OPTICAL MEASUREMENTS OF CHEMICAL REACTION
BY GAS DISSOLUTION IN A GAS-LIQUID MICROCHANNEL FLOW

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Abstract  The present study focuses on the mass transfer process through a gas-liquid interface in a microchannel flow. The objective is to investigate the CO₂ dissolution process in water as the model of the gas-liquid mass transfer process by a simultaneous measurement of liquid velocity and pH distribution by PTV and LIF with a confocal microscope and a 3CCD color camera. In order to accomplish the measurement, it is needed to realize the gas-liquid interface in a microchannel. The parallel gas-liquid flow with keeping the static gas-liquid interface in the microchannel is realized by controlling the fluid pressure and the surface tension with the step shaped channel and surface modified glass. The CO₂ concentration distribution was calculated from pH distribution by considering the CO₂ chemical equilibration in water. Spatial resolution of velocity and CO₂ concentration measurement was 6.2 × 24.8 μm and 5.2 × 5.2 μm, respectively. The simultaneous measurement was conducted at variable liquid flow rates. The result of liquid velocity measurement showed the presence of the liquid velocity at the gas-liquid interface. The results obtained by LIF indicated that the CO₂ concentration was increased with decreasing the liquid velocity. The convection and diffusion fluxes were calculated from PTV and LIF measurement data. From the profiles of molar flux, it is observed that the convection flux is much more dominant than the diffusion flux. The diffusion flux in the vicinity of the wall is almost same at every flow rate. This result shows that the amount of the CO₂ flux from gas phase into water is almost constant based on Henry’s law. The difference of the concentration at the gas-liquid interface is derived from the effect of the convection flux, which is attributed to the presence of liquid velocity at the gas-liquid interface.

1. Introduction

Microfluidic devices comprising multiple submilliorder channels enables the miniaturization of the system integrated overall operations for bio/chemical analysis and chemical reactor system, e.g., micro-TAS (Reyes et al. 2002) and microreactor (Watts and Wiles 2007) and so forth. In order to extend the ability of these devices, the addition of the gas phase operations was strongly desirable. Especially, the reaction and the analysis which could not be conducted in microspace is realized by the mass transfer operation accompanied gas-liquid contact in the microchannel. In the previous work, the microfluidic devices achieving the gas-liquid contact was studied by the different approaches. Jong et al. (2008) generated the proton concentration gradient in microchannel by absorption of the acidic and alkaline gases into liquid sample through gas permeable membrane. However, because the gas permeable membrane has the gas selectivity, the range of application is limited to the small molecules gases which can pass through the gap of membrane structure. The gas-liquid co-flowing regime was most applicable to realize the gas-liquid operation. Günter et al. (2004) investigated the gas-liquid segmented flow characteristic and synthesized the nano particles. However the undesired structures for gas sample rejection had to be set and resulted in the complexity of the device. Hibara et al. (2005) realized the gas-liquid two phase laminar flow in the microchannel by patterning the wettability of channel walls and conducted the degassing operation. Generation of the gas-liquid interface without merging each phases has advantages such as the ease of controlling the time of the gas-liquid contacting, the wide range of gases and so on. The precise analysis and effective reaction involving the gas sample operation will be conducted by utilizing the devices for mass transfer operation. For the practical application and the improvement of the devices realizing the gas-liquid interface, it is required to obtain detailed information about the
process of the gas-liquid mass transfer from microscopic viewpoint, that is, the integrated investigation of flow structure and mass transfer characteristics with optical visualization.

The optical measurement techniques have been studied for a few decades. For a fluid velocity measurement in microspace, Park *et al.* (2004) enhanced the depth wise resolution of micron resolution particle image velocimetry (micro-PIV) by utilizing the confocal microscopy. While, for a concentration measurement, Shinohara *et al.* (2005) investigated the fast proton diffusion in a chemical reacting flow by laser induced fluorescence (LIF) with pH sensitive fluorescent dye. Ichiyanagi *et al.* (2007) developed the simultaneous measurement system for velocity and pH distributions by utilizing micro-PIV/LIF with a confocal scanner and a 3CCD camera for investigation of a fluid mixing field involved neutralization reaction.

The present study focuses on the mass transfer process through a gas-liquid interface for realizing the practical application and the design optimization of gas-liquid controlling devices. The objective of the present study is to investigate the CO$_2$ dissolution process in water as the model of gas-liquid mass transfer process. To generate the static gas-liquid interface in a microchannel, the interfacial tension and the fluid pressure is controlled by optimizing the shape and the surface wettability of microchannel. The process of the CO$_2$ transfer in water is investigated by utilizing a simultaneous measurement technique of pH and velocity of the liquid flow. The velocity measurement is conducted by temporally and spatially averaging of the instantaneous velocity vectors obtained by particle tracking velocimetry (PTV). LIF gives the pH distribution from the fluorescent intensity by the calibration curve. The CO$_2$ concentration distribution is obtained from pH distribution by considering the relationship with pH from the chemical equilibration in water. Furthermore the convection and diffusion fluxes of CO$_2$ are obtained from the measurement data of velocity and CO$_2$ concentration, which enable to evaluate the CO$_2$ transfer process interacted with convection and diffusion.

2. CO$_2$ dissolution process through the gas-liquid interface

Figure 1 shows that a schematic illustration of CO$_2$ dissolution process. At a gas-liquid interface, the physical absorption and release of CO$_2$ keep the equilibrium relationship described as follow, CO$_2$ (gas) $\Leftrightarrow$ CO$_2$ (liquid). In general, if the absorption medium is a dilute solution and the solubility of gas is relatively small, the concentration of dissolved gas in the vicinity of the liquid surface is represented by the Henry’s law, $C_{CO_2} = H \cdot p$, where $p$ [Pa] is the CO$_2$ partial pressure in gas phase, $H$ [mol/(l·Pa)] is Henry’s constant and $C_{CO_2}$ [mol/l] is dissolved CO$_2$ concentration. This relationship shows that the mass transfer across the gas-liquid interface is dependent on partial pressure of CO$_2$ in gas phase. The CO$_2$ dissolution process into water has been considered to be described as chemical equilibrium depicted as Equations (1), (2). Dissolved CO$_2$ in water partially reacts and result in the generation of proton.

![Fig. 1. Schematic illustration of CO$_2$ dissolution process.](image-url)
The almost all amount of dissolved CO$_2$ is unreacted and H$_2$CO$_3$ which generates as the result of hydration is less than 0.4% of whole CO$_2$. These chemical reaction rate is represented with the use of dissociation constant $K_a$ [mol/l] which is given by

$$K_a = \frac{[H^+][HCO^-]}{[CO_2 + H_2CO_3]} = 4.3 \times 10^{-7}. \tag{3}$$

The relationship between pH and dissolved CO$_2$ concentration derived from Equation (3) is shown in Equation (4).

$$C_{CO_2} = 10^{pK_a - 2pH}, \tag{4}$$

where $pK_a = -\log_{10}K_a = 6.35$. The CO$_2$ concentration distribution in water is able to be calculated from the pH distribution by utilizing this relationship.

### 3. Microchannel

The microchannel was designed so that it generates the static gas-liquid interface. The interfacial tension and the fluid pressure were controlled by optimizing the channel structure and the surface wettability of microchannel. In the constant flow rate, the pressure drop is proportional to the fourth power of hydraulic diameter. Thus, it is required to increase the hydraulic diameter of liquid channel for the reduction of the liquid pressure to the gas phase. On the other hand, the pressure caused by the surface tension of liquid $\Delta P_S$ [Pa] is described with the modified Young-Laplace equation defined as

$$\Delta P_S = \frac{2\gamma \sin(\theta - 90^\circ)}{d}, \tag{5}$$

where $\gamma$ [N/m] is the surface tension, $\theta$ [deg] is the contacting angle which represents the wettability of materials and $d$ [m] is the depth of interface. This equation indicates that the surface tension is dependent on the wettability of the channel wall and the channel depth.

The microchannel was designed by taking into account the three parameters, the cross sectional area of liquid channel, the interfacial depth and the wettability of the channel wall. Figure 2 shows the microchannel comprising of a poly-(dimethilsiloxane) (PDMS) chip and a borosilicate cover glass with a thickness of 170 $\mu$m (Matsunami glass ind., LTD.). First, the step structure in the span-wise direction was built in the microchannel. Second, the deep part of channel is expanded cross sectional area. The microgroove provided in the PDMS substrate was processed by cryogenic micromachining (Kakinuma et al. 2007). The hydrophilic glass wall of channel shown in Figure 2 (c) was treated by the hydrophobic surface modification of octadecyltrichrolosilane (OTS) (Ulman, 1996) depicted in Figure 2 (d). The surface modification was conducted by immersing the glass in hexadecane solution (Sigma-Aldrich Corp.) containing 10 mmol/l OTS (Shin-Etsu Chemical Co., Ltd.) for 5 minutes and flushing hexane (Sigma-Aldrich Corp.) and ethanol (Wako pure chemical Inc.). The liquid was driven in left-hand side channel without entering the right-hand side channel for gas sample and the static gas-liquid interface was realized in the microchannel by providing these operations.
4. Experimental setup

A schematic of the optical measurement system based on an inverted microscope is illustrated in Figure 3. A laser beam from the continuous Ar laser at a wavelength of 488 nm and a power of 100 mW was introduced into the confocal scanner (Yokogawa Electric Corp., CSU22 β) and collected through a 20× magnification objective lens (Nikon Corp., CFI S Fluor) with a numerical aperture (NA) of 0.75 into microchannel. The fluorescence from particles (Molecular Probes Inc., TransFluoSpheres T8883) and dye (Wako pure chemical Inc., Sodium Fluorescein) whose fluorescent properties are shown in Table 1 and 2 was passed through objective lens and emitting filter transmitting wavelengths longer than 520 nm and introduced into the confocal scanner. The out-of-focus fluorescence was excluded by the pinhole in the confocal scanner and only in-focus fluorescence was detected by a 3CCD camera (Hamamatsu Photonics, K.K., C7780-20, 1344 × 1024 pixels, 8 bits × 3). In the present measurement condition, the measurement depth is reduced to 5 μm by utilizing the confocal scanner (Park et al. 2004). The peak values of fluorescence wavelengths from dye and particle are different. Thus the red and green sensors of the 3CCD camera could detect the different band of fluorescent wavelength simultaneously. The focal plane was able to be shifted well-aligned to control the position of an objective lens with the piezo actuator (Sigma Koki Co., Ltd., SFS-OBL-01). The position resolution of the piezo actuator was 20 nm.
Table 1. Property of fluorescent particle

<table>
<thead>
<tr>
<th>Material noun</th>
<th>Polystyrene</th>
</tr>
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<tbody>
<tr>
<td>Diameter</td>
<td>1 [μm]</td>
</tr>
<tr>
<td>Density</td>
<td>1.055 [g/cm³]</td>
</tr>
<tr>
<td>Absorption wavelength</td>
<td>488 [nm]</td>
</tr>
<tr>
<td>Emission wavelength</td>
<td>645 [nm]</td>
</tr>
</tbody>
</table>

Table 2. Property of fluorescent dye

<table>
<thead>
<tr>
<th>Material noun</th>
<th>Sodium Fluorescein</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₂₀H₁₂O₅Na₂</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>376.82</td>
</tr>
<tr>
<td>Absorption wavelength</td>
<td>494 [nm]</td>
</tr>
<tr>
<td>Emission wavelength</td>
<td>518 [nm]</td>
</tr>
</tbody>
</table>

5. Measurement method

In this section, the measurement method of velocity and pH distribution of liquid phase by utilizing fluorescent particles and dye is explained.

For the velocity measurement, particle tracking velocimetry (PTV) is utilized with 1 μm diameter particles as flow tracer. The velocity profile is obtained by spatially and temporally averaging of 99 instantaneous velocity vectors measured by PTV in the every set of measurement under the laminar flow condition with no temporal velocity variation.

For the pH distribution measurement, LIF is applied with pH sensitive dye. Fluorescent intensity $I_f$ [W/m²] is represented by following relationship given by Coppeta and Rogers (1998)

$$I_f(\lambda, \text{pH}) = I_e(\lambda)C\phi\epsilon(\text{pH}),$$

where $I_e$ [W/m²] is the excitation light intensity, $\lambda$ [nm] is the excitation wavelength, $C$ [kg/m²] is the concentration of fluorescent dye, $\phi$ [-] is the quantum efficiency and $\epsilon$ [m²/kg] is the absorption coefficient which is dependent on the pH value.

The calibration between the fluorescent intensity and pH were performed at five points over the measurement area as depicted in Figure 4 by using the five aqueous solutions (pH 5.5, 6.0, 6.6, 6.9 and 7.3). The aqueous solutions at pH 6.0-7.3 were prepared by mixing the sodium dihydrogenphosphate solution and the disodium hydrogenphosphate solution (Wako Pure Chemical Industries, Inc.). The aqueous solution at pH 5.5 was prepared by mixing the acetic acid solution and the sodium hydroxide solution (Wako Pure Chemical Industries, Inc.). The influence of the background noise from the CCD camera was eliminated by subtracting the background intensity from the detected intensity. To reduce the pixel error, an average per 8 × 8 pixels was performed and this resulted in a spatial resolution of 5.2 μm × 5.2 μm. To eliminate the influence of the nonuniform excitation light intensity, normalized fluorescent intensity was calculated by dividing the each values of fluorescent intensities by the values at pH 6.9 chosen as a reference value pH$_{ref}$. Normalized fluorescent intensity was represented by the following equation.

$$I_c = \frac{I_e(\lambda, \text{pH}) - I_{back}}{I_{ref}(\lambda, \text{pH}_{ref}) - I_{back}}.$$  (7)

$I_c$ [-] is normalized fluorescent intensity, $I_{ref}$ [W/m²] is fluorescent intensity at reference value and $I_{back}$ [W/m²] is back ground intensity which is captured at no excitation light. A normalized single calibration curve was exhibited in Figure 5. In a set of the experiments, the measured fluorescent intensity was corresponded to the pH value by using the normalized calibration curve. A pH resolution of 0.1 was achieved, which was evaluated by the RMS value of the fluctuation of pixels and that of the excitation light intensity.
6. Results and discussion

6.1 Two-dimensional distribution of velocity and dissolved CO$_2$ concentration

CO$_2$ dissolution into water was visualized by simultaneous measurement with PTV/LIF. The ion-exchanged water (IEW) containing fluorescent dye and particles was injected into the wide channel inlet and moved by pressure-driven flow. Cylindrical reservoirs were attached on the PDMS at the inlet and outlet of wide channel and the liquid velocity was changed by altering the hydraulic head of IEW in the inlet and outlet reservoirs. The gas phase sample containing CO$_2$ at 95 % vol. was imposed in the narrow channel by a syringe pump (KD Scientific Inc., KDS210) at a constant flow rate of 700 $\mu$L/min. The fluorescence images were captured at $z = 7.5$ $\mu$m under the condition that the flow and the concentration field was fully developed and the steady state reached in the steady state. Measurement region was set to the junction area of the gas-liquid flow as shown in figure 6 (a). The measurements were conducted at the maximum liquid flow rate $u_{max}$ of 172 $\mu$m/s, 299 $\mu$m/s and 433 $\mu$m/s in the measurement plane. An instantaneous image at the measurement region was depicted in Figure 6 (b). Figure 7 shows the velocity profile and CO$_2$ concentration distribution at $u_{max} = 299$ $\mu$m/s. In this study, spatial resolution is $6.2 \times 24.8$ $\mu$m and $5 \times 5$ $\mu$m in velocity and CO$_2$ concentration measurement, respectively. Figure 7 indicates that the trapezoidal velocity profile, which agrees well with the theoretical flow profile in the rectangular...
channel (Brody et al. 1996), even in the case that one side boundary is a gas-liquid interface. The cross-sectional velocity profiles averaged in stream-wise direction at various liquid flow rates are plotted in Figure 8. The error bar indicates the RMS value. All profiles indicate the asymmetric shapes and the liquid velocity appears in the vicinity of the gas-liquid interface unlike the side of the PDMS wall. It is considered that the gas-liquid interface is moving and acts as the slip boundary, which differs from the solid wall case. On the other hand, the CO₂ concentration gradient was generated by absorbing CO₂ through the gas-liquid interface as shown in Figure 7. Figure 9 represents the cross-sectional CO₂ concentration gradient profiles at \( x = 150 \mu \text{m} \). These profiles indicate that the amount of concentration increases with the decreasing of the liquid flow rate, which shows that the CO₂ transfer is significantly affected by the convection.

![Fig. 7. Velocity vector map and CO₂ concentration contour at \( u_{\text{max}} = 299 \mu \text{m/s} \).](image)

![Fig. 8. Velocity profiles averaged in the stream wise direction.](image)

![Fig. 9. CO₂ concentration profiles at \( x = 150 \mu \text{m} \).](image)
6.2 Convection and diffusion fluxes of CO₂

For further investigation of the mass transfer phenomena, the convection and diffusion fluxes of CO₂ were evaluated by using the measured data of velocity and CO₂ concentration. The convection flux, \( J_c \) [mol/m²s], is described as

\[
J_c = C_{CO₂} \begin{pmatrix} u \\ v \end{pmatrix} \tag{8}
\]

And the diffusion flux, \( J_d \) [mol/m²s], is expressed as

\[
J_d = -D \begin{pmatrix} \partial C_{CO₂} / \partial x \\ \partial C_{CO₂} / \partial y \end{pmatrix}, \tag{9}
\]

where \( D \) [m²/s] is the diffusion coefficient of CO₂ in water. In the present experiment condition, \( D \) is calculated at \( 1.73 \times 10^{-9} \) m²/s (Melachlan and Danckwerts 1972). The velocity component is exist only in \( x \) direction and the concentration gradient in the stream-wise direction is negligible. Thus, the convection and diffusion fluxes are simplified as \( J_c = C_{CO₂}u \) and \( J_d = -D \partial C_{CO₂} / \partial y \), respectively. Therefore, the two dimensional molar flux \( J \) is represented as follows,

\[
J = J_c + J_d = \begin{pmatrix} C_{CO₂}u \\ -D \partial C_{CO₂} / \partial y \end{pmatrix}. \tag{10}
\]

For the calculation of the convection flux in the \( x \) direction and the diffusion flux in the \( y \) direction, the \( C_{CO₂} \) distributions were obtained in the span-wise direction by using the third polynomial equation in order to smooth the \( C_{CO₂} \) measurement data. Calculation points of the convection and diffusion fluxes were based on the interval of velocity vector. Figure 9 shows the molar flux vector map which combined \( J_c \) and \( J_d \). It is observed that the convection flux is more dominant than the diffusion flux and large CO₂ flux is distributed in the right-hand side half of the liquid flow field.

![Molar flux vector map at \( u_{max} = 299 \) μm/s.](image)
Figure 10 indicates the absolute value of the convection and diffusion fluxes at $x = 100 \, \mu m$. The convection molar flux was dominant compared with the diffusion flux at all liquid flow rates. The diffusion flux at the gas-liquid interface ($y = 400 \, \mu m$) is assumed to be the molar flux of CO$_2$ from the gas phase into water. The profiles of diffusion flux indicate that the amount of CO$_2$ flux from gas phase into water is almost same even if liquid flow rates differ. This result can be taken into account by Henry’s law as described in Section 2. Therefore, the difference of CO$_2$ concentration at the gas-liquid interface as shown in Figure 9 can be attributed to the convection flux in the vicinity of the liquid surface. In other words, the liquid velocity near the interface carried CO$_2$ in the vicinity of interface downstream and reduced the contact time of gas and liquid.

7. Conclusions

The CO$_2$ dissolution process in water was investigated by utilizing simultaneous measurement of velocity and CO$_2$ concentration distribution in order to obtain the detailed information of the mass transfer process through the gas-liquid interface. The important conclusions obtained from this work are summarized below.

(1) The static gas-liquid interface was realized in the microchannel by optimizing the channel depth and the wettability of channel walls. The simultaneous measurement of velocity and pH distribution was conducted by PTV/LIF in the gas-liquid microchannel flow. Spatial resolution was $6.2 \times 24.8 \, \mu m$ and $5.2 \times 5.2 \, \mu m$ in velocity and pH measurement, respectively. The CO$_2$ concentration distribution was calculated by considering the partial hydration of CO$_2$.

(2) In the velocity measurement, the velocity profiles indicated the higher value at the gas-liquid interface as compared with PDMS wall side. Decrease of the CO$_2$ concentration accompanied by the increase of the liquid velocity was attributed to the presence of the velocity at gas-liquid interface, which reduced the contact time of gas and liquid.
(3) The convection and diffusion mass flux was obtained from the experimental data. The amount of the convection flux was much larger than that of the diffusion flux, thus the convection was much dominant in CO2 transfer process.

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References


