Multiphase CO₂ Dispersions in Microfluidics: Formation, Phases, and Mass Transfer

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ABSTRACT

The dissolution and microfluidic mass transfer of carbon dioxide in water at high-pressure conditions are crucial for a myriad of technological applications, including microreactors, extractions, and carbon capture, utilization, and sequestration (CCUS) processes. In this experimental work, we use a high-pressure microfluidic method to elucidate the mass transfer process of CO₂ in water at high pressure. An intriguing multiphase CO₂ flow and dispersions are observed when operating at the pressure-temperature (P-T) condition close to the CO₂ gas-liquid phase boundary (P = 6.5 MPa and T = 23.5 ± 0.5 °C). We propose a series of strategies to unravel this complex multi-phase dynamics by calculating each phase’s volume and mass change in a gas-liquid coexistent CO₂ dispersion, estimating the possible CO₂ concentration change in water, and comparing with the CO₂ solubility data. Finally, we quantify the CO₂ mass transfer by directly calculating the CO₂ dissolution rate in water and estimating the volumetric mass transfer coefficient (kₐ,a). The results show that the mass transfer may be influenced by the specific area (a), CO₂ concentration gradient in the water slug, and the traveling speed of a dispersion.

1. Introduction

The technologies of carbon capture, utilization, and sequestration (CCUS) are essential to reduce CO₂ emissions and consequently mitigate global warming issues (Orr et al., 2018; Zhang et al., 2020). CCUS integrates methods to gather and transport CO₂ from large emission sites, such as power plants and oil refineries (Wulfhorst et al., 2019). The concentrated CO₂ can be utilized for enhanced oil recovery (EOR) (Adasani and Bai, 2011) and enhanced coalbed methane (Prabu and Mallick, 2015; Mukherjee and Misra, 2018) for energy fuel production while sequestering CO₂, and the further purified CO₂ can be used for chemical synthesis (Meunier et al., 2020; Branco et al., 2020). Alternatively, the captured CO₂ can be stored in various geological formations, such as in ocean (Adams and Caldeira, 2008; Aminu et al., 2017), in sub-seabeds (Carroll et al., 2014; Teng and Zhang, 2018), and in deep saline aquifers for a long time (Bachu, 2015).

The CO₂ mass transport behavior, therefore, plays a critical role in many CCUS processes, including the CO₂ absorption in the capture process (Abolhasani et al., 2014; Wulfhorst et al., 2019) and the CO₂ dissolution in the pore fluids of sequestration sites. For example, in EOR engineering precise data of CO₂ dissolution in the pore-fluids helps estimate the required injection pressure to reach the minimum miscibility pressure for a better recovery efficiency (Adasani and Bai, 2011). The CO₂ dissolution and mass transfer processes affect the storage capacity of deep saline aquifers during the early injection stage (via structural and residual trapping of CO₂ in micropores) as well as the long-term solubility trapping and mineralization of CO₂ with the host, porous rock (Huppert and Neufeld, 2014; Bachu, 2015; Aminu et al., 2017). Furthermore, understanding the CO₂ mass transport processes helps evaluate the sealing integrity and calculate the pressure build-up and CO₂ leakage (Singh, 2018), which are essential for mitigating potential environmental impacts (Carroll et al., 2014; Blackford et al., 2014).

The early experimental investigations for measuring the CO₂ dissolution rate and mass transfer include both in-situ field experiments (Brewer et al., 1999, 2002; Blackford et al., 2014; Sellami et al., 2015) and laboratory measurements using stirred vessels (Van’t Riet, 1979) or bubble columns reactors (Shah et al., 1982; Kantarci et al., 2005). However, the field experiments usually are time- and budget-consuming, and most of the previous laboratory experiments require large apparatuses to handle working fluids at high pressure safely (Teng and Yamasaki, 2000; Ogasawara et al., 2001; Maalej et al., 2001) and therefore more space, resources, and experimental time. Hence, it motivates us to explore alternatives for acquiring essential mass transfer data at elevated pressure more efficiently since the relevant experimental studies are crucial but rare currently.

Microfluidics has become an emerging and useful tool for fluid physics (Anna, 2016; Amstad et al., 2017) as well as energy and environmental technologies due to its time and economic efficiency (De Jong et al., 2006; Kjeang et al., 2009; Sinton, 2014; Lifton, 2016). A variety of microfluidic platforms have been utilized to investigate the mass transfer rate of gases (e.g., CO₂ (Yue et al., 2007; Sun and Cubaud, 2011; Abolhasani et al., 2012), air (Yue et al., 2009), and ozone (Ren et al., 2012)) in different solvents, the CO₂ take-up capacity of physical solvents for CO₂ capture applications (Sun and Cubaud, 2011; Lefortier et al., 2012; Abolhasani et al., 2012), and the influence of temperature (Tumarkin et al., 2011) and surfactants (Shim et al., 2014) on CO₂ solubility in water. Moreover, the development of high-pressure microfluidic devices in the last decade enables ex-
periments to operate in a broader pressure ($P$) and temperature ($T$) range up to $P = 45$ MPa and $T = 500$ °C (Marre et al., 2012). A few of microfluidic studies exploiting high-$P$ platforms provide insights into the CO$_2$ behaviors in different carbon storage scenarios, including the invasion patterns of CO$_2$ displacing the pore fluid (Zhang et al., 2011; Morais et al., 2016), the applications in the enhanced oil recovery (EOR) (Nguyen et al., 2015; Sharbatian et al., 2018), the physical properties at the supercritical state (Pinho et al., 2015), fast screening the CO$_2$ phase state in different solvents (Pinho et al., 2014; Bao et al., 2016), and the CO$_2$ solubility in brine (Liu et al., 2012).

Microfluidic studies addressing the mass transfer rate of CO$_2$ in water/brine at high $P$-$T$ conditions, especially for the liquid and supercritical CO$_2$, are still limited (Sell et al., 2013; Yao et al., 2015, 2017; Qin et al., 2017, 2018). Sell et al. (Sell et al., 2013) reported a minor influence of pressure on the CO$_2$ diffusion coefficient as $P$ increased from 0.1 to 5 Mpa. In contrast, the salinity significantly hinders CO$_2$ diffusion process in water, with a decrease in the diffusion coefficient by 60% with increasing salinity (from 0 to 5 M).

Yao et al. studied the pressure effects on the CO$_2$ mass transfer rate in water by measuring the liquid side volumetric mass transfer coefficient, $k_{L}a$, under elevated pressure from 0.1 to 3 M Pa. They found that $k_{L}a$ increased with the rising pressure and attributed this to the enlarged cross-sectional area of a CO$_2$ bubble at high pressure, which increases the CO$_2$-water contact area and enhances CO$_2$ mass transfer (Yao et al., 2015). Interestingly, they did not observe a significant influence of pressure on the CO$_2$ absorption in the chemical solvent DEA (diethanolamine) from their later experiments. They attributed to the shrinking interfacial area due to the altering flow patterns and the channel geometry (Yao et al., 2017).

Qin et al. calculated the mass transfer coefficient ($k_{L}$) from the shrinkage of supercritical CO$_2$, at 8 MPa and 40 °C according to the 3-D morphology of an ideal Taylor bubble in a rectangular channel (Qin et al., 2017). Their results showed that $k_L$ rose from $1.5 \times 10^{-4}$ to $7.5 \times 10^{-4}$ m/s as the water volume fraction increased from 0.28 to 0.9. Additionally, CO$_2$ droplets with a faster-moving speed had a higher $k_L$ due to the strong inner recirculation in the water slugs, enhancing the mixing of CO$_2$ and water (Qin et al., 2018).

In this work, we experimentally investigate the dissolution of liquid CO$_2$ in water at the injection pressure $P_{inj} = 6.5$ MPa and room temperature, $T = 23.5$ °C. To the best knowledge of ours, we observe intriguing and remarkable multiphase-coexisting CO$_2$ dispersions at high pressure, for the first time, generated by a two-phase CO$_2$ flow merging with water at the microfluidic T-junction (see Figure 1), while most similar microfluidic studies using two-phase flow have focused on the generation of monodisperse segmented flows and associated fluid dynamics and patterns (Zhu et al., 2016; Laborie et al., 2016; Eggersdorfer et al., 2018; Chakraborty et al., 2019; Salari et al., 2020; Fan et al., 2020). To analyze the complex dynamics of the multi-component CO$_2$ droplets, which involves phase change and dissolution processes, we first differentiate the phase state of CO$_2$ inside the dispersion by comparing the mass change and the solubility limit in water (for a particular $P$ and $T$ condition). A detailed discussion is provided according to two different phase combinations. Based on these results, we further quantify the mass transfer process by calculating the dissolution rate of CO$_2$, $M_{dis}$, and calculating the volumetric mass transfer coefficient, $k_{L}a$. We find that the estimated $k_{L}a$ decreases rapidly with time, which may attribute to the change of the specific area, CO$_2$ concentration in the water slug, and the moving speed of dispersions.

2. Material and methods

We experimentally observed an intriguing two-phase CO$_2$ flow with a clear interface in the CO$_2$ injection channel before the microfluidic T-junction. Consequently, the multiphase coexisting CO$_2$ dispersions were formed in the T-junction microchannel after merging with Milli-Q water, as shown in Fig. 1a. The experiments were operated at the in-
jection pressure, $P_{\text{inj}} = 6.5 \pm 0.05 \text{ MPa}$ and the chip temperature, $T_{\text{chip}} = 23.5 \pm 0.5 \degree C$, as pointed by the blue circle in Fig. 1b. The microchannel was fabricated using the deep reactive ion etching method (DRIE) (Franssila, 2010; Ho and Tsai, 2020). The main channel is 100 $\mu$m in width and 30 $\mu$m in height. The side-channel for introducing CO$_2$ is 50 $\mu$m in width and has the same height as the main channel.

2.1. Experimental

The microfluidics was installed in a metal platform that can sustain high-pressure. CO$_2$ pressure was ramped up from the atmospheric condition (0.1 MPa and 23.5 $\degree C$) to a high-pressure condition for transforming to the liquid state (6.5 MPa and 23.5 $\degree C$). This process was controlled by a high-pressure gas pump (ISCO 100DX), which directly connects with the gas tank (Praxair, RES K CO$_2$ 99.998%). A backpressure regulator (TESCOM BP 25 – 4000 PSI) was connected to the system’s outlet to control the CO$_2$ flow rate by regulating a proper pressure gradient across the channel. Milli-Q water was loaded in stainless steel syringes and pumped by a syringe pump (Chemyx Inc. Fusion 6000) after one hour of degassing in a vacuum chamber. Water is injected at the flow rate of 10 $\mu$l/min for the bubbly, intermittent, and annular-1 flow. The water injection rate for the annular-2 flow is lower, at 5 $\mu$l/min. A thermocouple (K-type) was attached to the microfluidic chip and to monitor the temperature. The flow was observed by using an inverted microscope (Zeiss Axio Observer 7 Materials, with a 5× objective) and recorded by a high-speed camera (Phantom V710L) at 5,000 frames per second (fps).

2.2. Image analysis

We applied a series of post-image processing functions in ImageJ (NIH Image) (Abramoff et al., 2004) to measure the size of a single dispersion and track its movement with respect to time. We first calibrated these data by comparing them with the manually measured results. The maximum difference between them is within 2.3 % in length. The measured data were further analyzed by using a customized code written in MATLAB (MathWorks ®). The variation between dispersions was evaluated by calculating the standard deviation of at least five bubbles for each representative flow pattern. The result showed good consistency in the size and position. The variance is about 2.5 % maximum in dispersion’s length and within 2.9 % in displacement.

2.3. Estimations of the total volume and surface area of a CO$_2$ dispersion

From our experimental images we notice that a dispersion comprises a brighter area surrounded by the black contour, as shown in Fig. 2a. We consider this black contour line resulting from the curved CO$_2$-water interface, which reflects the light and reduces the interface’s brightness. The width of the black contour is measured to be about 8 $\mu$m. Therefore, we assume the geometry of a CO$_2$ dispersion is a planar disk, with two spherical caps on both ends (see Fig. 2b). The red area represents the curved CO$_2$-water interface. Fig. 2c and 2d show the schematic shape of the CO$_2$ dispersion from the top view and the side view, respectively. The volume of a dispersion, $V_T$, is the sum of the center planar part and the two-sided caps:

$$V_T = 2V_{\text{cap}} + V_{\text{body}}.$$  

The volume of the cap $V_{\text{cap}}$ equals the volume of the fan region (OP1P2) highlighted in color green in (c). (e) The detailed dimensions of the gray area $A_s$ in (d). (f) The drawing of the quarter cross-section of the center body through the B-B plane.

The volume of the cap $V_{\text{cap}}$ equals the volume of the triangle OP1P2, from Fig. 2c. The volume of the green fan, $V_{\text{fan}}$, and triangle OP1P2, $V_{\text{tri}}$, can be written as:

$$V_{\text{fan}} = \frac{1}{2} \int_{\frac{\pi}{2} - \theta_t}^{\frac{\pi}{2} - \theta_t} A_s R_1 \cos \left( \frac{\pi}{2} - \theta_t \right) \cos \left( \frac{\pi}{2} - \theta_t \right) \sin \left( \frac{\pi}{2} - \theta_t \right) \, d\theta,$$

$$V_{\text{tri}} = \frac{1}{2} (W - 2\delta_f) R_1 \cos \left( \frac{\pi}{2} - \theta_c \right) (H - 2\delta_f),$$

where $W$ and $H$ are the width and height of the channel, $R_1$ is the radius of the circular cap, $\theta_c$ represents the con-
The contact angle between the (outer) cap and the microchannel (see Fig. 2c), and $\delta_f$ denotes the thickness of water film between CO$_2$ dispersion and the sidewall. $A_s$ in Eqn. (2) is the cross-sectional area of the green fan through the A-A plane, as the gray area in Fig. 2d. The dimensions of $A_s$ can be seen in Fig. 2c; note that the dimensions presented are exaggerated for better demonstration. $A_s$ can be expressed as:

$$A_s = (R_1 - C)(H - 2\delta_f) + \beta r^2 - \frac{1}{2} r \cos \beta (H - 2\delta_f). \quad (4)$$

where $r$ is the radius of the circular cap projected from the side view, and $\beta$ is half of the central angle. We acquired these two parameters according to their geometrical relations:

$$r \cos \beta = r - C, \quad (5)$$

$$r \sin \beta = \frac{H}{2} - \delta_f. \quad (6)$$

The volume of the center body of a CO$_2$ dispersion is calculated as $V_{body} = A_s (L_{drop} - 2L_{cap})$, where $L_{cap} = R_1 \cos (\frac{\pi}{2} - \theta_f)$ is the length of the circular cap on both ends. $A_s$ denotes the cross-sectional area of the center body through the B-B plane. We assume the center section’s cross-sectional area is constant. Fig. 2f schematically demonstrates the idealized dimensions of this cross-section. We consider the shaded region of the body section is due to the curvilinear CO$_2$-water interface. $A_c$ hence can be expressed as:

$$A_c = (W - 2\delta_f)(H - 2\delta_f) - (4 - \pi)(C - \delta_f)^2. \quad (7)$$

By substituting Eqn. (2), (3), and (7) into Eqn. (1), the volume of CO$_2$ dispersion is acquired. This calculation result agree well with the 3-D model built using computer-aided design software (PTC Creo), with an estimated, average error of 1.5%. Furthermore, a close examination of the CO$_2$ bubble/droplet shows a slightly asymmetric shape of 1 $\mu$m difference between the front and rear radii. We calculate the corresponding CO$_2$ bubble’s volume using Eqn. (1) to Eqn. (7). The volume difference due to the asymmetric bubble geometry is about 0.4%.

3. Results and discussion

3.1. Multiphase CO$_2$ flow and dispersions

Fig. 3a-c are experimental snapshots, showing three distinct CO$_2$ multiphase flow patterns observed in the CO$_2$ channel before the T-junction (when $P_{inj} = 6.51$ and 6.48 MPa, $P_{back} = 6.15$ MPa and $T_{chip}$ $\approx 23.5^\circ$C, close to the CO$_2$ gas-liquid phase boundary). The multiphase flow quickly transited from a segmented flow pattern (Fig. 3a) to a parallel flow with an upstream pinch-off nose, emitting segmented flow periodically (Fig. 3b). This parallel flow kept propagating along with the CO$_2$ channel and finally anchored at the T-junction, seen in (c). These three flow modes are similar to the classic condensation flows observed when flowing the vapor state of water (Wu and Cheng, 2005; Chen et al., 2014) or refrigerants (Coleman and Garimella, 2003; Al-Zaidi et al., 2018) in the microchannel as the sidewall temperature ($T_{wall}$) is lower than the vapor temperature of the fluid. We hence follow the same naming convention, calling the first segmented flow the “Bubbly flow” (Fig. 3a), the “Intermittent flow” for the second transitional pattern (in Fig. 3b), and the “Annular flow” for the final stratified flow pattern (in Fig. 3c). We artificially dyed the central or inner dispersed phase in light green in the images for better visualization.

At the microfluidic T-junction, the multiphase CO$_2$ flow periodically generates and emits dispersions in the main channel after being sheared off by the water flow. Fig. 3d shows such image sequences of the development of CO$_2$ dispersions for the different CO$_2$ flow patterns shown in Fig. 3a-c. These dispersions are multiphase with a clear interfacial boundary observed between the phases. Although each of the multi-phases is known to be either gas or liquid CO$_2$, because of the experimental pressure condition, without presumptions each exact phase was not certain and needed to be determined first. From the sequential images in Fig. 3a-c, the inner phase (artificially dyed in light green) prefers to stay on the right side of a CO$_2$ dispersion, while the outer phase accumulates on the left. For clarification and convenience, we call the phase on the right side of the CO$_2$ dispersion the “inner (dyed) phase” and the other the “outer (undyed) phase” based on their appearance before the microfluidic T-junction (see Fig. 3a-c).

Fig. 3e shows the total length of CO$_2$ dispersions, $L_{drop}$, changing with traveling time. The size change of the inner (dyed) phase seems to influences $L_{drop}$ greatly. For dispersions generated by the bubbly flow (depicted by ◆) and the intermittent flow (depicted by ▲), $L_{drop}$ decreases due to the shrinkage of the inner (dyed) phase. $L_{drop}$ reaches the steady-state when the inner phase completely vanishes. In general, we observe the same behavior for most dispersions generated by the annular flow, as depicted by ♦ in Fig. 3d. However, we surprisingly observed a different size change behavior of inner (dyed) phase in some dispersions generated by the annular CO$_2$ flow. As shown in Fig. 3 (d4), the inner phase shrank at the beginning when the dispersion detached from the T-junction. However, it started to expand after the dispersion traveled around 60 ms in the main channel, leading to the growth of CO$_2$ dispersions after moving 55 mm away from the T-junction (depicted by ▲).

3.2. Determination of the phase states of a multiphase CO$_2$ dispersion

Before detailed analyses on CO$_2$ flow and dissolution dynamics, we have to first differentiate and analyze the exact phases in the multiphase CO$_2$ droplets/bubbles without any presumptions. Based on the experimental condition ($P_{inj} = 6.5$ MPa and $T_{chip}$ $\approx 23.5^\circ$C), we knew the coexistence of liquid and gas CO$_2$ in a dispersion before the T-junction. However, it is challenging to identify the phase states from the experimental grayscale images directly. These phases’ grayscale values were close, measured to be 133.7 (±5.8) and 132.3 (±6.3) for the inner (dyed) and outer (undyed)
phases, respectively. In addition, the surface tension at the water-gas CO₂ interface ($\sigma_{W/G} = 31.7$ mN/m) is very close to that at the water-liquid CO₂ ($\sigma_{W/L} = 30.8$ mN/m) (Pereira et al., 2016). This implies that both gas and liquid CO₂ could affix to the water and wrap the other phase. Here, we discuss the processes determining the phase state of CO₂ dispersions in more detail by analyzing the volume change, density difference, mass loss, and solubility in water.

Fig. 4a demonstrates the total volume of CO₂ dispersions, $V_T$, changing with time, while 4b and 4c show the volume fraction of the inner (dyed) phase ($V_{in}$) and of outer (undyed) phase ($V_{out}$), respectively. From the observations, $V_{in}$ initially decreases dramatically for all representative cases, while $V_{out}$ increases in the range of 25% - 30% of the change of $V_{in}$, implying the mass exchange between two phases inside a CO₂ dispersion. Dispersions with a larger initial $V_{out}$ result in a bigger final size in the steady-state (flat regime), as seen in the bubbly flow (depicted by ●), comparing to other cases with larger $V_{in}$ (depicted by ▲, ◆, and △).

To systematically determine each phase (gas or liquid) for the multiphase CO₂, we furthermore consider two different phase combinations and look into their corresponding mass change with time. By comparing with the CO₂ solubility data at 6.5 MPa and 23.5 °C, this data would help differentiate the phase state in a CO₂ dispersion. The first presumption considers that the inner (dyed) phase is liquid CO₂ and the outer gas. The second presumption is the other way, assuming that the inner (dyed) phase is gas and the outer liquid.

Fig. 5 shows the calculation results according to the two presumptions by showing the total cumulative mass, $M_T$, the net mass change, $\Delta M_T$, and the estimated CO₂ concentration in water slugs, $|\Delta M_T|/V_{slug}$. Under the first presumption (assuming the inner (dyed) phase is liquid CO₂), $M_T$ dramatically decreases in the first 20 ms and reaches the steady-state for dispersions of the bubbly, intermittent, and annular-1 flow, as shown in Fig. 5a. The net mass change, $\Delta M_T$, during this period is between $-5 \times 10^{-11}$ to $-20 \times 10^{-11}$ kg, shown in Fig. 5b. Notably, dispersions in Annular-2 (▲) show a gradual gain of the mass after 40 ms of traveling time, which is different from the previous three cases. Here, we consider that the mass transfer in a CO₂ dispersion includes two processes: (1) the phase transition between the two phases and (2) the dissolution of CO₂ into the surrounding water. The phase change processes should follow mass conservation, resulting in zero (or negligible) mass change (see Appendix A for a detailed analysis). Therefore, the net mass change, $\Delta M_T$, should always be negative due to the dissolution.

We further estimate the CO₂ concentration in the water changing with time by dividing the absolute value of $\Delta M$ by the volume of the adjacent water slug, $V_{slug}$. Fig. 5c shows that the estimated CO₂ concentration for all repre-
The above analyses show that the second presumption yields consistent results with the CO₂ solubility data given by the method introduced in Section 2.3 using Eq. (1)-(7), and \(V_{r,i}^{*}\) denotes the initial volume of a dispersion, i.e., \(V_{r,i}^{*}(t = 0)\). The corresponding fractional volume change of the inner (dyed) and outer phase inside the dispersion is presented in (b) and (c), respectively. Dispersions generated by the three distinct CO₂ flow patterns are shown, including the bubbly flow (.), the intermittent flow (■), and the two different CO₂ phase change behavior observed in the annular flow [annular-1 (•) and annular-2 (▲)].

Figure 4: (a) The dimensionless volume of CO₂ dispersions changes with time, where \(V_{r,i}^{*}\) is estimated according to the method introduced in Section 2.3 using Eq. (1)-(7), and \(V_{r,0}\) denotes the initial volume of a dispersion, i.e., \(V_{r,i}^{*}(t = 0)\). The corresponding fractional volume change of the inner (dyed) and outer phase inside the dispersion is presented in (b) and (c), respectively. Dispersions generated by the three distinct CO₂ flow patterns are shown, including the bubbly flow (.), the intermittent flow (■), and the two different CO₂ phase change behavior observed in the annular flow [annular-1 (•) and annular-2 (▲)].

Figure 5: Results of time-varying CO₂ mass change estimated according to the presumption 1 and 2. (a) and (b) compare the cumulative mass of a CO₂ dispersion, \(M_{T} = M_{in} + M_{out}\) (kg), changes with time, where \(M_{in}\) and \(M_{out}\) represent the mass of the inner (dyed) and outer phase of the dispersion, respectively. (c) and (d) show the net mass change of CO₂ dispersions, where \(\Delta M_{T} = M_{T} - M_{T}(t = 0)\) (kg). Here, the negative sign of \(\Delta M_{T}\) implies the dissolution of CO₂ in the water. (e) and (f) demonstrate the CO₂ concentration change in water, estimated by dividing the absolute value of \(\Delta M_{T}\) by the volume of adjacent water slug, \(V_{inj}\) (m³). The black dash line denotes the theoretical solubility of CO₂ in water at \(P = 6.3\) MPa and \(T = 23.5\) °C (Diamond and Akinfiev, 2003).

The above analyses show that the second presumption yields consistent results with the CO₂ solubility data given \(P\) and \(T\). Therefore, we confirm that the inner (dyed) phase is CO₂ gas state, and the outer phase is the liquid state. This conclusion is further validated due to the following two reasons. First, the volume change ratio of the outer to inner phase, \(V_{inj}/V_{inj}^{*}\), is about 0.25 – 0.3. This value is also close to the density ratio of gas to liquid CO₂, \(\rho_{g}/\rho_{l} = 0.33\), suggesting the shrinkage of the inner (dyed) phase in a CO₂ dispersion is the process combining the phase transition from the gas to liquid and the dissolution into the surrounding water. Second, presumption one yields an unusual increase in the total mass of case Annular-2 (demonstrated in Fig. 4a),
implying that this assumption is incorrect because there are no other external mass sources. Besides, the presumption one overestimates the amount of dissolving CO$_2$ in water.

### 3.3. Formation of multiphase CO$_2$ dispersions

We further look into how the multiphase flow is formed in the CO$_2$ channel and what happens to such a CO$_2$ dispersion evolving in the microchannel, as seen in Fig. 3. These multiphase patterns are observed when increasing $P_{inj}$ from 1 atm up to 6.5 MPa at room temperature, and CO$_2$ in the pump started to phase change from the gas to liquid state slowly. Most of CO$_2$ likely stayed in the gas state as the oversaturated CO$_2$ vapor.

As CO$_2$ entered the microfluidics, CO$_2$ in the gas state flows in the center of the CO$_2$ channel, while the liquid CO$_2$ stayed on side walls because it is more viscous than the gas state. The formation of three distinct flow patterns observed might be similar to the jetting flow generated using the co-flow (Utada et al., 2007) and the cross-type microchannel (Cubaud and Mason, 2008). This kind of flow pattern may occur when the central fluid’s velocity (gas CO$_2$) is greater than the outer one (liquid CO$_2$). The upstream annular flow may form because the inertia force from CO$_2$ gas stream stabilizes with the viscous force and surface tension at the gas-liquid interface (Utada et al., 2007). At the nose of the central CO$_2$ stream, gas bubbles detached and became the downstream bubbly flow, which might be triggered by the amplified capillary waves due to the surface tension gradient (Utada et al., 2008). The intermittent flow may be the transition between the bubbly and the annular flow. We observed that the intermittent flow emits droplets/bubbles downstream while upstream became an annular flow.

After the CO$_2$ flow merging with the continuous water phase, the multiphase CO$_2$ dispersions were formed periodically. The vapor CO$_2$ in a dispersion (i.e., the dyed inner phase) continued to transform from the gas to the liquid state, resulting in the rapid shrinkage of inner phase when moving in the main channel, as shown in Fig. 3d (first three rows). The expansion of dispersion in Annular-2 case (as demonstrated by ▲ in Fig. 3d and 3e) might due to the lower CO$_2$ vapor temperature than the microchannel’s sidewall temperature. The local pressure along the channel keeps decreasing due to the hydraulic pressure gradient that drives the movement of a CO$_2$ dispersion (Kundu et al., 2011). CO$_2$ vapor temperature drops with the descending pressure, based on the Clausius-Clapeyron relation (Bejan, 2016), leading to the $P-T$ condition moving toward the phase boundary (Fig. 1b). Once the vapor temperature decreases to the sidewall temperature, CO$_2$ starts phase change from the liquid to gas state and expands $L_{drop}$.

### 3.4. Mass transfer of the multiphase CO$_2$ dispersions

To unravel the dissolution process while phase change is taking place, we develop an analysis to estimate the volumetric mass transfer coefficient, $k_{L}a$ (1/s), of CO$_2$ in water according to the dissolution rate of CO$_2$. $M_{dis}$, and mass conservation. We first assume that the continuous phase, water, is initially free from CO$_2$. Both gas and liquid CO$_2$ are incompressible due to the negligible density variation in a small pressure difference (estimated $\sim 22$ kPa). The CO$_2$ dissolution rate equals the net mass change rate of a dispersion, which can be expressed to the sum of the liquid and the gas parts:

$$M_{dis} = \frac{dM_T}{dt} = \rho_i \frac{dV_i}{dt} + \rho_g \frac{dV_g}{dt}, \tag{8}$$

where $\rho_i$ ($\rho_g$) is the density of CO$_2$ in the liquid (gas) state. $V_i$ ($V_g$) denotes the volume of liquid (gas) CO$_2$. By integrating Eqn. (8), the total mass of dissolving CO$_2$ is expressed as:

$$\int_{t_0}^{t} M_{dis} dt = \rho_i(V_i - V_{i,0}) + \rho_g(V_g - V_{g,0}), \tag{9}$$

where $V_{i,0}$ and $V_{g,0}$ (m$^3$) denotes the volume of liquid and gas CO$_2$ at $t = 0$, respectively.

The dissolved CO$_2$ increases its concentration in a water slug, and the convective mass transfer can be expressed as: (Yao et al., 2015; Ho et al., 2021)

$$M_{dis} = -k_L A_T (C^* - C(t)) = -V_{slug} \frac{dC}{dt}. \tag{10}$$

Here, $k_L$ (m/s) denotes the mass transfer coefficient of CO$_2$ in water. $A_T$ (m$^2$) is the surface area of a dispersion, and $V_{slug}$ is the volume of the adjacent water slug. $C^*$ and $C(t)$ represent the saturation concentration of CO$_2$ in water and the mean CO$_2$ concentration in a water slug, respectively.

The CO$_2$ concentration change in the water slug, $C^* - C(t)$, can be written as an exponential function by integrating the second identity in Eqn. (10), so

$$C^* - C(t) = (C^* - C_0)e^{-k_La t} = S e^{-k_La t}. \tag{12}$$

The dissolved CO$_2$ in water as a function of time thus can be expressed as:

$$M_{dis} = -k_L a SV_{slug} e^{-k_La t}, \tag{11}$$

where $C_0$ is the initial CO$_2$ concentration in water. Because we assume water is initially free from CO$_2$, $C^* - C_0$ represents the CO$_2$ solubility in the water (S) in the unit of kg/m$^3$. $a \equiv \dot{A}_d/V_{slug}$; The volumetric mass transfer coefficient, $k_L a$, is associated with the mass change of CO$_2$ with time via integrating Eqn. (9) after substituting $M_{dis}$ by Eqn. (11):

$$k_L a = -\frac{1}{t} \ln \left( 1 + \frac{1}{SV_{slug}} [\rho_i (V_i(t) - V_{i,0}) + \rho_g (V_g(t) - V_{g,0})] \right). \tag{12}$$

It should be noted that Eqn. (10) and Eqn. (11) consider a flat CO$_2$-water interface for the mass transfer. Studies have shown that the Laplace pressure between the two phases can enhance gas molecules’ transport of a stationary gas bubble into the surrounding solvent due to the overpressure. This enhancement becomes significant when the bubble radius is
smaller than 15 \mu m and the solvent is nearly saturated (Kloek et al., 2001; Duncan and Needham, 2004). In our experiments, we degas water for an hour to ensure it is initially free from any dissolving gases, including CO_2. A large concentration difference between CO_2 dispersion and adjacent water would primarily drive the mass transfer of CO_2 (Duncan and Needham, 2004). In addition, the Laplace pressure at \( P_{\text{mi}} = 6.5 \) MPa is estimated to be 1.5 kPa (about 0.023% of \( P_{\text{mi}} \)). Therefore, the influence of the Laplace pressure or surface curvature on the CO_2 mass transfer is likely negligible in our cases.

Fig. 6a shows the semi-log plot of the estimated \( k_L a \) for four representative cases by using Eqn. (12). All cases show a decreasing trend of \( \log(k_L a) \) with a slope of \(-7.5 \pm 2.2\). The black dashed line depicts the linear function as an eye guide. Overall, the average \( k_L a \) is estimated to be 25 (1/s), which is consistent with our previous experimental results from injection pressures smaller than 8.5 MPa, giving the value of 29 (1/s) on average (Ho et al., 2021). This dynamic change in \( k_L a \) was also observed and reported in a recent sub-millimeter scale experimental study of CO_2 mass transfer in water (Zhang et al., 2018).

The decreasing trend of \( k_L a \) may attribute to the three following factors. First, the specific area (a) decreases with the reducing length of CO_2 dispersion \( L_{\text{drop}} \) due to phase change and dissolution, where \( a \) is defined by the ratio of the surface area of a CO_2 dispersion \( (A_T) \) and the sum of \( V_T \) and \( V_{\text{slug}} \). Second, the CO_2 concentration across the water-CO_2 interface is initially high as water contacts with CO_2 at \( t \approx 0 \), leading to the large \( k_L a \) because CO_2 molecules dissolve in water in a very short time. The dissolution rate of CO_2 would quickly drop due to the surrounding water gradually saturated with CO_2. Finally, we found that the traveling speed of CO_2, \( u_e \), influences \( k_L a \) significantly.

Fig. 6b shows that \( k_L a \) is the linear function of \( a \cdot u_e + \beta \) for all representative cases. The fitting coefficient \( a \) shows a larger value of 9150.9 \((\pm 1383.9)\) for the bubbly (●), intermittent (■), and annular-1 (▲) cases. A smaller \( a \) of 1162.9 is found for the annular-2 (▲). The faster \( u_e \) allows fluid elements to pass the body part of CO_2 dispersions in a shorter time, preventing the fluid element from saturated with CO_2 and therefore increasing the mass transfer rate. Also, a high \( u_e \) induces more intensive inner circulation inside the water slug, enhancing the mixing of dissolving CO_2 in the water (Gunther et al., 2005; Kuhn and Jensen, 2012).

Furthermore, the annular-2 flow shows a smaller estimated \( k_L a \) than the other three flow patterns. The data suggest that the pattern of the multiphase CO_2 flow and the water injection rate play a significant role in CO_2 mass transfer. The annular-2 flow is observed at the water injection rate of 5 \( \mu l/\text{min} \), whereas the other cases are generated at a high water injection rate of 10 \( \mu l/\text{min} \). The small water injection implies the weaker shear stress exerting from the continuous water on the dispersed CO_2 phase. As a result, the water phase takes a longer time to rupture the multiphase CO_2 stream and thus generates longer CO_2 dispersions (177.2 ±2 \( \mu m \)) and water slugs (216.8±1.6 \( \mu m \)). The average length of CO_2 dispersions and water slugs for the bubbly, the intermittent, and the annular-1 flows are 162.9 ± 4 \( \mu m \) and 109.1 ± 4 \( \mu m \), respectively. The long CO_2 dispersion may prohibit the CO_2 mass transfer due to the inactive liquid film surrounding the CO_2 dispersion (Irdouin et al., 1992; Pohorecki, 2007). In addition, a long water slug may also hinder the mass transfer of CO_2 to water due to the inefficient mixing inside the water slug (Bercic and Pintar, 1997; Yao et al., 2021). As a result, the annular-2 flow shows a small \( k_L a \) than the other cases.

4. Conclusions

We experimentally investigate an intriguing dissolving dynamics of multiphase CO_2 dispersions in water at the P-T condition close to the gas-liquid phase boundary of CO_2 (\( P = 6.5 \) MPa and \( T = 23.5\pm0.5 \) °C). The multiphase CO_2 dispersions are generated by merging the gas-liquid CO_2 flow with water using a microfluidic T-junction. Three flow patterns were observed sequentially, from the bubbly flow to the intermittent flow and the annular flow, representing the gaining dominance of the central CO_2 vapor stream over the liquid. A series of strategies are proposed and discussed to differentiate the phase state of CO_2 inside a dispersion, including estimating the volume of two distinct phases, calculating the corresponding mass change, and evaluating the
possible CO₂ concentration change in the water. We find that the gas CO₂ with lower viscosity traveling faster at the center of the CO₂ channel and could be pitched off to form bubbles surrounded by liquid CO₂.

We further estimate the volumetric mass transfer coefficient, \( k \), from the multiphase dispersion dissolving into the surrounding water by considering both dissolution and the phase change processes. The estimated \( k \) in our experiments (≈ 25 s⁻¹) is greater than those from previous experimental data (of 0.3 < \( k \) < 1.6 s⁻¹) obtained when \( P \) between 0.1 and 3 MPa (Yue et al., 2007, 2009; Ren et al., 2012; Yao et al., 2015). The larger \( k \) value found is likely due to the smaller hydraulic diameter used in our design (\( d_h \approx 50 \mu m \)), giving rise to a larger specific area (a) compared to previous work. Finally, the resultant \( k \) of the multiphase CO₂ dispersion shows an exponential decay with time due to decreasing \( a \) and, moreover, a significantly linear increase with the CO₂ traveling speed, \( u_c \).

Conflict of Interest

There are no conflicts to declare.

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Appendix

A. Detailed calculations of mass change of each phase due to phase change and dissolution

This appendix shows the case bubbly flow’s detailed mass change calculations for supporting the discussions regarding Fig. 5. Each representative case demonstrated in Fig. 5 has gone through this type of analysis for determining the phase state of a CO₂ dispersion. For a CO₂ dispersion flowing in the microchannel, the total volume and mass is the sum of the inner (dyed) and outer phase, as seen in Fig. 7a–c. Fig. 7b and 7c demonstrate the mass of a CO₂ dispersion varying with time based on the two different phase combinations, using presumption 1 and 2.

The total CO₂ volume and mass can be estimated from the contributions of the inner (dyed) and outer phases:

\[
V(t) = V_{in}(t) + V_{out}(t),
\]

\[
M(t) = \rho_{CO₂}V_{in}(t) + \rho_{CO₂}V_{out}(t).
\]

The mass change of each phase comes from two primary parts: due to the phase change and the dissolution in water (denoted by the subscript \( P \) and \( D \), respectively):

\[
M_{out}(t) - M_{out}(t_0) = m_{out}^P + m_{out}^D,
\]

\[
M_{in}(t) - M_{in}(t_0) = m_{in}^P + m_{in}^D,
\]

where \( M_{out} \) (\( \text{in} \)) denotes the mass of the outer (dyed inner) phase. \( m_{out}^P \) represents the mass change due to the phase transition between the outer and inner phases; \( m_{out}^D \) is the mass loss due to its dissolution in water.

We consider the mass conservation during a phase change process and assume \( m_{in}^P = -m_{out}^P \). The mass change of a CO₂ dispersion can be obtained by adding Eqn. (15) and Eqn. (16):

\[
\Delta M_T(t) = M(T) - M(t_0) = m_{out}^P + m_{in}^P.
\]

The results calculated from Eqn. (19) are shown in Fig. 7g.

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Figure 7: The detailed calculations of a CO$_2$ dispersion based on the mean value from five dispersions in the case of the bubbly flow. (a) The volume fractions, $V(t)$, of the outer phase ($V_{\text{out}}$), the (dyed) inner phase ($V_{\text{in}}$), and the total volume ($V_T = V_{\text{out}} + V_{\text{in}}$) changing with time ($t$). (b) The mass of the outer phase, $M_{\text{out}} = \rho_{\text{CO}_2} V_{\text{out}}$, and the dyed, inner phase, $M_{\text{in}} = \rho_{\text{CO}_2} V_{\text{in}}$, changing with time based on Presumption 1 (assuming the inner phase is the liquid CO$_2$). The total mass of a CO$_2$ dispersion, $M_T = M_{\text{out}} + M_{\text{in}}$. (c) Results of $M_{\text{out}}$, $M_{\text{in}}$, and $M_T$ calculated from Presumption 2 (assuming the outer phase is the liquid CO$_2$). (e) and (f) present the net mass change of a dispersion varying with time calculated according to presumption 1 and 2, respectively. $\Delta M$ represents the volume of mass from its initial value, $M(t_0)$. The data for the outer phase is denoted by $\bullet$, while the dyed inner phase by $\diamond$. $\bigcirc$ represents the sum properties. (d) The estimated CO$_2$ concentration, $C(t)$, changes with time according to presumption 1 (●) and 2 (○). The black dashed line denotes the theoretical CO$_2$ solubility in the water. (g) The estimated mass change of the dyed, inner phase resulted from the phase transition.
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