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## Microfluidic mass transfer of CO<sub>2</sub> at elevated pressures: implications for carbon storage in deep saline aquifers†

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Carbon capture and sequestration (CCS) in a deep saline aquifer is one of the most promising technologies to mitigate anthropologically emitted carbon dioxide. Accurately quantifying the mass transport of CO<sub>2</sub> at pore-scales is crucial but challenging for successful CCS deployment. Here, we conduct high-pressure microfluidic experiments, mimicking reservoir conditions up to 9.5 MPa and 35 °C, to elucidate the microfluidic mass transfer process of CO<sub>2</sub> at three different states (*i.e.*, gas, liquid, and supercritical phase) into water. We measure the size change of CO<sub>2</sub> micro-bubbles/droplets generated using a microfluidic T-junction to estimate the volumetric mass transfer coefficient ( $k_{l,a}$ ), quantifying the rate change of CO<sub>2</sub> concentration under the driving force of concentration gradient. The results show that bubbles/droplets under high-pressure conditions reach a steady state faster than low pressure. The measured volumetric mass transfer coefficient increases with the Reynolds number (based on the liquid slug) and is nearly independent of the injection pressure for both the gas and liquid phases. In addition,  $k_{l,a}$  significantly enlarges with increasing high pressure at the supercritical state. Compared with various chemical engineering applications using millimeter-sized capillaries (with typical  $k_{l,a}$  measured ranging from  $\approx 0.005$  to  $0.8 \text{ s}^{-1}$ ), the microfluidic results show a significant increase in the volumetric mass transfer of CO<sub>2</sub> into water by two to three orders of magnitude,  $O(10^2\text{--}10^3)$ , with decreasing hydrodynamic diameter (of  $\approx 50 \mu\text{m}$ ).

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## 1 Introduction

The technology of CCS in saline aquifers is one of the most promising options to store a large volume of anthropogenic CO<sub>2</sub> captured from major emission sites due to the abundant storage capacity (estimated to be greater than  $10^3 \text{ Gt}$ ).<sup>1,2</sup> Understanding the dissolution and mass transfer of CO<sub>2</sub> in the pore fluid (water or brine) is critical because these processes affect the storage capacity of the early trapping mechanisms (*i.e.*, structural and residual trapping) as well as the long term solubility trapping and mineralization with the host rock.<sup>3,4</sup> In addition, CO<sub>2</sub> is a sustainable “green” solvent widely utilized in cleaning, drying, and extraction, particularly the supercritical state due to its low viscosity and surface tension with a high diffusivity.<sup>5</sup>

Conventional methods of measuring CO<sub>2</sub> dissolution rates and mass transfer include bubble column reactors<sup>6,7</sup> and stirred vessels.<sup>8</sup> A bubble column consists of a cylindrical

vessel with a gas distributor at the bottom. The gas is sparged in the form of bubbles into a liquid phase or a liquid–solid slurry.<sup>9,10</sup> Stirred vessels usually have similar configurations to bubble columns, but they are equipped with an additional stirrer and motor to enhance the mixing and increase the interfacial area.<sup>11</sup> However, the drawbacks of these methods include considerable back mixing in the collecting tank, bubble coalescence, and requirement of relatively large operation space and fluid volume<sup>6,8</sup> and, hence, motivate efficient alternative approaches.

Microfluidics has offered emerging and promising platforms for a variety of energy and environmental technologies.<sup>12–16</sup> To name a few, microfluidics has been beneficially utilized for visualizing the multiphase flow patterns of viscous fingering during the gas–liquid and liquid–liquid displacement in a porous medium<sup>16–18</sup> as well as measuring the mass transfer rates of CO<sub>2</sub> (ref. 19–22) and ozone,<sup>23</sup> gas diffusivity in different solvents,<sup>24</sup> and CO<sub>2</sub> solubility (under the temperature effect,<sup>25</sup> under surfactant influence,<sup>26</sup> and in different solvents<sup>22,24</sup>).

Very recently, high-pressure microfluidic platforms have been developed to investigate the behaviors of CO<sub>2</sub> with a background fluid at high pressure and temperature to simulate the conditions of deep saline formations, which

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typically have the pressure ( $P$ ) range of  $6 \text{ MPa} < P < 27 \text{ MPa}$  and the temperature ( $T$ ) range of  $26 \text{ }^\circ\text{C} < T < 110 \text{ }^\circ\text{C}$ .<sup>27</sup> For example, the investigations using high-pressure microfluidics have focused on the flow patterns of  $\text{CO}_2$  displacing fluid,<sup>28,29</sup> the applications of  $\text{CO}_2$  in oil recovery processes,<sup>30,31</sup> physical properties (e.g., density and viscosity) at the supercritical state,<sup>32</sup> fast screening of the  $\text{CO}_2$  phase state in different solvents,<sup>33,34</sup> and solubility of  $\text{CO}_2$  in brine.<sup>35</sup>

Nevertheless, microfluidic experimental studies regarding the  $\text{CO}_2$  transport rate in water or brine under  $P$ - $T$  conditions close to or under reservoir conditions are relatively limited.<sup>36–39</sup> Sell *et al.* applied a sodium fluorescein tracer to measure the diffusivity of  $\text{CO}_2$  in brine (up to 5 M) at a pressure ranging from 0.1 to 5 MPa using a PMMA microfluidic cell. They reported that the salinity had a significant impact on the  $\text{CO}_2$  diffusivity, while the system pressure seemed to have a minor effect on the measured diffusion coefficient.<sup>36</sup> Yao *et al.*<sup>37</sup> performed microfluidic T-junction experiments and found a gradual increase in the mass transfer coefficient,  $k_L$  (from  $1.8 \times 10^{-4}$  to  $5.3 \times 10^{-4} \text{ m s}^{-1}$ ), of  $\text{CO}_2$  bubbles in water with rising pressure (from  $P = 0.1$  to  $P = 3 \text{ MPa}$ ). In 2017, Yao *et al.* investigated the influence of elevated pressure on  $\text{CO}_2$  absorption in water and a chemical solvent DEA (diethanolamine) by adjusting  $P$  ranging from 0.1 to 4 MPa. They reported a decrease in  $k_L a$  with rising pressure in both physical and chemical absorption processes due to the shrinkage of the interfacial area at high pressure.<sup>38</sup> Qin *et al.* experimentally estimated the mass transfer coefficient  $k_L$  to be  $1.5 \times 10^{-4} < k_L < 7.5 \times 10^{-4} \text{ m s}^{-1}$  for supercritical  $\text{CO}_2$  in water (at  $P = 8 \text{ MPa}$  and  $T = 313 \text{ K}$ ), based on the three-dimensional morphology of a shrinking Taylor bubble in a rectangular channel.<sup>40</sup> Additionally, the results showed that a higher water volume fraction results in a larger  $k_L$ , and a faster-moving droplet generally has a higher  $k_L$ .<sup>39</sup>

In this study, we experimentally investigated the influence of different thermodynamic states on the microfluidic  $\text{CO}_2$  mass transfer, which is not fully addressed in the literature, particularly the supercritical state. A  $\text{CO}_2$  bubble/droplet was generated in a T-junction microchannel under various conditions ranging from the standard state ( $P = 0.1 \text{ MPa}$  and  $T = 24 \text{ }^\circ\text{C}$ ) to reservoir conditions ( $P = 9.5 \text{ MPa}$  and  $T = 35 \text{ }^\circ\text{C}$ ). The mass transfer rate is characterized by the volumetric mass transfer coefficient,  $k_L a$ , extracted from the length change of a  $\text{CO}_2$  slug when traveling in a microchannel. The influence of pressure on the mass transfer rate was examined. We further investigate other key parameters that may affect the mass transfer rate, such as the capillary number ( $Ca$ ) and the Reynolds number ( $Re$ ), and compare them with other existing experimental results, which used different hydrodynamic diameters.

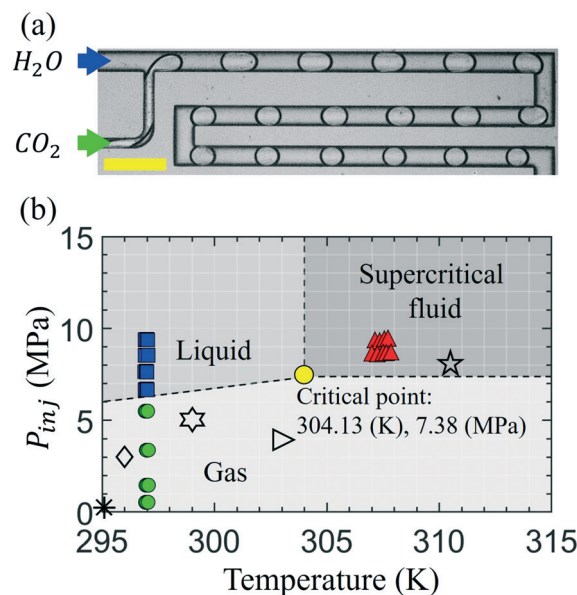
## 2 Materials and methods

We experimentally generated  $\text{CO}_2$  bubbles/droplets in Milli-Q water using T-junction microfluidics<sup>41,42</sup> and measured the

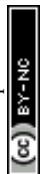
size change of traveling  $\text{CO}_2$  to acquire the mass transfer data. Microchannels were fabricated using silicon wafers and bound with a cover glass after applying the deep reactive ion etching (DRIE) technique.<sup>43,44</sup> Fig. 1a is an experimental snapshot illustrating the generation of  $\text{CO}_2$  bubbles at the T-junction with an injection pressure of 1.45 MPa. The water (illustrated by the blue arrow) directly enters the main microchannel (whose width and depth are  $100 \text{ }\mu\text{m}$  and  $30 \text{ }\mu\text{m}$ , respectively) as the continuous phase, while  $\text{CO}_2$  is injected *via* the narrower side-channel (of a width of  $50 \text{ }\mu\text{m}$ ) to form the dispersed phase.

### 2.1 Experimental procedures

The microfluidics was installed in a metal platform that allows operation from standard atmospheric conditions ( $P = 0.1 \text{ MPa}$  and  $T = 24 \text{ }^\circ\text{C}$ ) to reservoir conditions ( $P = 9.5 \text{ MPa}$  and  $T = 35 \text{ }^\circ\text{C}$ ), covering the gas, liquid, and supercritical states of  $\text{CO}_2$ , as shown in Fig. 1b. A heating plate and two thermocouples (K-type) were attached to the platform to heat up and monitor the assembly's temperature, respectively. 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.  $\text{CO}_2$  was



**Fig. 1** (a) The snapshot of  $\text{CO}_2$  bubbles generated using a microfluidic T-junction while subsequently moving in the channel. The water inlet has the same width as the main microchannel ( $100 \text{ }\mu\text{m}$ ), and the  $\text{CO}_2$  channel is  $50 \text{ }\mu\text{m}$  in width. The depth of the microchannel is  $30 \text{ }\mu\text{m}$ . The (yellow) scale bar represents  $300 \text{ }\mu\text{m}$ . (b) The  $\text{CO}_2$  thermodynamic phase diagram near the critical point (yellow ●). Colored symbols show our various experimental conditions for the  $\text{CO}_2$  injection pressure,  $P_{inj}$ , facilitating different  $\text{CO}_2$  phases: liquid (■), gas (●), and supercritical (▲). Other symbols represent the experimental conditions from previous studies, including works under atmospheric conditions (\*),<sup>19,20,23</sup> by Sell *et al.* (☆),<sup>36</sup> Yao *et al.* (◇<sup>37,45</sup> and ▷<sup>38</sup>), and Qin *et al.* (⋄).<sup>39</sup> The image of the phase diagram is adapted from the National Institute of Standards and Technology (NIST).<sup>46</sup>



controlled by a high-pressure gas pump (ISCO 100DX), directly connected to the gas tank (Praxair, RES K CO<sub>2</sub> 99.998%). A backpressure regulator (TESCOM BP 25-4000PSI) was connected to the system's outlet to keep a suitable pressure gradient across the channel. The flow pattern was observed by using an inverted microscope (Zeiss Axio Observer 7 Materials) and recorded by a high-speed camera (Phantom V710L) at a rate of 5000 frames per second (fps).

## 2.2 Image analysis

We processed the recorded images using ImageJ (NIH Image)<sup>47</sup> to measure the size of a single bubble and track its position varying with time. The measured data were further analyzed by using a customized code written in Matlab (MathWorks®). The data variation was evaluated by calculating the standard deviation of at least five bubbles for each pressure condition. The results showed good consistency in both the bubble size and position. The variance is about 3% in bubble length and ≈4% in displacement.

## 2.3 Determining the volumetric mass transfer coefficient

As revealed by the experimental observation, *e.g.*, Fig. 1a, CO<sub>2</sub> bubbles gradually dissolve in water, resulting in shrinkage in size, when they move along the microchannel. We hence analyze the change of the CO<sub>2</sub> bubble length,  $L_b$ , with time ( $t$ ) to extract the (liquid-side) volumetric mass transfer coefficient ( $k_L a$ ) as it moves at a speed,  $u_b$ , downstream (adjacent to a liquid slug of water with a length of  $L_s$ ) in a microchannel width ( $d_c$ ), schematically illustrated in Fig. 2a.

To estimate  $k_L a$ , we used the so-called unit cell model<sup>37,45,48</sup> by analyzing the mass transfer between one single bubble and its adjacent liquid slug, illustrated by the red dotted-line compartment in Fig. 2a. Assuming that the liquid slug is initially free from CO<sub>2</sub> and in time CO<sub>2</sub> gradually dissolved while well-mixed in the adjacent liquid slug, based on the mass balance concept, the mass transfer of CO<sub>2</sub> from the bulk phase (bubble) through the phase boundary to the liquid slug can be mathematically described by

$$\dot{M}_{\text{CO}_2} = -\frac{\rho dV_b}{dt} = V_L \frac{dc}{dt}, \quad (1)$$

where  $V_L$  and  $V_b$  are the volumes of the liquid slug and CO<sub>2</sub> bubble/drop, respectively. The CO<sub>2</sub> density,  $\rho$ , is assumed to be a constant. The volume of the liquid slug  $V_L$  remains unchanged because of the fixed water injection rate ( $Q_L = 15 \mu\text{l min}^{-1}$ ).  $c$  denotes the CO<sub>2</sub> concentration in a liquid slug as a function of position ( $x$ ) and time ( $t$ ). Here, the unit-cell model also assumes no mass transfer between different unit cells.<sup>37,48</sup>

Eqn (1) correlates the CO<sub>2</sub> concentration changes in a fluid element to the decrease in the bubble volume. As CO<sub>2</sub> bubbles/droplets move, fluid elements (in the liquid slug) repeatedly move from the bulk fluid phase onto the phase boundary (coming into contact with CO<sub>2</sub>) and stay for a

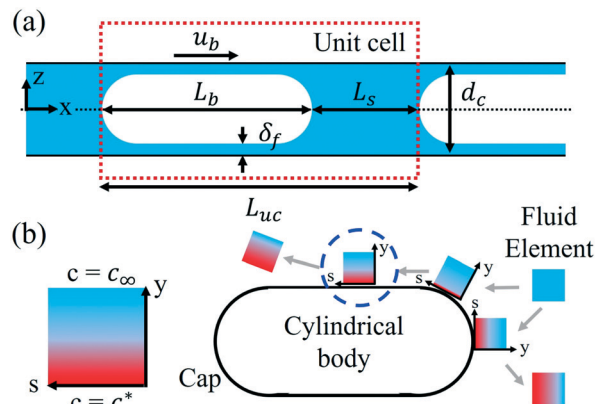


Fig. 2 The schematic of the theoretical, conceptual model: (a) a unit cell. The  $x$ -axis denotes the downstream location of a bubble after being released from the T-junction.  $L_{uc}$ , the length of a unit cell, is the sum of  $L_b$  and  $L_s$ , where  $L_b$  and  $L_s$  represent the length of the CO<sub>2</sub> bubble/drop and liquid plug, respectively. A bubble is surrounded by the thin liquid film of  $\delta_f$  in thickness. It travels at a velocity of  $u_b$  in a microfluidic channel of the width of  $d_c$ . (b) Higbie's penetration theory:<sup>49</sup> a fluid element from the bulk phase may come into contact with the phase boundary at a finite time. During this period, the mass transfer is assumed only *via* molecular diffusion at the interface. The  $s$ -axis represents the streamline direction, and the  $y$ -axis denotes the mass transport direction of CO<sub>2</sub>, which is normal to the streamline.

limited time,  $\delta t$ . The process is schematically illustrated in Fig. 2b, showing CO<sub>2</sub> concentration variation in the liquid bulk and along the phase boundary. The initial concentration of CO<sub>2</sub> in a liquid element equals that in the bulk fluid phase, denoted as  $c(x)$ , varying with the downstream location ( $x$ ) as the CO<sub>2</sub> bubble/drop travels downstream. Due to the direct contact, the phase boundary (at  $y = 0$ ) is always saturated with CO<sub>2</sub>, whose saturation concentration is denoted as  $c^*$  ( $P, T$ ) as a function of  $P$  and  $T$ . In short, these boundary conditions at the phase boundary and the liquid bulk can be expressed as  $c(y = 0) = c^*$  and  $c_\infty \equiv c(y \approx \infty) = c(x)$ , respectively.

The mass transfer rate from a CO<sub>2</sub> bubble to the surrounding liquid is the integral of the mass flux through a fluid element over the surface area of the phase boundary around a bubble,  $A_b$ :

$$\dot{M}_{\text{CO}_2} = \int_{cs} J_{\text{CO}_2} dA_b = k_L A_b (c^* - c_\infty). \quad (2)$$

The CO<sub>2</sub> mass flux,  $J_{\text{CO}_2}$ , can be further expressed using the mass transfer coefficient,  $k_L$ , which by definition is determined by the ratio of CO<sub>2</sub> mass flux to the concentration gradient.

The rate change of CO<sub>2</sub> concentration in a liquid slug equals the mass transfer of CO<sub>2</sub> through the phase boundary; we therefore combine eqn (1) and (2):

$$\frac{dc}{dt} = k_L \frac{A_b}{V_L} (c^* - c(x)) = k_L a (c^* - c(x)), \quad (3)$$

where  $a$  is the specific area and defined by the ratio of  $A_b$  to  $V_L$ . The prefactor  $k_L a$  in eqn (3) is the volumetric mass



transfer coefficient, an important measure for the CO<sub>2</sub> transport efficiency in a unit cell.

By integrating (3) and using the chain rule of total time-derivative, the CO<sub>2</sub> concentration change in a liquid slug can be modeled by:

$$c^* - c(x) = (c^* - c_0) \exp\left(-\frac{k_L a}{j_L} x\right), \quad (4)$$

where  $c_0$  is the initial concentration of CO<sub>2</sub> in water,  $c_0 \equiv c_{\infty}$  ( $t = 0$ ).  $j_L$  is the superficial velocity of liquid, that is,  $j_L = Q_L/A$ , the ratio of the liquid injection rate ( $Q_L$ ) to the cross-sectional area of the microchannel ( $A$ ).

Eqn (4) describes the concentration difference with an exponential decay at a rate of  $k_L a/j_L$ . Substituting eqn (4) into eqn (3), the change of bubble size (or length) relates to the concentration change of liquid slugs ( $\Delta c = c^* - c_0$ ) and  $k_L a$ :

$$\rho \frac{DV_b}{Dt} = \rho A_c u_b \frac{dL_b}{dx} = -k_L a V_L (c^* - c_0) \exp\left(-\frac{k_L a}{j_L} x\right). \quad (5)$$

Here,  $A_c$  is the cross-sectional area of a CO<sub>2</sub> bubble and assumed to be a constant.  $L_b$  denotes the bubble length, changing with the downstream position,  $x$ .

By integrating eqn (5) and dividing by the initial bubble length ( $L_{b0}$ ), the dimensionless size (or length) change of a moving (CO<sub>2</sub>) bubble with the position away from the origin (T-junction) is described by:

$$\frac{L_{b0} - L_b}{L_{b0}} = \frac{1}{L_{b0}} \frac{j_L V_L}{A_c u_b \rho} (c^* - c_0) \left[1 - \exp\left(-\frac{k_L a}{j_L} x\right)\right]. \quad (6)$$

The first term of the prefactor determines the maximum size change at the equilibrium state, and the second one ( $k_L a/j_L$ ) determines the speed to reach equilibrium. Eqn (6) is used to obtain  $k_L a$  from the size change of bubbles in a microfluidic system without measuring the concentration change in liquid slugs.<sup>37,45</sup> We extracted  $k_L a$  using a best nonlinear fit of eqn (6) with our data measured at elevated CO<sub>2</sub> injection pressures to investigate the influence of pressure on the CO<sub>2</sub> mass transfer, *i.e.*,  $k_L a$ .

## 3 Results and discussion

### 3.1 CO<sub>2</sub> bubble/droplet size change at different phases

Our experiments were operated from gas ( $P_{inj} = 0.25, 1.45, 3.45, \text{ and } 5.45$  MPa) to liquid ( $P_{inj} = 6.45, 7.5, 8.5, \text{ and } 9.5$  MPa at room temperature) and supercritical ( $P_{inj} = 8.5$  and  $9.5$  MPa at  $35 (\pm 0.5)$  °C) states of CO<sub>2</sub> to reveal the dynamics of CO<sub>2</sub> transfer in water and the influence of pressure. For each injection pressure, we conducted the experiments at least three times independently to check the reproducibility. In total, thirty-four sets of experimental data were summarized and presented in this work. The complete experimental data are shown in Fig. S1 in the ESI.† Revealed in Fig. 3a are representative snapshots (taken from five fixed, downstream locations along the channel), including the T-junction's origin point. The initial length of CO<sub>2</sub> bubbles/droplets ( $L_{b0}$ ) was controlled within  $212 (\pm 7)$  μm, with the

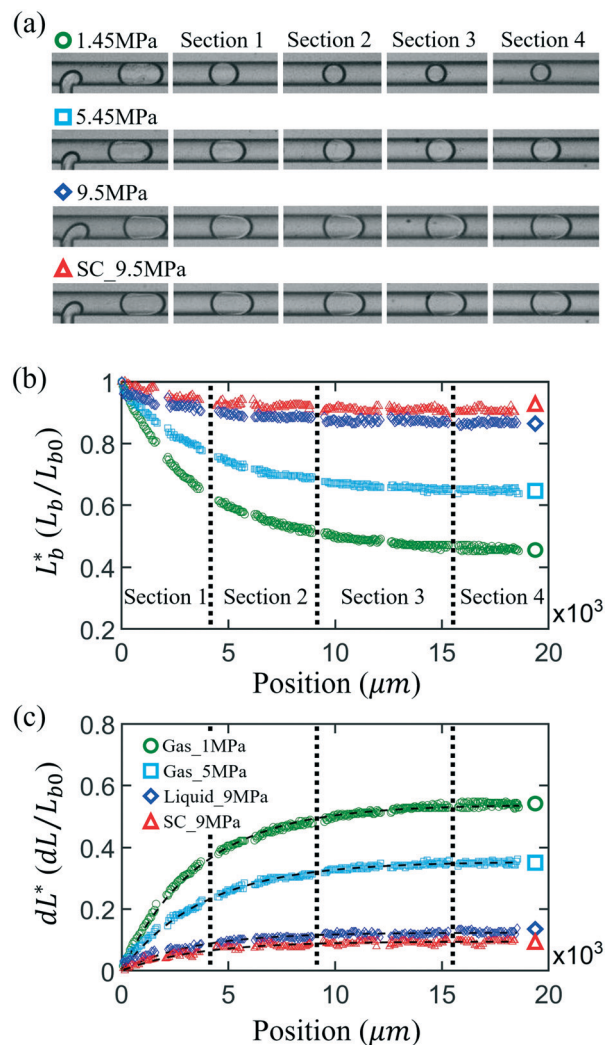


Fig. 3 (a) Experimental snapshots of CO<sub>2</sub> bubbles or droplets in water in the microchannel for four different injection pressures, covering the CO<sub>2</sub> phase state from gas (○ and □) to liquid (◇) and supercritical state (△). As a reference of scale, the width of the channel is 100 μm. CO<sub>2</sub> bubbles/droplets shown in (a) correspond to different locations: at the initial position ( $x = 0$ ), 4000 μm (section 1), 9000 μm (section 2), 15000 μm (section 3), and 18600 μm (section 4) away from the T-junction. Dimensionless length and length change of the CO<sub>2</sub> bubbles/droplets measured from the image sequences are shown in (b) and (c), respectively. In (c), the comparison of the measured CO<sub>2</sub> length change with the results of nonlinear regression fitting of the simplified form of eqn (6):  $dL^* = \alpha(1 - \exp(-\beta x))$  is shown. The volumetric mass transfer coefficient,  $k_L a$ , is obtained by multiplying the fitting coefficient,  $\beta = k_L a/j_L$ , by the inlet water flux,  $j_L$ .

length of liquid slugs being  $194 (\pm 11)$  μm and the mean CO<sub>2</sub> bubble/droplet speed being  $0.33 (\pm 0.07)$  m s<sup>-1</sup>.

Fig. 3b and c show the dimensionless length,  $L_b^* = L_b/L_{b0}$ , and dimensionless length change,  $dL^* = 1 - L_b/L_{b0}$ , of CO<sub>2</sub> vs. the traveling distance recorded from (a), respectively. It is noteworthy that all CO<sub>2</sub> bubbles/droplets experienced a rapid shrinkage when they departed from the T-junction and later reached a final steady state. Under high-pressure conditions, the size change became subtle. As seen in Fig. 3b, CO<sub>2</sub>



bubbles shrank more than half of their initial length at low system pressure (e.g., 1.45 MPa depicted by ○). As the pressure increased, the range of drastic size change became smaller, shown by the data of 5 MPa (depicted by □). In the liquid (◇) and supercritical state (△), the shrinkage of a droplet decreased to about 10% of its initial length. Meanwhile, these high-pressure CO<sub>2</sub> drops reached the final steady-state size faster than the low-pressure ones. It took 12 ms on average for liquid and supercritical CO<sub>2</sub> droplets to reach a final steady state, whereas the CO<sub>2</sub> bubbles at 1 MPa needed more than 30 ms to reach their stable size.

To examine the above distinct observations, we correlated the dimensionless maximum size change of CO<sub>2</sub> ( $dL_{\max}^*$ ) with the CO<sub>2</sub> density,  $\rho(P,T)$ , bubble velocity,  $u_b$ , and liquid volume fraction,  $\nu_{\text{slug}}$ , measured from experiments to investigate their influences on the (quasi-)equilibrium size (see section 2 in the ESI†). The  $dL_{\max}^*$  was determined using the mean value of  $dL^*$  in the plateau region of Fig. 3c. The results showed that the CO<sub>2</sub> density has a strong but negative correlation with its size change. The significant difference in size change at the different states is likely attributed to the increase in CO<sub>2</sub> density with increasing  $P$ , as it transforms from the gas, to liquid, and to supercritical state. For instance, the CO<sub>2</sub> density increases by  $\approx 25\times$ , rising from  $\rho = 28.19$  to  $693.95$  Kg m<sup>-3</sup>, when  $P$  increases from  $P = 1.45$  MPa to  $P = 9.5$  MPa for the same  $T = 24$  °C, as shown in Table S1 in the ESI†. Although the CO<sub>2</sub> solubility in water, i.e.,  $c^* - c_0$ , also increases with pressure, this solubility increase (by  $\approx 3\times$ , from  $21.86$  Kg m<sup>-3</sup> at 1.5 MPa (ref. 50) to  $\approx 67.3$  at 9.63 MPa (ref. 51)) is smaller than the contribution from the increase in CO<sub>2</sub> density.

The bubble velocity and the liquid volume had only a minor influence on the size change of gas CO<sub>2</sub> ( $P \leq 6.29$  MPa). The influences of these two parameters (for the ranges explored) are negligible when the CO<sub>2</sub> phase changed to liquid and supercritical CO<sub>2</sub> (as shown in Fig. S2 in the ESI†).

### 3.2 Volumetric mass transfer coefficient, $k_L a$ , under elevated pressure

We extracted the volumetric mass transfer coefficient,  $k_L a$ , by applying a nonlinear regression method with a reduced form of eqn (6):  $Y = \alpha(1 - \exp(\beta X))$ , to fit the experimental data of dependent variable  $Y$  as a function of parameter  $X$ , which is the downstream location  $x$  from the T-junction. Fig. 3c reveals the dimensionless size-change of CO<sub>2</sub>  $dL^*/L_{b0}$  under different pressure conditions and the resultant fitting of the nonlinear regression (depicted by the black dashed lines). Overall, eqn (6) models well our experimental data. At the gas states ( $P \leq 6.29$  MPa), the  $R$ -squared values were between 0.97 and 0.99. The standard deviation of fitting coefficients was smaller than 1% for the prefactor  $\alpha$  and within 3.2% for the mass transfer coefficient term  $\beta$ . For the results in the liquid and supercritical CO<sub>2</sub> phases, the uncertainty of  $\alpha$  increased to 5% and 10–15% for the error of  $\beta$ . The larger percentage errors in the latter cases are associated with the

experimental resolution (corresponding to  $\approx 4$   $\mu\text{m}$  per pixel) and due to the relatively smaller change in the CO<sub>2</sub> size in the high- $P$  regime. In addition, a close examination of CO<sub>2</sub> bubble/droplet geometry shows a slightly asymmetric shape as we measure a difference of 1  $\mu\text{m}$  between the front and rear spherical radii of CO<sub>2</sub>. Using eqn (6) and calculating the corresponding change in  $A_c$ , we estimate that this asymmetric CO<sub>2</sub> shape would contribute  $\approx 5\%$  error in  $k_L a$ .

The data reveals that the majority of CO<sub>2</sub> transports in the rapid shrinkage stage at the initial time, as seen in section 1 in Fig. 3, especially for high-pressure cases. We hence focused on this short period (about 9 ms) to highlight the influence of pressure on CO<sub>2</sub> mass transfer in water. Fig. 4 shows the resultant volumetric mass transfer coefficient,  $k_L a$ , in the rapid shrinkage stage and the data from previous experiments,<sup>19,20,23,37,39</sup> which primarily focused on low pressures. As seen in the figure,  $k_L a$  does not change significantly for low injection pressure when  $P_{\text{inj}}$  is smaller than 8 MPa, with an average  $k_L a = 28.85$  s<sup>-1</sup>. When  $P_{\text{inj}}$  raises to above 8 MPa,  $k_L a$  increases to  $45.4$  s<sup>-1</sup> on average for liquid CO<sub>2</sub> and greatly enlarges to a mean value of  $100$  s<sup>-1</sup> for supercritical CO<sub>2</sub>. Our data reveal that the average volumetric mass transfer coefficient,  $k_L a$ , is increased from the gas, liquid, to supercritical state for a comparative CO<sub>2</sub> traveling speed (of  $u_b \approx 0.33$  m s<sup>-1</sup>) in a microfluidic channel. This significant gain in  $k_L a$  for the supercritical state may be primarily attributed to the temperature increase, from 24 °C (room temperature) to 35 °C for a comparable  $u_b$  range in our experiments. The rising temperature activates both water

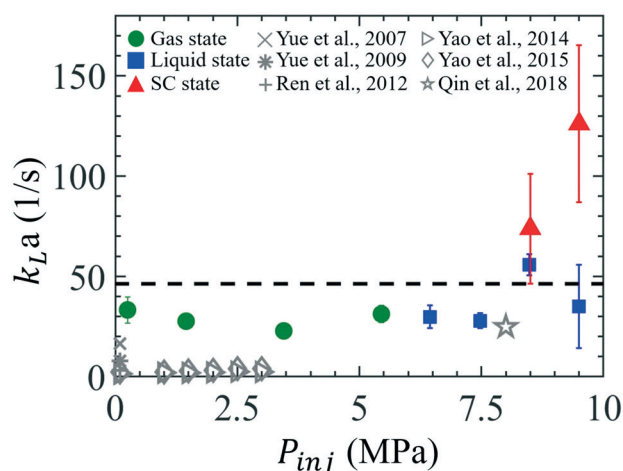


Fig. 4 The volumetric mass transfer coefficients,  $k_L a$ , during the rapid shrinkage stage (section 1) against elevated injection pressures,  $P_{\text{inj}}$ . Our data span a wide range of  $P_{\text{inj}}$ , covering three different states, gas (●), liquid (■), and supercritical (▲), of CO<sub>2</sub>. The shown points represent the average value of at least three independent experiments repeated for the same experimental conditions. Error bars denote the standard deviations. The black dashed line presents the mean value over all the presented data,  $\langle k_L a \rangle = 46.4$  (s<sup>-1</sup>). Grey symbols are the maximum  $k_L a$  available from previous microfluidic experimental results,<sup>19,20,23,37,39</sup> which mostly focused on the low range of  $P_{\text{inj}}$  and used a microchannel of a size greater than 100  $\mu\text{m}$ .



and CO<sub>2</sub> molecules and thus enhances the mass transfer processes by increasing CO<sub>2</sub> diffusivity. As a reference, the diffusion coefficient of CO<sub>2</sub> in water increases from 1.88 × 10<sup>-9</sup> to 2.18 × 10<sup>-9</sup> (m<sup>2</sup> s<sup>-1</sup>) as measured in the temperature at 25 °C and 35 °C, respectively.<sup>52</sup>

Overall, CO<sub>2</sub> droplets in the rapid shrinkage stage give an average value of  $k_L a = 46.4$  (1/s) (black dashed line in Fig. 4) in a microfluidic channel of a small hydrodynamic diameter (of  $d_h = 46$  μm). This value is greater than those from previous microfluidic data operated under lower pressure conditions (0.1–3 MPa) and at room temperature, with their  $k_L a$  values ranging between 0.3 and 16 (1/s).<sup>19,20,23,37</sup> The  $k_L a$  measured in our experiments was improved by 3× to 150× compared to those from the previous data. Since the range of CO<sub>2</sub> traveling speed,  $u_b$ , is comparable between the experiments, the significant increase in  $k_L a$  measured in our experiments compared to previous low- $P$  data likely comes from the larger specific area ( $a$ ) created by our microchannel, as elaborated below.

The specific area,  $a$ , is conventionally defined as the ratio of the interfacial area to the volume of the two phases.<sup>53</sup> For a similar total volume of the two phases,  $a$  can greatly enhance the mass transfer process by increasing the contact area of the multiphase. According to the calculation proposed by Vandu *et al.*,<sup>48</sup> the specific area consists of two parts, namely two spherical caps and a cylindrical body of the drop or bubble (*i.e.*, CO<sub>2</sub>), as follows:

$$a = a_{\text{cap}} + a_{\text{body}} \approx \frac{4}{L_s} + \frac{4(L_b - d_h)}{d_h L_s}. \quad (7)$$

The specific area hence is inversely related to the microfluidic hydraulic diameter,  $d_h$ .

Most of the microfluidic experiments studying the mass transfer rates for the segmented gas–liquid flow applied hydraulic diameters larger than 200 μm, which could generate bubbles with the specific area ( $a$ ), calculated based on eqn (7), ranging from 3400 to 10<sup>4</sup> m<sup>-1</sup>.<sup>19,20,23,37</sup> As a comparison, our microchannel has a low hydraulic diameter of 46 μm, which significantly enlarges the specific area of CO<sub>2</sub> bubbles/droplets up to 10<sup>5</sup> m<sup>-1</sup> on average, approximately 10× to 30× greater than those of previous microfluidic experiments.<sup>19,20,23,37</sup> In addition, the recent high-pressure microfluidic experiment (with  $P_{\text{inj}} = 8$  MPa and  $T \approx 313$  K) done by Qin *et al.*<sup>39</sup> found the mass transfer coefficient,  $k_L$ , to be between 1.5 × 10<sup>-4</sup> and 7.5 × 10<sup>-4</sup> m s<sup>-1</sup>, consistent with the low-pressure regime data.<sup>19,20,23,37</sup> With a large specific area of 33 200 m<sup>-1</sup>, this high-pressure microfluidic data also yields a large  $k_L a$  up to 24.9 (s<sup>-1</sup>) (depicted by \*),<sup>39</sup> consistent with our microfluidic data in the comparable pressure range. In short, these comparisons reveal that a smaller microfluidic channel enhances the volumetric mass transfer coefficient significantly by increasing the specific interfacial area, thereby benefiting various chemical reactions using a smaller  $d_h$ .

Furthermore, the mass transfer coefficient,  $k_L$ , at room temperature in this work is estimated to be 3.4 (±0.71) × 10<sup>-4</sup>

m s<sup>-1</sup> on average. This result is consistent with the  $k_L$  reported in previous micro-scale experiments (1.8 × 10<sup>-4</sup> ≤  $k_L$  ≤ 7.3 × 10<sup>-4</sup> m s<sup>-1</sup>).<sup>19,20,23,37</sup> For supercritical CO<sub>2</sub>, the  $k_L$  is calculated to be as high as 9.96 × 10<sup>-4</sup> m s<sup>-1</sup> on average, which is about three times larger than the values estimated in the gas and liquid states. The higher  $k_L a$  value of supercritical CO<sub>2</sub> compared to the liquid/gas counterpart may be attributed to the greater temperature (35 °C) and shorter contact time of a fluid element on the CO<sub>2</sub>–water interface. The latter is suggested by Higbie's penetration theory,<sup>49</sup> where the mass transfer coefficient is modeled to be proportional to the square root of diffusivity:

$$k_L \sim \sqrt{\frac{D}{\pi \tau_c}}, \quad (8)$$

where  $D$  is the diffusivity and  $\tau_c$  denotes the contact of a fluid element on the CO<sub>2</sub>–water interface.  $D$  generally has a linear correlation to temperature, reported by previous experimental<sup>52,54,55</sup> and simulation works.<sup>56</sup>

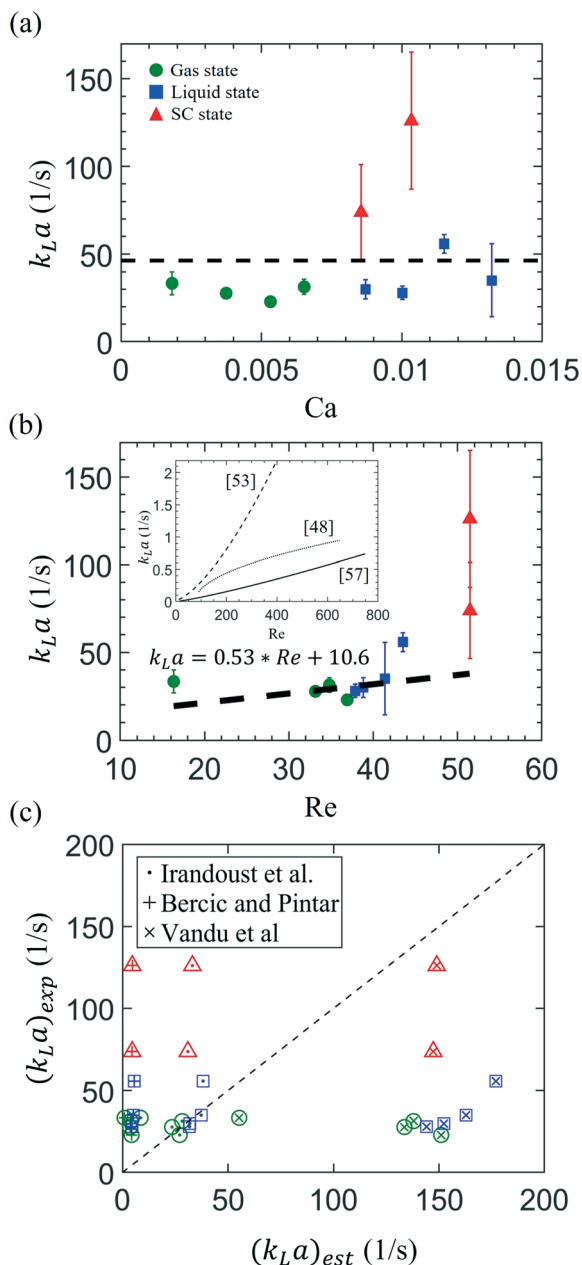
### 3.3 CO<sub>2</sub> mass transfer rate

We further investigate the influence of the Capillary number (Ca) and Reynolds number (Re) of the injected water on  $k_L a$  (see Fig. 5). Here,  $\text{Ca} = \mu_1 u_b / \sigma$ , representing the ratio of the viscous drag of the carrier liquid (*i.e.*, water) to the interfacial tension between CO<sub>2</sub> and water,  $\sigma$ .  $\text{Re} = \rho_1 u_b d_h / \mu_1$  is calculated by comparing the inertial force of a moving bubble to the liquid's viscous force, where  $\rho_1$  is the liquid density,  $u_b$  is the CO<sub>2</sub> traveling speed, and  $d_h$  is the hydrodynamic diameter of the microfluidic channel. The values of these thermodynamic parameters used are given in Tables S2 and S3 in the ESI.†

On the one hand, as shown in Fig. 5a, the volumetric mass transfer coefficient does not significantly correlate with the Capillary number, Ca, ranging from 1.9 × 10<sup>-3</sup> to 1.4 × 10<sup>-2</sup> in this study. The change in Ca primarily stems from the decrease in the CO<sub>2</sub>–water surface tension ( $\sigma$ ) as the CO<sub>2</sub> phase changed from gas to the supercritical state. On the other hand, we correlated the  $k_L a$  with the Reynolds number in Fig. 5b, to study the influence of CO<sub>2</sub> velocity. As an approximation, the black dashed line represents the result of linear regression analysis from all the experimental data, showing that  $k_L a$  grows linearly with a prefactor of 0.53 (±0.58) with Re.

The dependence of  $k_L a$  on Re, observed from our data, indicates the significance of CO<sub>2</sub> bubble velocity,  $u_b$ , on enhancing the mass transfer. This observation generally agrees with approximations proposed previously, considering the bubble velocity ( $u_b$ ), a critical parameter that determines  $k_L a$ .<sup>48,53,57</sup> Illustrated in Fig. 5b inset are the empirical results of  $k_L a$  found in millimeter-scale capillaries, and here we plot their data as a function of Re based on their experimental conditions. All of the empirical results show a rising  $k_L a$  with increasing Re, *i.e.*, the moving speed of bubbles. This dependent relation between  $k_L a$  and Re may be associated with the fact that a faster  $u_b$  enhances the mixing of fluid





**Fig. 5** The correlation of the measured volumetric mass transfer coefficient,  $k_La$ , with (a) the capillary number,  $Ca = \mu_l u_b / \sigma$ , and (b) the Reynolds number,  $Re = \rho_l u_b d_h / \mu_l$  of the continuous liquid phase.  $u_b$  is the mean velocity of a moving bubble/droplet, and  $d_h$  denotes the hydraulic diameter of the microchannel, which is  $46 \mu\text{m}$  in this study.  $\rho_l$ ,  $\mu_l$ , and  $\sigma$  represent the density and dynamic viscosity of the water and the  $\text{H}_2\text{O}-\text{CO}_2$  interfacial tension varying with pressure, respectively. Presented in the inset are the three empirical approximations of  $k_La$  previously proposed by Irandoust *et al.*<sup>53</sup> [dashed line (with  $y_m = 0.5$ )], Berčič and Pintar<sup>57</sup> (solid line), and Vandu *et al.*<sup>48</sup> (dotted line). (c) The comparison of experimental data from this study,  $(k_La)_{\text{exp}}$ , and values estimated using the above empirical approximations,  $(k_La)_{\text{est}}$ , previously proposed by Irandoust *et al.* (.),<sup>53</sup> Berčič and Pintar (+),<sup>57</sup> and Vandu *et al.* (x).<sup>48</sup> Three different colors represent the experimental conditions in three phase states of  $\text{CO}_2$ : green color denotes the gas state, and blue and red symbols represent the conditions using liquid and supercritical  $\text{CO}_2$ , respectively.

elements on the phase boundary and the fresh bulk fluid due to the more intensive liquid slug's internal recirculation.<sup>58,59</sup> Also, from the perspective of Higbie's penetration theory,<sup>49</sup> the more intensive internal recirculation implies the more frequent contact of fluid elements with the phase boundary and the shorter contact time for a fluid element on the phase boundary, thereby increasing  $k_L$  [based on eqn (8)].

Besides the dimensionless parameters, both temperature and the viscosity of water affect  $\text{CO}_2$  diffusion in water. Under uniform temperature conditions, the diffusivity of  $\text{CO}_2$  is inversely proportional to water viscosity.<sup>60</sup> The water viscosity  $\mu_l$  varies from  $9.14 \times 10^{-4}$  to  $7.22 \times 10^{-4}$  ( $\text{Ns m}^{-2}$ ) as the injection pressure elevates from 0.15 MPa at room temperature up to 9.5 MPa at 35 °C. This decrease in water viscosity may lead to a 26% increase in  $\text{CO}_2$  diffusivity in water, which may partially explain the greater  $k_La$  measured for supercritical  $\text{CO}_2$ . Studies also show that surface tension could play a role in mass transfer for a stationary micron-sized gas-bubble when the bubble radius  $\leq 15 \mu\text{m}$  and the solvent is nearly saturated.<sup>61,62</sup> Under these conditions, the Laplace pressure between the two phases can enhance gas molecules' transport into the surrounding solvent due to overpressure. In our experiments, we degas water for an hour to make sure it is initially free from any dissolving gases, including  $\text{CO}_2$ . The large concentration difference between the  $\text{CO}_2$  bubble/droplet and adjacent water would primarily drive the mass transfer of  $\text{CO}_2$ .<sup>62</sup> In addition, the surface tension between  $\text{CO}_2$  and water and, hence, the Laplace pressure decreases at elevated pressure [by about three times compared to that at 1 atm (see Table S2 in the ESI†)]. Therefore, the influence of the Laplace pressure (estimated to be 1 kPa) or surface tension on the  $\text{CO}_2$  mass transfer at elevated pressure (of  $P_{\text{inj}} = 9.5$  MPa) is likely negligible in our cases.

How do our microfluidic results compared with the  $k_La$  obtained using the segmented gas-liquid flow (so-called Taylor flow) in millimeter-sized capillaries,<sup>53</sup> which are beneficially used in monolithic chemical catalyst reactors? Fig. 5c shows such a comparison between our experimental results and the  $k_La$  estimated by three empirical approximations with millimeter-scale capillaries. Our experimental results of  $(k_La)_{\text{exp}}$  are plotted in the Y-axis, whereas the correspondingly estimated values,  $(k_La)_{\text{est}}$ , in the X-axis, by substituting our experimental conditions into the previous empirical equations, described below.

First, the semi-theoretical model developed by Irandoust *et al.* (depicted by \*) considers the bubble speed ( $u_b$ ) playing a crucial role in the mass transfer on both cap sides and the center cylinder of a Taylor bubble:<sup>53</sup>

$$k_La = 4[\delta_f(d_h - \delta_f)U_{\text{av}} y_m + D \text{Sh}(d_{\text{hc}} - 2\delta_f)]/(d_h^2 L_{\text{uc}}), \quad (9)$$

where  $U_{\text{av}}$  is the mean velocity of the liquid film passing through the cylindrical part of a bubble, which is a function of  $u_b$  (Re). Sh denotes the Sherwood number, defined by the ratio of convective to diffusive mass transport.<sup>63</sup>  $y_m$  is defined



as the mix cup concentration of the solute in the liquid film (in contact with the cylindrical part of the Taylor bubble)<sup>53</sup> and represents the dimensionless fraction of dissolving gas in the liquid film ( $0 < y_m < 1$ ). The higher  $y_m$  implies more solute dissolving in the solvent *via* the cylindrical part of a bubble. Previous experimental data of  $k_L a$  (for  $11 < Re < 824$ ) using millimeter-scale capillaries showed consistent results,<sup>53</sup> albeit  $\approx 30\%$  lower, compared to the (semi-)theoretical predictions. Notably, this model performs a good prediction on our results at room temperature if assuming  $y_m = 0.052$ , as depicted by blue and green symbols. The low  $y_m$  implies that the film contribution is small and inactive for mass transfer [see eqn (9)].

Second, results calculated using Berčić and Pintar's model underestimate the  $k_L a$  compared to our measurements (depicted by +):

$$k_L a = p_1 \times u_b^{p_2} / L_s^{p_3}, \quad (10)$$

where  $p_1 = 0.111$ ,  $p_2 = 1.19$ , and  $p_3 = 0.57$ ,<sup>57</sup> respectively. This empirical model was developed to fit the results measured from experimental conditions of long  $L_{b0}$  ( $28 \text{ mm} < L_{b0} < 110 \text{ mm}$ ) and relatively low  $u_b$  ( $0.076 \text{ m s}^{-1} < u_b < 0.15 \text{ m s}^{-1}$ ). In the previous experiments, the long gas bubble and slow velocity make the mass transfer from the cylindrical side of a bubble inactive, *i.e.*, corresponding to the case of  $y_m = 0$  in eqn (9). Therefore, without modeling the contribution from the thin film, this model would underestimate and result in smaller  $k_L a$  for our experimental conditions (as shown in Fig. 5c).

Third, the empirical model proposed by Vandu *et al.* suggests that the mass transfer happens primarily *via* the cylindrical body to the liquid film. The contribution from the cap side can be neglected because of the small specific area  $a$  of the cap side compared to the cylindrical body;<sup>48</sup> therefore

$$k_L a = C_1 \sqrt{\frac{DU_g}{L_{uc}}} \frac{1}{d_h} \approx C_1 \frac{\sqrt{Du_b L_{b0}}}{L_{uc} d_h}, \quad (11)$$

where the prefactor  $C_1$  is found to be 4.5 to fit their results the best,  $D$  is the diffusion coefficient of the solvent, and  $U_g = u_b \cdot (L_{b0}/L_{uc})$ . This model considering only the film contribution, however, overestimates the  $k_L a$  under our experimental conditions (depicted by  $x$ ). This model corresponds to another extreme condition of eqn (9) as  $y_m \approx 1$ , when the fluid elements on the cylindrical body remain active.

In brief, our microfluidic measurements of  $k_L a$  for the segmented gas-liquid are significantly greater than those obtained by millimeter-size capillaries. Consistently,  $k_L a$  generally increases with increasing  $u_b$  and, hence,  $Re$ . Compared with various empirical models developed for the millimeter-size capillaries, our microfluidic segmented Taylor flow measurements show the contributions of mass transfer from both the spherical caps and the thin liquid film.

## 4 Conclusions

We experimentally investigated the microfluidic  $\text{CO}_2$  mass transfer rate in water under high-pressure conditions, ranging from the normal state on the ground (0.25 MPa and  $24 \text{ }^\circ\text{C}$ ) to the deep formation's reservoir conditions (9.5 MPa and  $35 \text{ }^\circ\text{C}$ ) for CCS applications. With the microfluidic measurements of the segmented flow's size-change in a high-pressure microfluidic device, we extracted the liquid-side volumetric mass transfer coefficient  $k_L a$  to quantify the dynamic mass transport of  $\text{CO}_2$  bubbles/droplets in gas, liquid, and supercritical states. The resultant  $k_L a$  reveals a more intensive mass transfer for supercritical  $\text{CO}_2$ . The measurement of  $k_L a$  also shows an approximately linear dependency on the Reynolds number of the continuous phase with a factor of 0.53. Our microfluidic results with  $d_h \approx 50 \text{ } \mu\text{m}$  show a significant increase of  $k_L a$ , by  $O(1-10^2)$  compared to other low-pressure microfluidic measurements (with  $d_h \approx 200 \text{ } \mu\text{m}$ ) and by  $O(10^2-10^3)$  compared to those obtained using millimeter-size capillaries. Future work could extend the current parameter scope to investigate the important effect of temperature and microchannel size on microfluidic (two-phase) mass transfer, which is crucial for the technologies of microreactors and intensified extraction.

In terms of CCS applications, our experimental results revealed intensive mass transfer ( $k_L a$ ) of  $\text{CO}_2$  in the supercritical state at the micro-pore scale ( $d_h \approx 50 \text{ } \mu\text{m}$ ), leading to fast saturation in water at the early stage and benefiting subsequent sequestration of  $\text{CO}_2$ . In addition, the increase in the  $\text{CO}_2$ 's traveling velocity ( $u_b$ ) considerably enhances its mass transfer. These two primary outcomes can help assess the relevant time-scale and volume of supercritical  $\text{CO}_2$ 's mass transfer in water for the  $P$ - $T$  conditions and fluid inject rates used. Furthermore, the microfluidic platform presented can be extended for beneficial applications of microfluidic visualizations of  $\text{CO}_2$ -EOR under different reservoir conditions and intensive extractions using the green solvent supercritical  $\text{CO}_2$ .

## Author contributions

Tsaihsing Martin Ho: investigation, methodology, software, formal analysis, writing – original draft, visualization. Junyi Yang: software. Peichun Amy Tsai: conceptualization, methodology, validation, software, writing – revision, visualization, supervision, funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

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