into a heavy (10 kg) steel holder. The bottom of the cell was equipped with a valve and a piston pump, which permitted injection of liquid into the cell. The top of the cell was connected to a high-pressure gas cylinder. The gas pressure was measured with a calibrated pressure transducer with an accuracy of 5 mbar. Moreover, a safety valve was placed at the top part of the set-up. A calibrated data acquisition system was provided to record the pressure and temperature in the cell during the experiment. The experimental data were recorded every 10 sec by the computer. To avoid thermal fluctuations, the cell was located inside a liquid bath. In all experiments, the bath was kept at  $25 \pm 0.1^\circ\text{C}$ .

## 2.2. Materials and Methods

### 2.2.1. Gas

The gas used to carry out the experiments was 99.98% pure carbon dioxide.  $\text{CO}_2$  is highly soluble in water (Fogg and Gerrard, 1991), i.e., the Henry constant is  $2,980.1 \text{ mol/m}^3/\text{Pa}$  (Sander, 1999). The diffusion coefficient of  $\text{CO}_2$  in water is  $(1.97 \pm 0.10) \times 10^{-9} \text{ m}^2/\text{s}$  (Gertz and Loeschcke, 1954). Nitrogen ( $\text{N}_2$ ) was used to detect possible leakages in the setup.

### 2.2.2. Surfactant

The surfactant used to perform the experiments was sodium dodecyl sulfate (SDS) with the chemical formula of  $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$  and a molecular weight of 288 g/mol. It was dissolved in distilled water ( $\text{pH} = 5.5 \pm 0.1$ ).

Before starting the experiments, the critical micelle concentration (CMC) of the surfactant was measured. To that end, solutions of SDS and distilled water with the concentrations of 2, 2.5, 3, 3.5, 4, 5, and 6 mmol/l were prepared. The surface tension of these solutions was measured by the DuNouy ring method at room temperature. The apparatus was first calibrated with distilled water (the surface tension of distilled water at the room temperature is 72.6 mN/m). The critical micelle concentration of the SDS was measured to be 0.3 mM at our experimental conditions.

## 2.3. Experimental Procedure

In the pressure depletion experiments, the liquid phase was either pure distilled water or surfactant solutions with different surfactant concentrations. The concentration of the surfactant in some experiments was above the CMC and in some experiments below the CMC. For this purpose, an appropriate

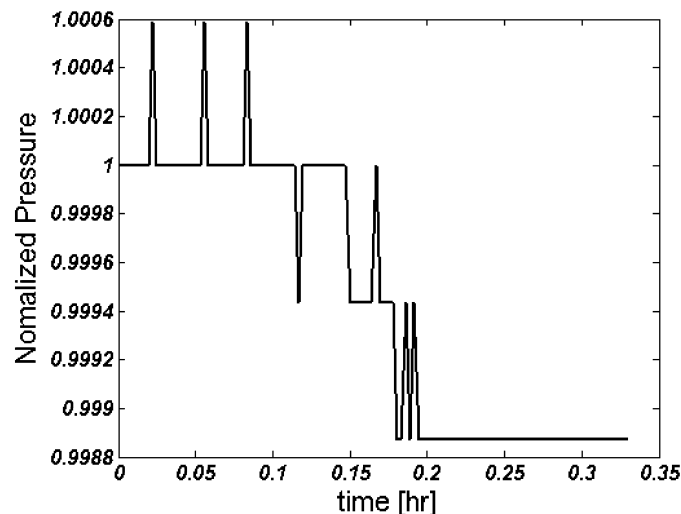
amount of SDS was weighed and dissolved in distilled water. Originally some foam is formed at the surface, which collapses after leaving it undisturbed for a few minutes.

Before performing the experiments, the dry cell was filled with nitrogen to a certain pressure to assure that there is no leakage in the system. Figure 2 shows the pressure versus time-plot for a leakage test. The small fluctuations in the first part of the plot are due to small fluctuations in the temperature and the difference between the temperature of the gas cylinder and the liquid bath. The experimental procedure is as follows: First, the liquid was injected from the bottom via an accurate piston pump into the cell until it reached the desired level. After that, pumping of the liquid was stopped and the valve at the bottom of the cell was closed. Next CO<sub>2</sub> was slowly injected into the cell from the top, for about 30 sec. When the CO<sub>2</sub> pressure reached the desired value, the valve was closed and the cell was isolated. This was the starting time of the experiment. Each experiment was run for several days. All the experiments were repeated to show the reproducibility.

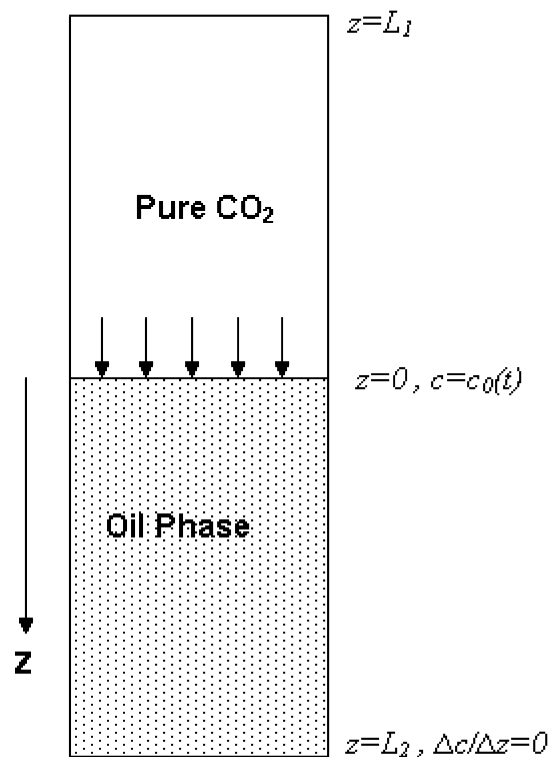
### 3. PHYSICAL MODEL

#### 3.1. Formulation

A physical model has been developed to describe the mass transfer based on Fick's Law taking into account the solubility of the gas by Henry's Law. The



**Figure 2.** Leakage test: The set-up was checked for any possible leakage by injecting nitrogen. The pressure should be constant with time in the range of accuracy of the pressure transducer.



**Figure 3.** Schematic outlay of the process: The total length of the tube is  $L$ , the height of water is  $L_2$ , and the height of the gas is  $L_1$ . There is no gas flowing out at the end of the tube. The gas-liquid interface is fixed. The liquid concentration at the interface is related to the gas pressure through Henry's Law and changes with time.

geometry of the problem under scrutiny is depicted in Figure 3. The vessel consists of an upper column filled with gas and a lower column filled with a stagnant liquid layer. The model disregards convection and capillary effects. Moreover, it is assumed that the density of CO<sub>2</sub> in the gas phase only depends on time. We disregard both water evaporation (the contribution of water vapor to the gas pressure is 0.03 bar at 25°C (Greenwood and Earnshaw, 1997)) and water swelling due to CO<sub>2</sub> dissolution. Consequently, we assume that the boundary remains fixed. The CO<sub>2</sub> concentration at the liquid surface is related to the gas pressure by assuming instantaneous thermodynamic equilibrium at the interface. We assert that the transfer of gas molecules through the gas-liquid interface can be described as a one-dimensional, unsteady-state diffusion process, i.e., by Fick's Law. We take  $z$  positive in the downward direction ( $z = 0$  at the gas-liquid interface) and assume that diffusion coefficient does not change significantly with concentration. Since the liquid

column is large, the concentration is zero at  $z = L_2$ . The gas inside the vessel follows the real gas law and the gas pressure can be calculated by  $PV = ZRT$ .

### 3.2. Equations

For this system, Fick's Second Law can be written as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \quad (1)$$

$$0 \leq z \leq L_2, 0 \leq t \leq \infty,$$

where  $D$  is the effective diffusion coefficient and  $c$  is the concentration of CO<sub>2</sub> in the liquid phase. Initially, there is no gas inside the liquid, i.e.,

$$c(z, t = 0) = c_0 = 0. \quad (2)$$

Since the diffusion process is slow and the liquid column is large, we can assume that the concentration of the gas is zero at the end of the tube ( $L_2 \rightarrow \infty$ ). The second boundary condition is given by Henry's Law which states that the pressure of a gas above a solution is proportional to the mole fraction (concentration) of the gas in the solution, i.e.,

$$P(t) = Hc(t), \quad (3)$$

where  $H$  is taken as Henry's Law proportionality constant.

An additional condition to the present problem can be written in accordance with the fact that the change of the total moles of gas in the system is due to diffusion into the liquid. The mass flux of the gas at the interface for real gas can be written as

$$\left. \frac{dn_g}{dt} \right|_{z=0} = \left. \frac{V}{ZRT} \frac{dP_g}{dt} \right|_{z=0} = -DS \left. \frac{\partial c}{\partial z} \right|_{z=0}, \quad (4)$$

where  $V$  and  $S$  are the gas volume and the cross-sectional area of the cell, respectively.  $R$  is the universal gas constant and  $Z$  is the compressibility factor.  $V$  is also assumed to be constant (no moving boundary).

By substituting Henry's Law for the gas pressure in Eq. (4) we obtain

$$-DS \left. \frac{\partial c}{\partial z} \right|_{z=0} = \left. \frac{VH}{ZRT} \frac{\partial c}{\partial t} \right|_{z=0}. \quad (5)$$

### 3.3. Analytical Solution

Equation (1) has a time-dependent boundary condition and can be solved by Laplace transform method. Laplace form of Eq. (1) is

$$\frac{\partial^2 \bar{C}}{\partial z^2} - \frac{s}{D} \bar{C} = 0. \quad (6)$$

The final solution of Eq. (6) with the given boundary conditions is

$$\bar{C}(s) = \frac{1}{\frac{H}{P_i} s - \frac{ZRT\sqrt{D}}{L_1 P_i} \sqrt{s}} \exp\left(-\sqrt{\frac{s}{D}} z\right). \quad (7)$$

Applying Laplace transform to Eq. (4) and using Eq. (7) yields

$$\frac{L_1}{ZRT} (s \bar{P}_g - P_i) = -\frac{1}{\frac{H}{P_i \sqrt{D}} \sqrt{s} - \frac{ZRT}{P_i L_1}}, \quad (8)$$

from which we can obtain

$$\frac{\bar{P}_g(s)}{P_i} = \frac{1}{s} - \frac{1}{\frac{L_1 H}{ZRT \sqrt{D}} s^{3/2} - s}. \quad (9)$$

The gas pressure as a function of time is found by Laplace inversion as

$$P_g(t) = P_i [2 - \exp(\kappa^2 t) \operatorname{erfc}(-\kappa \sqrt{t})], \quad (10)$$

where

$$\kappa = \frac{ZRT \sqrt{D}}{L_1 H}. \quad (11)$$

Due to our boundary condition—that the concentration is zero at the bottom of the cell ( $z = L_2$ )—we find as long time behavior that the pressure is declining indefinitely. However, that occurs for times much longer than relevant for the experiment.

It should also be mentioned that the solution of Fick's Second Law assuming a constant concentration at the gas-liquid interface suggests that after a long time, the concentration at the interface is linearly proportional to the square root of time, i.e., the plot of gas pressure versus the square root of time will be a straight line (Coulson and Richardson, 1977).

**Table 1.** List of experiments with water

Experiment number	Initial pressure, bar	Temperature, °C
Exp1	7.72	25 ± 0.1
Exp2	11.73	25 ± 0.1
Exp3	20.10	25 ± 0.1

## 4. RESULTS AND DISCUSSION

### 4.1. Pressure Decline

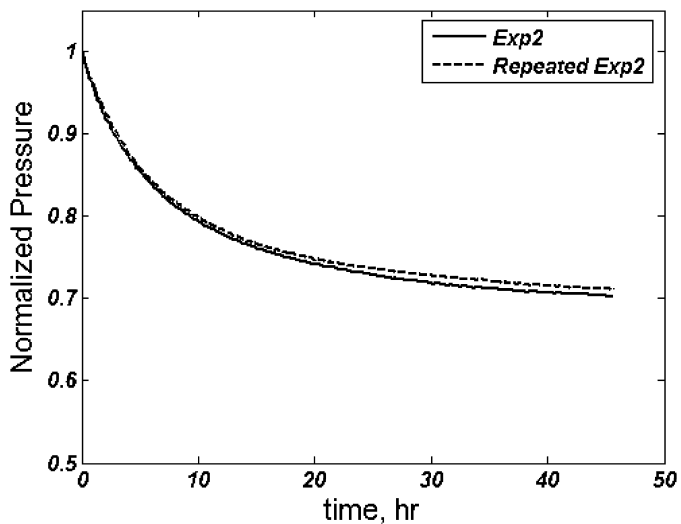
In this study, the quantification of the mass transfer rate is based on the measurement of the gas pressure in a closed volume containing a column of liquid below a gas column. The changes in the gas pressure are assumed to be only due to transfer of gas into the liquid phase. The measured gas pressure versus time for both distilled water and the surfactant solution are plotted for all experiments. The general trends of the curves for different initial pressures were similar. Thus due to these similarities only the curves of Exp2 will be presented in this article. However, the extracted data will be reported for all experiments (Tables 1 and 2).

Figure 4 shows normalized CO<sub>2</sub> pressure versus time during pressure decline measurements for Exp2. It shows that the gas pressure decreases with time due to the transfer of the CO<sub>2</sub> molecules into water. Comparison between the solid and dashed lines in the figure shows the reproducibility of the experiment. The small difference between these two curves is due to the difficulties in setting the initial pressure to the same value for the two experiments.

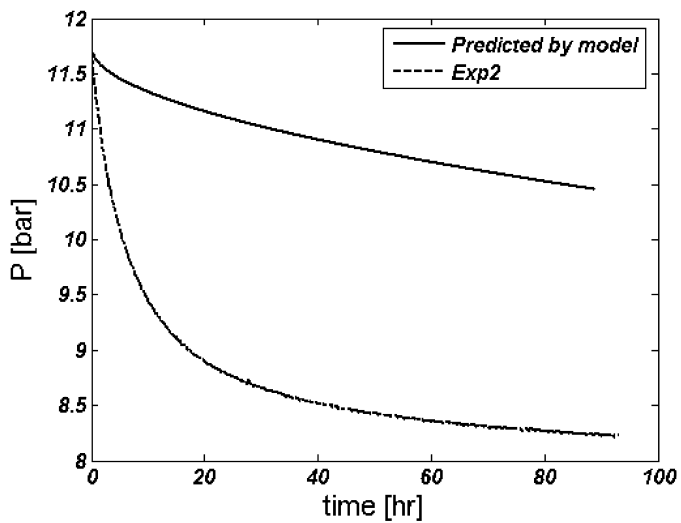
It becomes clear from Figure 4 that the gas pressure declines significantly at the initial stages of the experiment, i.e., has a steep slope at the early times of the experiment. However, the slope of the curve becomes less steep with time, also meaning that the mass transfer rate decreases with time. Figure 5 shows the comparison between the measured pressures and the model using the known diffusion coefficient of CO<sub>2</sub> in water (in this curve chosen to be

**Table 2.** List of experiments with SDS solution

Experiment number	Initial pressure, bar	T, °C	SDS concentration, mM
Exp4	11.80	25 ± 0.1	C = 30 mM > CMC
Exp5	11.76	25 ± 0.1	C < CMC
Exp6	11.75	25 ± 0.1	C = 30 mM + NaCl



**Figure 4.** Reproducibility test: All of the experiments were repeated to assure that the observed pressure decline is only due to the mass transfer of  $\text{CO}_2$  into water and the obtained data are reproducible.



**Figure 5.** Comparison between experiment and model: This curve shows the comparison between the model that is based on the modified Fick's second law and the experimental data. At the initial stages of the experiments, the rate of mass transfer of  $\text{CO}_2$  into water is higher than the predicted values by the physical model.

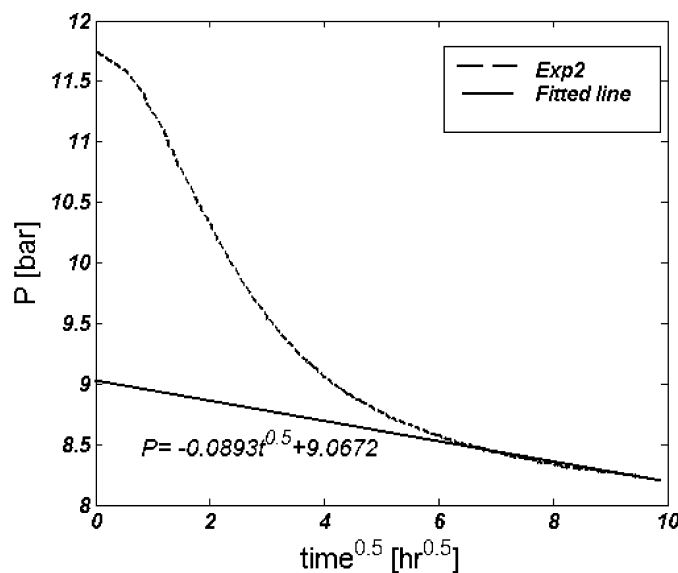
$D = 1.97 \times 10^{-9} \text{ m}^2/\text{s}$ ). The curve shows significant discrepancy between experimental and predicted values.

#### 4.2. Deviation from the Square Root of Time

Figure 6 shows the plot of the measured gas pressure versus the square root of time for Exp2. It shows that the initial behavior of this curve is faster than the square root of time. This is an indication of the higher mass transfer of CO<sub>2</sub> into water, which cannot be explained by a diffusion-like process. Interestingly, after about 1 day, the pressure vs. the square root of the time-curve becomes linear. It can be expected that at longer times the mass transfer of CO<sub>2</sub> into water is determined by molecular diffusion.

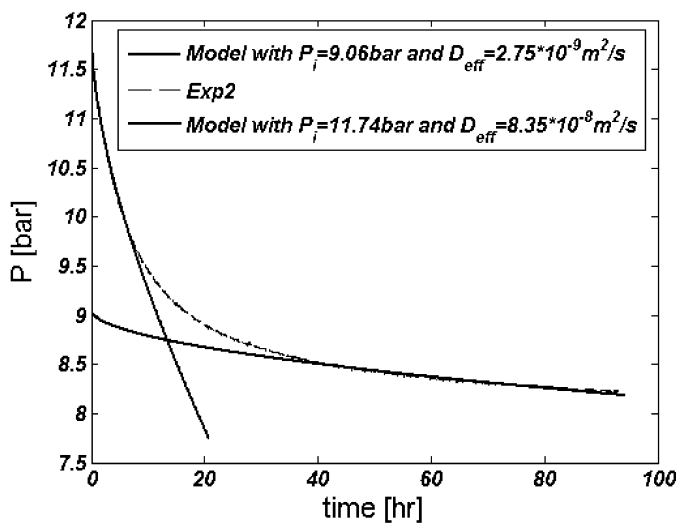
#### 4.3. Estimated Diffusion Coefficients

In this article two effective diffusion coefficients are extracted from the experimental data describing the initial and long-time behavior of the CO<sub>2</sub> mass transfer into water and surfactant solutions. The procedure is as follows: In the plots of pressure versus the square root of time (e.g., Figure 6 for Exp2), the late-stage experimental data are fitted to a straight line. The intercept of the fitted line in Figure 6 is the initial pressure with which the mass transfer



**Figure 6.** Measured pressure data plotted versus the square root of time. The long time part of the experiment can be fitted to a straight line.

process would have started if diffusion had been the only responsible mechanism for mass transfer of CO<sub>2</sub> into the liquid (no convection case). Therefore, to obtain the late-stage diffusion coefficient, this pressure is put as initial pressure in the physical model, for which the model equation is Fick's Second Law with a time-dependent boundary condition. The lower solid curve in Figure 7 is the predicted gas pressure by Eq. (10) using the initial pressure obtained from Figure 6 and choosing  $D = 2.75 \times 10^{-9} \text{ m}^2/\text{s}$  and inserting the literature value of Henry's coefficient ( $H = 2,980.1 \text{ mole/m}^3/\text{Pa}$ ). The dashed line shows the experimentally measured pressure data versus time. With a diffusion coefficient close to the molecular diffusion coefficient of CO<sub>2</sub> into the water, the predicted values by the model are in excellent agreement with the measured pressure values. To obtain the effective coefficients for early stages of the experiments, the experimental initial pressure was put in the model and the effective diffusion coefficient was obtained with the help of the data. The upper solid curve in Figure 7 is the predicted gas pressure by Eq. (10) choosing  $D = 8.35 \times 10^{-8} \text{ m}^2/\text{s}$  and  $H = 2,980.1 \text{ mole/m}^3/\text{Pa}$ . Alternatively, we can use the later stage diffusion coefficient  $D = 2.75 \times 10^{-9} \text{ m}^2/\text{s}$  but then the Henry's coefficient needs to be modified to  $H = 552.01 \text{ mole/m}^3/\text{Pa}$ . Such a small value has not been reported in the literature for CO<sub>2</sub> solubility in water. Therefore, we have chosen to use the literature value of Henry's coefficient in the interpretation of the experiments.



**Figure 7.** Extraction of diffusion coefficients, using Eq. (10): the data are fitted to two curves of the form suggested by Eq. (10). The lower solid line shows the predicted pressure values using the virtual initial pressure obtained from Figure 8 and  $D = 2.75 \times 10^{-9} \text{ m}^2/\text{s}$ . The dashed line is the measured pressure data. The left solid line shows the predicted pressure values using the real pressure obtained from Figure 8 and  $D = 8.35 \times 10^{-8} \text{ m}^2/\text{s}$ .

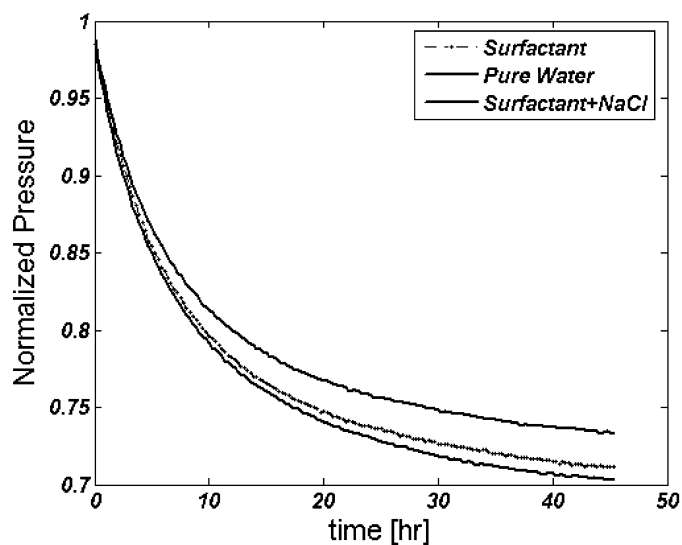
**Table 3.** The late stage and early stage effective diffusion coefficients extracted from experimental data. The effective diffusion coefficients in the third and fourth columns were extracted by choosing the literature value of Henry's coefficient,  $H = 2,980.1 \text{ mol/m}^3/\text{Pa}$

Experiment number	$\sqrt{D}/H$	$D_{eff}$ for early stages (m <sup>2</sup> /s)	$D_{eff}$ for later stages, m <sup>2</sup> /s
Exp1	$7.00 \times 10^{-8}$	$4.35 \times 10^{-8}$	$2.05 \times 10^{-9}$
Exp2	$9.50 \times 10^{-8}$	$8.35 \times 10^{-8}$	$2.75 \times 10^{-9}$
Exp3	$1.10 \times 10^{-7}$	$10.70 \times 10^{-8}$	$2.05 \times 10^{-9}$
Exp4	$9.46 \times 10^{-8}$	$7.95 \times 10^{-8}$	$2.50 \times 10^{-9}$
Exp5	$9.37 \times 10^{-8}$	$7.80 \times 10^{-8}$	$3.50 \times 10^{-9}$
Exp6	$9.00 \times 10^{-8}$	$7.20 \times 10^{-8}$	$1.95 \times 10^{-9}$

The extracted effective diffusion coefficients for different experiments are shown in Table 3. The obtained effective diffusion coefficients for the early stages of the experiments are one order of magnitude larger than the actual molecular diffusion of CO<sub>2</sub> into water, again indicating the faster mass transfer rate of CO<sub>2</sub> into water at the early stages of the experiment. However, the obtained effective diffusion coefficients for the later stages of the experiments imply that after a certain time, the mass transfer of CO<sub>2</sub> into aqueous solutions becomes slower compared to the initial stages. The early-stage diffusion coefficients increase with increasing initial pressure proving the fact that even at slightly high pressures for a CO<sub>2</sub>-water system, the diffusion coefficient is a strong function of the initial pressure, i.e., the initial concentration of CO<sub>2</sub> in the system. This means that at higher pressures, the effective diffusion coefficients will be even higher. This observation is also supported by the experimental results in Yang and Gu (2006) in which the authors found diffusion coefficients which were two orders of magnitude larger than the molecular diffusion coefficient of CO<sub>2</sub> into water at higher pressures. In addition, regardless of the initial pressure, after a certain time, diffusion becomes the dominant mechanism for mass transfer of CO<sub>2</sub> into water. The diffusion coefficient extracted from the long time behavior turns out to be independent of the initial experimental pressure.

#### 4.4. Influence of Surfactant

To study the influence of the soluble surfactants on the interfacial mass transfer, some of the experiments were done using surfactant solutions of SDS as liquid phase. Figure 8 shows the normalized pressure decline curve for the experiments with surfactant solution together with the experiment with pure water. It is evident from Figure 8 that at our experimental conditions the addition of SDS has no significant effect on the mass transfer rate of CO<sub>2</sub> into



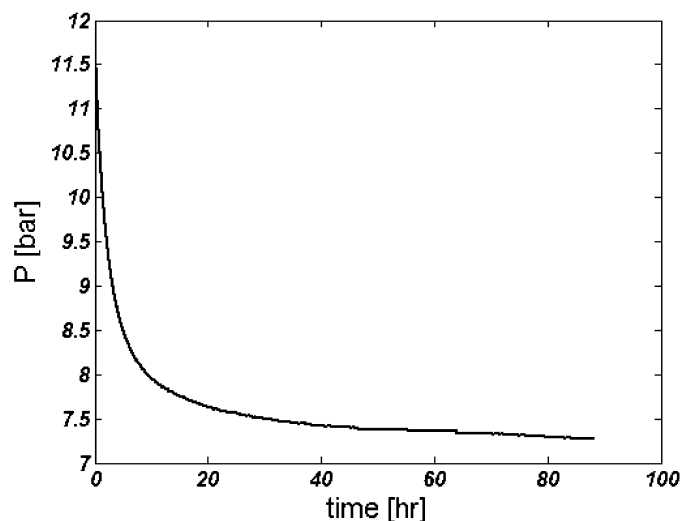
**Figure 8.** Comparison of measured pressure data for pure water, solution of water, and SDS and solution of water and surfactant with NaCl versus time.

water. However, it seems that the addition of salt slightly retards the mass transfer. Several parameters can be responsible for this behavior: (a) the addition of NaCl increases the viscosity of the solution and therefore the effective diffusion coefficient decrease by adding NaCl; (b) the addition of NaCl decreases the solubility of  $\text{CO}_2$  in water. Therefore, less  $\text{CO}_2$  is dissolved in water in the experiment with NaCl compared to experiments without NaCl; (c) the addition of salt increases the adsorption of the surfactant molecules at the interface (Santanu and Pak, 2006) and the interface becomes more packed which could be another possible reason for the differences of the curves in Figure 8. Our results are consistent with the results of other researchers (La Mer et al., 1963; Molder, Tenno, and Nigu, 1998; Raymond and Zieminski, 1971), i.e., the surface resistance for soluble surfactants is very small. However, the insoluble surfactants do have a significant effect on the transfer rates of gas through the gas-liquid interface.

The same procedure as previously discussed was also followed to extract the effective diffusion coefficients for surfactant solutions. Indeed, the obtained diffusion coefficient values for surfactant solutions are about the same as for the experiments with water and are presented in Table 3.

#### 4.5. Experiment with n-Decane

We carried out a few experiments to study the mass transfer of  $\text{CO}_2$  into hydrocarbons from which we report the obtained pressure curve from an



**Figure 9.** Pressure decline curve in the experiment with n-decane. The pressure behavior is similar to the water case, indicating an enhancement of mass transfer in the initial stages of the experiment. In long time, the conventional diffusion behavior is observed.

experiment with n-decane. The dissolution of CO<sub>2</sub> increases the density of the hydrocarbons (Ashcroft and Ben Isa, 1997). The experimental procedure and conditions were the same as explained in section 2. The initial pressure of the experiment was 11.85 bar. Figure 9 shows that initially the mass transfer of CO<sub>2</sub> is faster than at the later stages. We believe that this result has implications for enhanced oil recovery for CO<sub>2</sub> flooding and improved oil recovery in fractured oil reservoirs.

## 5. POSSIBLE MECHANISMS

As an explanation for the observed discrepancy between the physical model and the experimental data in Figure 5, the following possibilities have been considered: a) CO<sub>2</sub> may be adsorbed to the water “attached” to the gas-filled part of the glass tube. This explanation is unlikely, however, because it requires a water layer thickness of 2 mm. b) Other possibilities are related to the validity of Henry’s Law in relating the surface concentration of the fluid to the gas pressure. Even if we consider these possibilities less likely, they have to be investigated. c) When CO<sub>2</sub> is brought into contact with water, the dissolution and diffusion of CO<sub>2</sub> leads to a concentration gradient in the water and also a density gradient (Gmelin, 1973). As the density increases with increasing dissolution of CO<sub>2</sub> at the interface, the fluid on

top of the water near the interface becomes denser. This density gradient induces natural convection to the system, which speeds up the transfer of  $\text{CO}_2$  into water and results in a higher flux of  $\text{CO}_2$  at the interface. However, the density gradient, and therefore natural convection effects, decreases with time and after a certain time the density gradient is not large enough to sustain convection to the system.

In addition to the natural convection, the time-dependency of the boundary condition in Eq. (4) can be another reason why the early pressure history is not proportional to the square root of time. However, as we can see from Figure 6 the pressure decline is slow at the later stages and then the gas pressure can be considered constant for the boundary condition.

The observations previously mentioned can be quantified in terms of the effective diffusion coefficients. It is seen that regardless of the initial pressure, after a certain time, the enhancement effects will be less and diffusion becomes the dominant mechanism for  $\text{CO}_2$  mass transfer  $\text{CO}_2$  into water.

Furthermore, as can be seen from Figure 9, it appears that natural convection is also responsible for the mass transfer of  $\text{CO}_2$  into n-decane (oil phase). Once more, at the later stages, the effect of natural convection becomes less significant.

## 6. CONCLUSIONS

In this article it is shown that a relatively simple PVT cell can be used to study the enhanced mass transfer between gases and liquids.

A physical model based on the Fick's Second Law and Henry's Law can be used to interpret the experimental data. We use the model to extract two diffusion coefficients.

The mass transfer process cannot be modeled with a modified Fick's Second Law with a single, effective diffusion coefficient.

The initial stages and later stages of the experiments could be modeled individually with the described model and two effective diffusion coefficients could be obtained from the experimental data.

The obtained effective diffusion coefficient values for the initial stages of the experiments were one order of magnitude larger than the molecular diffusivity. It was suggested that at the early stages of the experiments, density-driven natural convection enhances the mass transfer of  $\text{CO}_2$  into water.

The effective diffusion coefficients for the initial stages of the experiments increase with increasing pressure.

The extracted diffusion coefficients for the later stages of the experiments agree with the molecular diffusivity of  $\text{CO}_2$  into water. It was asserted that after a certain time, the density-driven natural convection becomes less

important. At the later stages diffusion becomes the dominant mechanism for the mass transfer experiments of CO<sub>2</sub> into water and surfactant solutions.

The same behavior was seen from the surfactant solution experiments. Moreover, the results of experiments show that the addition of SDS to water has no measurable effect on the mass transfer rate in our experimental set-up.

A similar mass transfer enhancement was observed for the mass transfer between a gaseous CO<sub>2</sub>-rich phase with an oil (n-decane) phase. This has implications for the oil recovery.

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## NOMENCLATURE

$c$	Gas concentration, M
$\overline{C}$	Laplace transform of $c$ , M
$D_{eff}$	Effective diffusion coefficient, m <sup>2</sup> /s

**Mass Transfer of CO<sub>2</sub> Into Water****1511**

$H$	Henry's constant, Pa/mol/m <sup>3</sup>
$L$	Length of the experimental tube, m
$L_1$	Height of the gas in the experimental tube, m
$L_2$	Height of the liquid in the experimental tube, m
$P_g$	Gas pressure, Pa
$P_i$	Initial gas pressure, Pa
$R$	Universal gas constant, J/mol/K
$S$	Cross-sectional area of the tube, m <sup>2</sup>
$t$	Time, sec
$T$	Temperature, K
$V$	Volume of the gas in tube, m <sup>3</sup>
$Z$	Gas compressibility factor, –