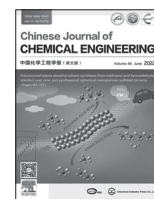




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Full Length Article

Formation characteristics of Taylor bubbles in a T-junction microchannel with chemical absorption

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ABSTRACT

This study focuses on the effect of chemical absorption on the formation dynamic characteristics and initial length of Taylor bubbles. The temporal evolutions of neck width and length of gaseous thread and initial length with and without chemical absorption were investigated with the Capillary number and Hatta number between 0.0010–0.0073 and 1.8–5.8 respectively. The squeezing regime with typical three stages, expansion, squeezing and pinch off is observed for both two processes. Compared with the non-absorption process, the increase of formation time in the chemical absorption process arises mainly from the expansion stage, and the decrease of initial length is from the necking stage. In addition, the temporal length evolution satisfies the power-law scale with the same exponent but a smaller pre-exponential factor. The correlations of neck width for stage transition and initial length with Hatta number demonstrate the enhancement effect of chemical absorption on bubble formation dynamics and initial length at relatively high chemical reaction rates and long formation time. This study provides insight into the bubble formation mechanism and helps to regulate the bubble initial size with chemical absorption.

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1. Introduction

Over the past two decades, microreactor technology has been developed rapidly as a potential means of process intensification technology in chemical engineering, due primarily to its metrics of high concentration/heat gradient and huge specific surface. A broad application prospect has been demonstrated in many fields, such as biochemistry, organic synthesis, separation, halogenation and so forth [1–4], where the gas–liquid two-phase flow and reaction are frequently encountered. Importantly, the reaction performance in gas–liquid microreactors depends highly on the hydrodynamics of gas–liquid two-phase flows.

Great efforts have been devoted to exploring the hydrodynamics and mass transfer performance of Taylor flow (slug flow or segmented flow) for applications in gas absorption, particle preparation, catalysis and polymerization, etc. [5–8]. Taylor flow is a common flow pattern consisting of alternative liquid slugs and elongated bubbles that are longer than channel width. The adjacent liquids are separated by bubbles and are connected only through the thin lubricant film and gutters between the bubble

and channel wall. Thus, this pattern contributes to a significant reduction in axial mixing and a great improvement in radial mixing. Until now, the overall mass transfer performance of Taylor flow regime in microreactors has received extensive attention, but few studies focus on the separate contributions of mass transfer of the three characteristic stages, i.e., bubble forming, bubble flowing and phase separation stages. Tan *et al.* [9] investigated the mass transfer performance of CO₂ absorption in NaOH aqueous solution at bubble formation stage in a T-junction microchannel, and the results showed that the mass transfer during the formation stage (0.2–0.4 s) played a significant role in overall mass transfer, accounting for 30%–40%. Yao *et al.* [10] observed that the gas absorption fraction at the inlet was proportional to the maximum mass transfer rate ($k_L a C^* t$). The gas absorption fraction was about 2%–10%, which was far less than the result of Tan *et al.* [9]. Moreover, Ganapathy *et al.* [11] observed that the volumetric mass transfer coefficient in the formation stage was lower than that in the flowing stage. Thereby, the understanding of the contribution of mass transfer stemmed from the formation stage is insufficient, which significantly limits the application and development of microreactors.

In addressing the hydrodynamics in the formation process, the bubble length is one of the key issues in determining the pressure

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drop and the mass transfer in the flowing stage. Several formation mechanisms have been proposed [12–14]. The regimes for bubble formation in T-junctions can be classified into squeezing regime, dripping regime, squeezing-to-dripping transition regime and jetting regime, according to the dominated force exerted on the gaseous thread and breakup model [15]. The bubble formation coupling with the gas–liquid mass transfer is usually governed by the squeezing mechanism at low Capillary numbers (10^{-4} – 0.0058) [16]. Moreover, at relatively high Capillary numbers (>0.21), the squeezing force can also play an important role even though the shear stress is absolute of great importance [17]. Currently, the squeezing regime has been studied extensively, and several models for predicting the initial bubble length have been proposed under the Taylor pattern [1,12,16,18–22], as summarized in Table 1. These models cover different factors affecting the initial bubble length, including inlet condition, fluid property and microchannel geometry. Regrettably, these studies focus mainly on the gas–liquid flow process without mass transfer or reaction, while the mass transfer encountered in gas–liquid two-phase systems is normally accompanied by chemical reactions. Thereby, the effect of chemical absorption on bubble formation in microchannels remains unclear.

Herein, the bubble formation dynamics in monoethanolamine (MEA) aqueous solutions with and without chemical absorption were studied in a T-junction microchannel. The temporal evolutions of neck width and the length of gaseous thread were elaborated in the squeezing regime. In addition, the formation frequency and bubble initial length were explored. The Hatta number was correlated with the critical bubble neck width (for stage transition) and initial length for better understanding the effects of chemical absorption and operation conditions on bubble formation.

2. Materials and Methods

2.1. Materials

The aqueous solutions with various concentrations of monoethanolamine (c_{MEA} , MEA with purity $> 99.0\%$, Shanghai Aladdin Chemical Reagent Co., Ltd., China) were utilized as liquid phase. Carbon dioxide (CO_2 , with purity $> 99.99\%$, Tianjin Liufang Gas Co., Ltd., China) and nitrogen (N_2 , with purity $> 99.99\%$, Tianjin Liufang Gas Co., Ltd., China) were employed as reference gas. The sodium dodecyl sulfate (SDS, 0.4% (mass)) was added into the liquid phase to stabilize gas–liquid flow by reducing the interfacial energy. The almost same surface tensions (Table 1) for all solutions indicate a similar effect on the bubble length. Table 2 summarizes the physical properties (viscosity, density and surface tension) of the liquid phase. Different chemical reaction rates can be achieved by adjusting MEA concentrations without obvious impact on physical properties, *i.e.* density, viscosity and surface tension. Generally, the reaction system is regarded as a fast pseudo-first-order reaction [23]. The Hatta number is represented as $Ha = \sqrt{Dk_1/k_L}$, where D , k_1 and k_L stand for the diffusion coefficient of CO_2 in the bulk liquid, the pseudo-first-order reaction rate constant and the physical mass transfer coefficient respectively. The k_1 can be calculated by reference [24]. In such short bubble formation period (<25 ms), the k_L can be determined by the permeation model [25], $k_L = \sqrt{D/\pi t_f}$, where t_f is the bubble formation time. Under current experimental conditions, Ha is between 1.8 and 5.8.

2.2. Methods

The schematic diagram of the experimental setup is depicted in Fig. 1. Two precision-controlled micro-syringe pumps (Harvard

Table 1
Previous correlations of bubble length in T-junction microchannels

Correlation	Geometry and size/mm	System	Operation condition	Refs.
$\frac{l_B}{w_c} = 1 + \alpha\varphi$	w_c : 0.05, 0.1, 0.2 h_c : 0.033 w_{in} : 0.05, 0.1 w_c (h_c): 0.8	Water– N_2	φ : 0.5–3, $Ca < 0.01$	[12]
$\frac{l_B}{w_c} = 1.5 + 1.5\varphi$		Ethanol–air	φ : 0.6–5	[18]
$\frac{V_B}{w_c^3} = 1 + 2\varphi$	w_c (h_c): no specified	No specified	φ : 0–2, $Ca < 0.01$	[19]
$\frac{l_B}{D_h} = 2 + \left(\frac{h_c}{w_c}\right)\varphi^{0.5}$	D_h : 0.25–0.55 h_c/w_c : 0.12–1	Water– N_2	Q_G : 2–30 $\text{ml}\cdot\text{min}^{-1}$ Q_L : 0.1–10 $\text{ml}\cdot\text{min}^{-1}$	[22]
$\frac{l_B}{w_c} = 1 + 1.72Re^{0.173}\varphi^{0.797}$	w_c : 0.594 h_c : 0.08	Water–air Glycerol/water–air	φ : 0.1–3.33	[21]
$\frac{l_B}{w_c} = 0.5\left(\frac{Q_G}{Q_L\sin\theta} + 0.4\cot\theta\right)^{0.5}Ca^{-0.2}$	w_c : 0.12 h_c : 0.04 θ : 30° , 60° , 90° , 120° , 150°	Glycerol/water–air	φ : 0.3–10, $Ca < 0.012$	[20]
$\frac{l_B}{w_c} = 0.32 + 0.64\varphi$	w_c : 0.12 h_c : 0.04	Water– N_2 Glycerol/water– N_2	Ca : 10^{-4} – 5.8×10^{-3}	[16]

Note: w_c , h_c and D_h are the width, height, hydraulic diameter of the main channel; l_B and V_B are the length and volume of bubbles, φ is the ratio of gas rate to liquid rate; θ is the angle between gas and liquid inlets; w_{in} is the width of the inlet; Re is two-phase Reynolds number ($Re = D_h(U_G + U_L)\rho_L/\mu_L$, U_G and U_L are the gas-phase velocity and liquid-phase velocity, ρ_L and μ_L are density and viscosity of liquid phase); Ca is two-phase Capillary number ($Ca = \mu_L(U_G + U_L)/\sigma$, σ is the gas–liquid surface tension).

Table 2
The properties of liquid phase used in this experiment

Concentrations of MEA, $c_{\text{MEA}}/\text{mol}\cdot\text{L}^{-1}$	Density, $\rho_L/\text{kg}\cdot\text{m}^{-3}$	Viscosity, $\mu_L/\text{mPa}\cdot\text{s}$	Surface tension, $\sigma/\text{mN}\cdot\text{m}^{-1}$	Pseudo-first-order reaction rate constant, k_1/s^{-1}
0.2	997.8	0.81	37.73	490.75
0.4	998.2	0.82	37.64	981.50
0.6	998.6	0.87	37.57	1472.26
0.8	999.0	0.85	37.43	1963.02

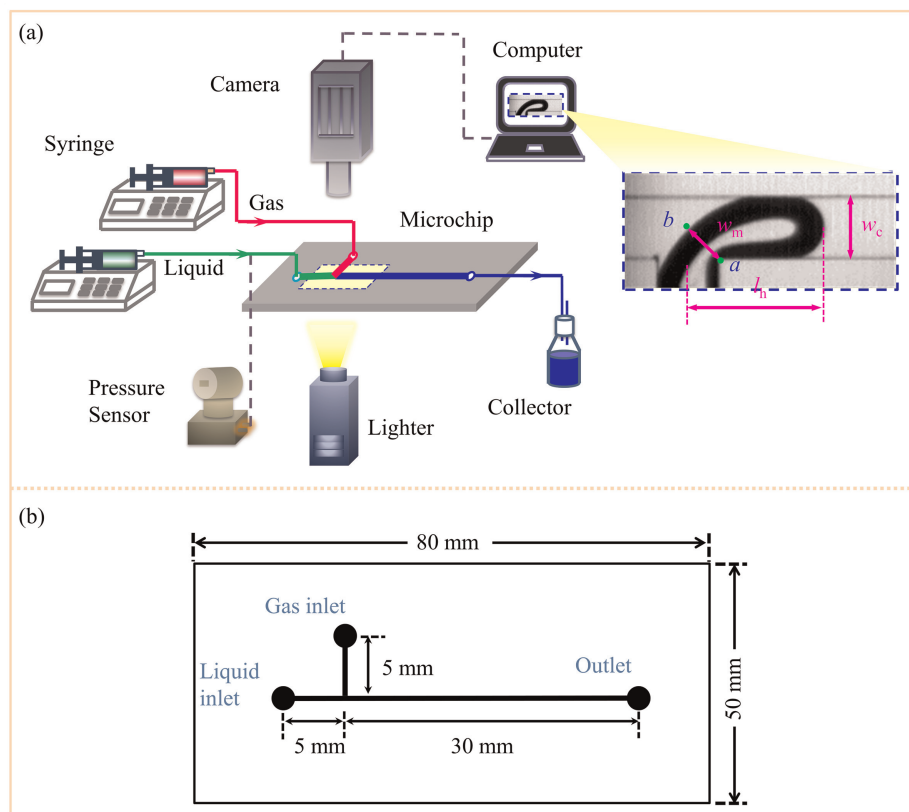


Fig. 1. Schematic overview of the experimental setup (a) and the structure of microchannel chip (b) (w_m , w_c and l_h are the minimum neck width, microchannel width and the extending length of bubble head in the formation process, respectively).

PHD 2000, USA) were used to drive the gas and liquid into the microchannel device. A cross T-junction microchannel was fabricated on a polymethyl methacrylate (PMMA) plate. The lengths of the two inlet microchannels and the main microchannel are 0.5 mm and 30 mm respectively. All microchannels have a square cross-section ($0.4 \text{ mm} \times 0.4 \text{ mm}$). The inlet of the branch microchannel was used for the introduction of gas phase, and the inlet of the main microchannel was allocated to the liquid phase. The liquid flowing out the microchannel was separated from the gas and collected into a collector. A high-speed camera (Motion Pro Y-5, USA) was located vertically above the interaction port of the microchannel to monitor the formation process of CO_2 bubbles, and the photographs were captured and recorded with 10,000 frames per second. The illumination required for photography was provided by a cold light source. The pressure drop between the gas inlet and outlet of the main channel was measured by a differential pressure sensor (ST3000, Honeywell, USA). The pressure at the outlet is atmospheric pressure, and thus the measured pressure drop can be used to determine the inlet pressure at gas phase. The formation process of Taylor bubbles was performed under two liquid volumetric rates (20 and $40 \text{ ml} \cdot \text{h}^{-1}$) and various gas volumetric rates ($20 < Q_G < 280 \text{ ml} \cdot \text{h}^{-1}$). The range of two-phase Capillary number Ca is 0.0010–0.0073. All experiments were conducted at ambient pressure and room temperature (0.1 MPa , 298.15 K).

3. Results and Discussion

3.1. Formation process of Taylor bubble

Figs. 2 and 3 show the evolutions of the emerging bubble in the squeezing regime (or confined breakup regime). The typical three

stages, expansion, squeezing and pinch off can be observed for bubble formation with and without chemical absorption. Importantly, in comparison with non-absorption process, the chemical absorption prolongs the formation process and conversely declines bubble length as illustrated in Fig. 2. This phenomenon confirms the effect of chemical absorption on bubble formation. Based on the fluid dynamic theory, the formation of bubble in squeezing regime is known to be controlled by gas dynamic pressure, liquid squeezing, liquid shear, and surface tension [12]. For better understanding the formation process with chemical absorption, the interfacial dynamics of CO_2 bubble formation are comprehensively investigated, with special attention to forces and effects of chemical absorption on them.

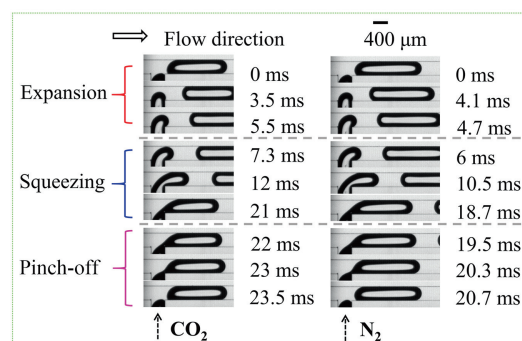


Fig. 2. Comparison of CO_2 bubble and N_2 bubble during the formation process in a cross T-junction microchannel, $c_{\text{MEA}} = 0.8 \text{ mol} \cdot \text{L}^{-1}$, $Q_G = 40 \text{ ml} \cdot \text{h}^{-1}$, $Q_L = 20 \text{ ml} \cdot \text{h}^{-1}$.

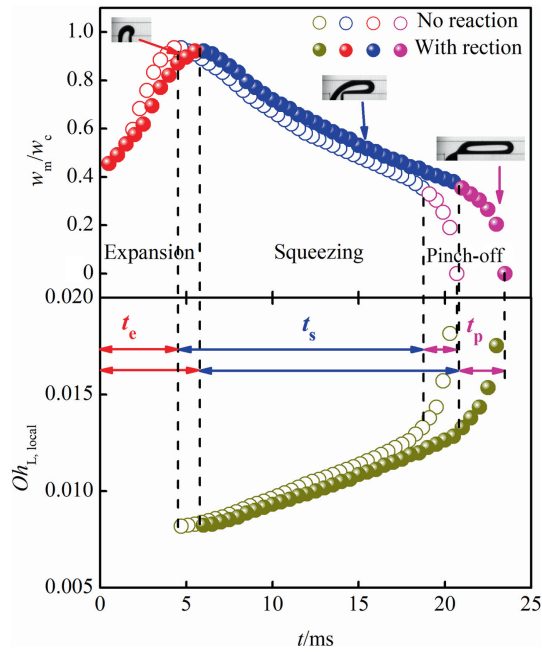


Fig. 3. Evolutions of the bubble minimum neck width (w_m) and the local Ohnesorge number of liquid phase ($Oh_{L,local} = \mu_L/(\rho_L \sigma w_m)^{0.5}$). The durations in the expansion, squeezing and pinch-off stages are defined as t_e , t_s and t_p respectively. $C_{MEA} = 0.8 \text{ mol}\cdot\text{L}^{-1}$, $Q_G = 40 \text{ ml}\cdot\text{h}^{-1}$, $Q_L = 20 \text{ ml}\cdot\text{h}^{-1}$.

3.1.1. Expansion stage

The expansion stage can be described as: after the pinch-off of the former bubble and a retracting and waiting time, the bubble tip gradually penetrates into the liquid phase and moves forward axially and radially until a neck is formed. At the end of this stage, the neck width normally reaches the maximum value. Nevertheless, there still exists a small gap between the bubble thread and channel wall on the opposite side. The distance between the interface (site *b* in Fig. 1) at the 45° direction to the right corner of the gas inlet and the corner (site *a* in Fig. 1) is defined as the characteristic width of gaseous thread. As illustrated in Fig. 4, compared with the liquid rate, the gas rate presents more significant impact on the characteristic width of gaseous thread and time duration in the expansion stage. Thereby, the gas dynamic pressure can still be the main control force during the expansion with chemical absorption [12,16].

From Fig. 4, the decrease of gas rate results in longer time duration and a larger neck width at the end of expansion stage. Since the gaseous thread moves slower at the lower gas rate, more liquid

flows through the gap between the gaseous thread and channel wall with relative ease, which negatively influences the accumulated rate of pressure in the liquid upstream of the gaseous thread, resulting in smaller liquid squeezing difference on both sides of gaseous thread. Consequently, the neck becomes thicker. The chemical absorption inhibits the growth of gaseous thread especially at low gas rates, resulting in longer expansion time. To be exact, chemical absorption will affect the balance of control forces. The chemical absorption can reduce the gas dynamic pressure (see Fig. 5). It can reduce the penetration rate of gaseous thread into the channel, allowing more liquid to bypass the gaseous thread, and thereby result in a smaller liquid squeezing force. The reduction of squeezing force may affect the following squeezing stage since it is the main driving force for neck thinning.

During the gradual penetration of gaseous thread into the main channel, the enhanced liquid shear and squeezing in the gap slows the radial growth of gaseous thread, as shown in Fig. 6. There is a power-law scale between the radial expansion distance and expansion time, i.e., $1-\varepsilon/w_c \sim at^b$ (ε is the width of the gap between the gaseous thread and channel wall). Both the gas and liquid rates have little impact on the exponent ($b \approx 2.0$), but positively increase the pre-exponential factor. When the gap ε reduces to $0.2w_c$, there exists a turning point in the radial displacement velocity of the gaseous thread, thereafter, the exponent decreases. This is because the far greater increment of squeezing (than the shear force) primarily promotes the axial diffusion of gaseous thread in the early stage of squeezing process. Nevertheless, an analogous power-law scale can be still satisfied (with a smaller exponent of 0.83). The chem-

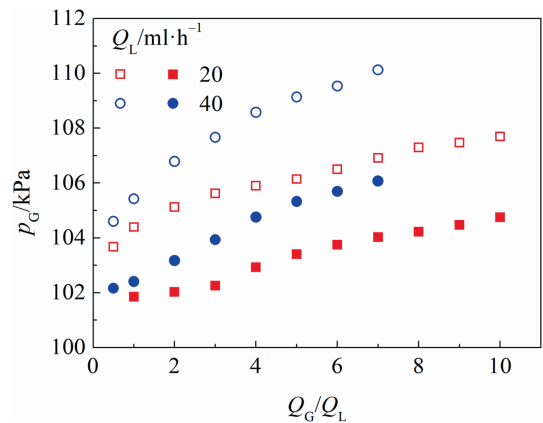


Fig. 5. The inlet pressure of gas phase for $C_{MEA} = 0.8 \text{ mol}\cdot\text{h}^{-1}$, solid symbols: with absorption, open symbols: without absorption.

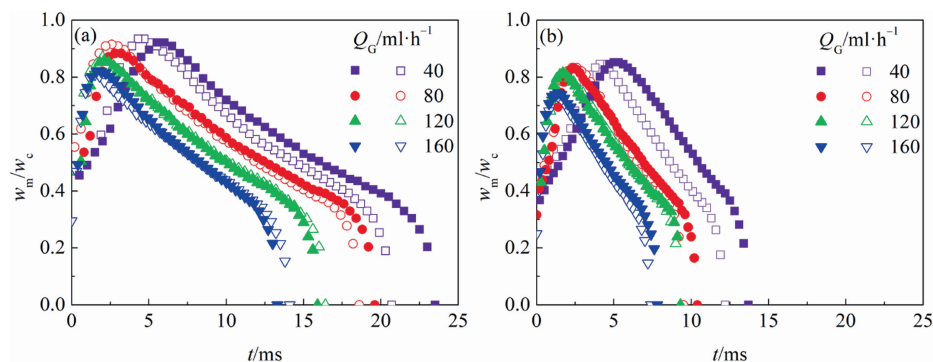


Fig. 4. Evolution of the minimum width of bubble neck with time under different experimental conditions ($C_{MEA} = 0.8 \text{ mol}\cdot\text{L}^{-1}$, (a) $Q_L = 20 \text{ ml}\cdot\text{h}^{-1}$ and (b) $Q_L = 40 \text{ ml}\cdot\text{h}^{-1}$, solid symbols: with absorption, open symbols: without absorption).

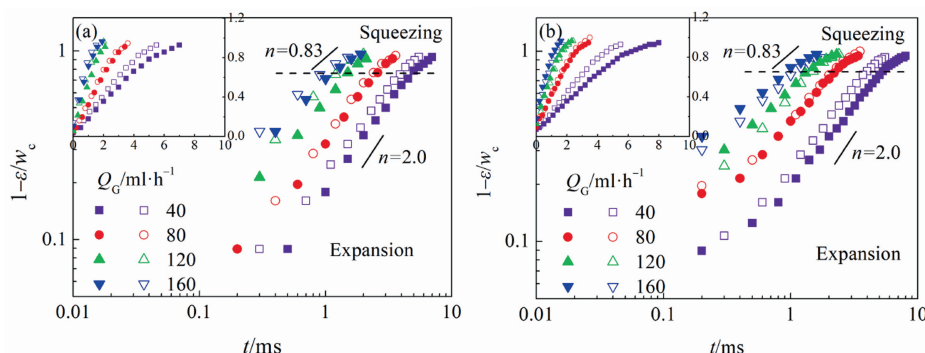


Fig. 6. Temporal evolution of radial penetration of gaseous thread ($c_{\text{MEA}} = 0.8 \text{ mol} \cdot \text{L}^{-1}$, (a) $Q_L = 20 \text{ ml} \cdot \text{h}^{-1}$ and (b) $Q_L = 40 \text{ ml} \cdot \text{h}^{-1}$, solid symbols: with absorption, open symbols: without absorption).

ical absorption has little impact on the exponent but affects the pre-exponential factor. At low liquid rate, the chemical absorption inhibits the radial development of gaseous thread by decreasing the gas dynamic pressure, and thus results in a smaller pre-exponential factor. At high liquid rate, the effect of chemical absorption changes from inhibition to promotion with the increasing gas rate (Fig. 7), because the decrement of gas dynamic pressure (due to chemical absorption) is dominant at the low gas rate, while it can significantly increase the leakage flow at the high gas rate, which decreases the liquid shear and squeezing in the gap, thereby promoting the radial development of gaseous thread. For the axial development of gaseous thread, the easier leakage of liquid reduces the pressure difference between the two sides of gaseous thread. Moreover, the absorbed CO_2 solute near the interfacial can be carried out by the leakage flow, thereby keeping high renewal and absorption rate around the interface [26]. These can result in a slower axial elongation of gaseous thread with absorption than that without absorption. However, the effect of chemical absorption on the axial elongation of gaseous thread is unobvious at the expansion stage (see inset in Fig. 7).

3.1.2. Squeezing stage

The squeezing stage is mainly characterized by the neck thinning of gaseous thread. Heretofore, the gaseous thread after the expansion stage still undergoes a short radial extension until its head can completely block the main channel. The further blockage of gaseous thread inhibits the leakage flow, thus rapidly increasing the pressure of liquid upstream of the gaseous thread. The clear neck is squeezed by liquid upstream and shrinks at the rate that is considered to be approximately equal to the mean flow velocity of liquid-phase fluid (Fig. 4) [12]. For both two processes, the neck shrinkage depends almost on the liquid rate,

moreover, the squeezing stress ranges between $\Delta p_s \approx 10^2$ – 10^3 , while the shear stress is approximately $\Delta p_\tau \approx 10^0$, $\Delta p_s \gg \Delta p_\tau$ [12], demonstrating the dominant role of liquid squeezing in controlling the squeezing process.

As presented in Fig. 4, due to the delay of squeezing arrival, the neck squeezing with chemical absorption always keeps larger width than the process without absorption. Nevertheless, the chemical absorption has little effect on the neck shrinking velocity. Consequently, under a new balance of forces, although the gas dynamic pressure (Fig. 5) and liquid squeezing decrease due to the chemical absorption, the net driving force controlling interface evolution remains unchanged. For better understanding the necking characteristics, the evolution of neck width with and without absorption is depicted on a dimensionless time scale (t/T , T represents the bubble formation period). Fig. 8 demonstrates that the chemical absorption has little influence on the neck evolution of gaseous thread in the squeezing process, i.e., the evolution trend and critical dimensionless time for stage transition is almost consistent between chemical absorption and non-absorption processes. The further development of gaseous thread in the squeezing process, on one side, increases the exposed surface area for mass transfer, which enables more CO_2 absorption and thus promotes neck shrinkage. On the other side, it prevents the liquid leakage and meanwhile the bypass of the absorbed CO_2 solute in the neck area, which allows the absorbed CO_2 solute to accumulate at the root region of gaseous thread, thereby inhibiting convective mass transfer and neck shrinkage. The high liquid velocity and low gas velocity are beneficial for leakage flow and accordingly convective mass transfer [27]. Nevertheless, the neck width with chemical absorption increases at the Q_L of $40 \text{ ml} \cdot \text{h}^{-1}$ and Q_G of $40 \text{ ml} \cdot \text{h}^{-1}$ (Fig. 8(b)), which infers a smaller squeezing force with absorption as the squeezing equilibrium is reached.

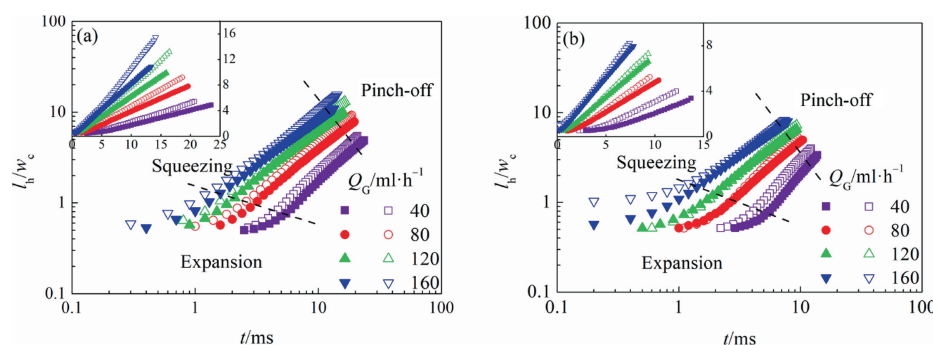


Fig. 7. Temporal evolution of axial extension of gaseous thread ($c_{\text{MEA}} = 0.8 \text{ mol} \cdot \text{L}^{-1}$, (a) $Q_L = 20 \text{ ml} \cdot \text{h}^{-1}$ and (b) $Q_L = 40 \text{ ml} \cdot \text{h}^{-1}$, solid symbols: with absorption, open symbols: without absorption).

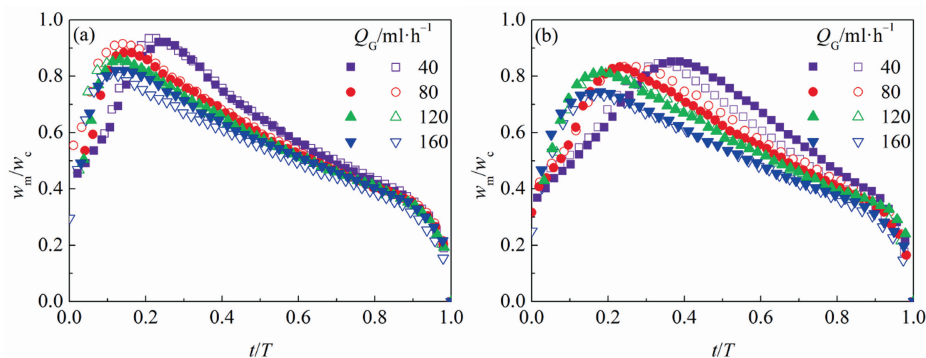


Fig. 8. Evolution of the dimensionless minimum width of bubble neck with dimensionless time ($c_{\text{MEA}} = 0.8 \text{ mol}\cdot\text{L}^{-1}$, (a) $Q_L = 20 \text{ ml}\cdot\text{h}^{-1}$ and (b) $Q_L = 40 \text{ ml}\cdot\text{h}^{-1}$, solid symbols: with absorption, open symbols: without absorption).

The axial elongation of gaseous thread in the squeezing stage still follows a power-law scale but with higher exponent than that in the expansion stage due to the increase of liquid upstream squeezing. The chemical absorption slows the elongation of gaseous thread, which increases the length difference during the squeezing process (see inset in Fig. 7). Moreover, the difference becomes more significant at high gas rate and low liquid rate or low gas rate and high liquid rate. The former is attributed to the increase of squeezing time, while the latter can be attributed to the enhancement of leakage flow.

3.1.3. Pinch-off stage

During the necking process, the pinch off of the neck with a drastic shrinkage occurs due to the Rayleigh–Plateau instability [28,29] and the reversed flow of liquid from the tip towards the neck [30]. In this stage, the liquid squeezing is still the main driving force by considering the magnitude of local Ohnesorge number of liquid phase ($Oh_{\text{L,local}} = \mu_L/(\rho_L \sigma w_m)^{0.5}$, which presents the ratio of viscous force to surface tension) in Fig. 3(b), even though the $Oh_{\text{L,local}}$ number experiences a slow to rapid increase from the squeezing to pinch-off stage.

The increase of liquid rate or gas rate accelerates the pinch off of the bubble neck and reduces the pinch-off duration (Fig. 4). However, the neck width on a dimensionless time scale is almost identical for all conditions (Fig. 8). This phenomenon may be related to the different forces exerted on the interface as gaseous thread starts to be pinched off and the fluid migrates from the lubricating film to gutters [30]. The axial movement of gaseous thread still continues as the squeezing process, and the accumulated effect of chemical absorption on its length maintains and continues in this short stage.

3.2. Minimum neck width for stage transition

Hatta number (Ha) is used to correlate the dimensionless minimum neck width for the transition of adjacent stages with chemical absorption. From Fig. 9, the dimensionless neck transition widths increase linearly with the increasing Ha . It implies that the shrinking of bubble neck in the latter two stages becomes more difficult at the higher reaction rate or/and longer formation time. The absorption, on one side, decreases the dynamic pressure in the gas phase and thus exacerbates the leakage of fluid upstream of the gaseous thread, resulting in lower squeezing force. Consequently, it becomes more difficult for squeezing force to resist surface tension for bubble formation. On the other side, it can decrease the dynamic surface tension due to the transfer of CO_2 molecules into the liquid layer, which weakens the asymmetric molecular force field in the gas–liquid interfacial region [2]. At high

reaction rates, the reaction can further restore the molecular force field on the interface due to the fast transfer rate of CO_2 molecules from the liquid layer to the liquid bulk [2]. Therefore, compared with the non-absorption process, the reduction of squeezing force caused by absorption is responsible for the transiting of larger neck width from expansion to squeezing stage. Moreover, at high reaction rate, the decrease of squeezing force and the increase of dynamic surface tension are unfavorable to the pinch off of bubble. In terms of the intercept, the minimum neck widths for transitions between different stages are approximately 0.66 and 0.28 times of the channel width, with a downward offset by comparing with the values obtained without reaction. In addition, the small slopes (0.042 and 0.015) indicate that a large enough Ha is required for chemical absorption to have a significant impact on the neck dynamics. In contrast, the critical neck width is more sensitive to Ha for process transiting from expansion to squeezing than from squeezing to pinch off.

3.3. Bubble extension proportion in each stage

The proportions of bubble extension length and duration time of each stage are depicted in Fig. 10. The bubble extension proportions are 9.7%–17.9% in the expansion stage, 59.3%–75.9% in the squeezing stage, and 12.3%–18.0% in the pinch-off stage for all processes. The dominant contribution to bubble initial length arises from the inflow of liquid-phase fluid into the bubble in the squeezing stage because the Q_G/Q_L is higher than 1 [12]. With the increase

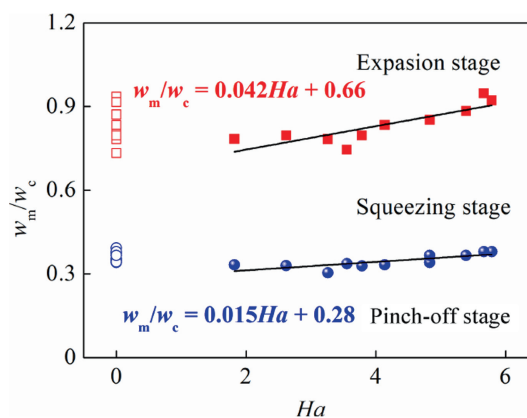


Fig. 9. The critical minimum neck width for bubble transition between adjacent stages as a function of the Hatta number, solid symbols: with absorption, open symbols: without absorption, block symbols: for bubble transition from expansion to squeezing stage, circle symbols: for bubble transition from squeezing to pinch-off stage, $Q_L = 20, 40 \text{ ml}\cdot\text{h}^{-1}$, $Q_G/Q_L = 0.5\text{--}8$, $c_{\text{MEA}} = 0.2\text{--}0.8 \text{ mol}\cdot\text{L}^{-1}$.

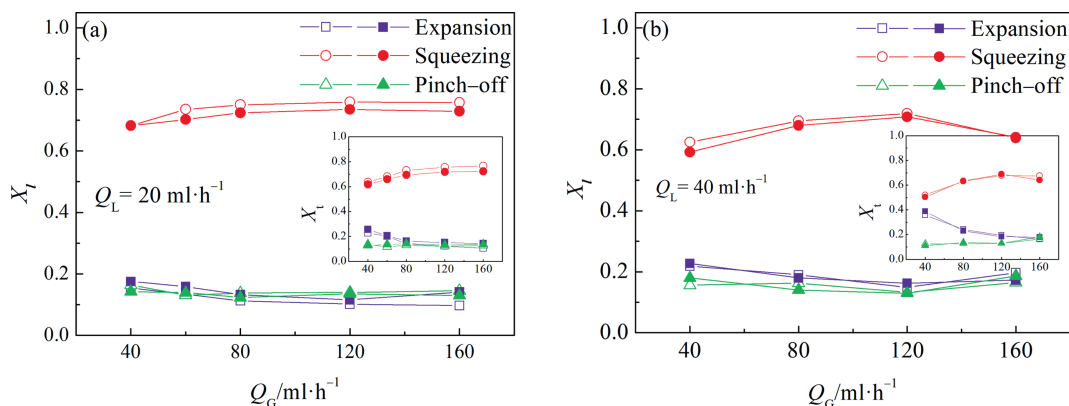


Fig. 10. The proportions of the extension length and time duration of the gaseous thread for each stage ($c_{\text{MEA}} = 0.8$ mol·L⁻¹, solid symbols: with absorption, open symbols: without absorption).

of gas rate, the proportion of bubble extension length initially decreases and then increases in the first and third stages, and thus there is a converse change in the second stage. This phenomenon can be attributed to the different proportion of duration time, which is consistent with the trend of bubble length (see the inset in Fig. 10). The increase of liquid rate shrinks the proportions of extension length and duration time in the squeezing stage and conversely prolongs them in the expansion and pinch-off stages. The dominant long duration time in the squeezing stage causes severe chemical absorption, resulting in the decrease of bubble extension proportion. The distributions of duration time and extension length in different stages can provide ideas to obtain the desired bubble size by regulating bubble formation process.

3.4. Overall bubble formation performance

3.4.1. Formation frequency

The average frequency of bubble generation is calculated by $f = N/\Delta t$, where Δt is the time for generating N numbers of bubbles. The increase of gas and liquid rates shortens the above discussed three stages, thereby increasing the formation frequency of bubble (Fig. 11(a)). However, the chemical absorption prolongs the bubble formation time, resulting in a slight decrease in formation frequency with the increasing reaction rate (Fig. 11(b)). This phenomenon is contrary to Soh *et al.*'s simulation results that the formation time was inversely correlated with the diffusion coefficient [26], since the increases of liquid shear and gas dissolution rate and the decrease of dynamic surface tension accelerated the neck thinning at a larger diffusion coefficient. Differently, the increment of chemical reaction rate can inhibit the accumulation of gas dynamic pressure, which hinders the entering of bubble into

the main channel. In this case, the enhanced leakage flow leads to the decrease of liquid squeezing force. In addition, the increase of reaction rate will increase the dynamic surface tension (as discussed in Section 3.2). All of these are detrimental to bubble formation and accordingly expand the formation time at a higher reaction rate. As described in Fig. 11, the frequency can be scaled with the ratio of gas rate to liquid rate as a power-law relationship. The exponent is approximately 0.3–0.4 regardless of absorption or not. This result implies that the chemical absorption has no significant influence on the dynamic characteristics of bubble formation.

3.4.2. Prediction of initial bubble length

As described above, the formation process of bubbles is mainly influenced by gas–liquid flow rates. The pressure drop over the whole main channel is less than 10 kPa, and thus the compression of bubble at the inlet of the main channel is negligible [10]. In this case, the initial bubble length was directly obtained by measuring the pixels occupied from the head to the tail of the regular-shaped bubble near the channel intersection (Fig. 12(a)).

The dependence of the normalized bubble length to channel width on the gas–liquid rate ratio is depicted in Fig. 12(a). As can be seen, the bubble length increases with the gas rate but decreases with the liquid rate. Previously, Garstecki *et al.* [12] observed that the length of gaseous thread was approximately equal to the width of the channel at the end of the expansion stage, and then the squeezing force thinned the bubble neck at a constant velocity, which was approximately equal to the liquid velocity u_L , $u_{\text{squeezing}} \approx u_L = Q_L/(hw_c)$. Thus, the time for the thread neck to shrink at a characteristic distance d (or minimum neck width w_m) of the neck was $t_{\text{collapse}} = d/u_{\text{squeezing}}$. Meanwhile, the gaseous thread grew at a velocity equal to the gas velocity, $u_{\text{growth}} \approx u_g = Q_g/$

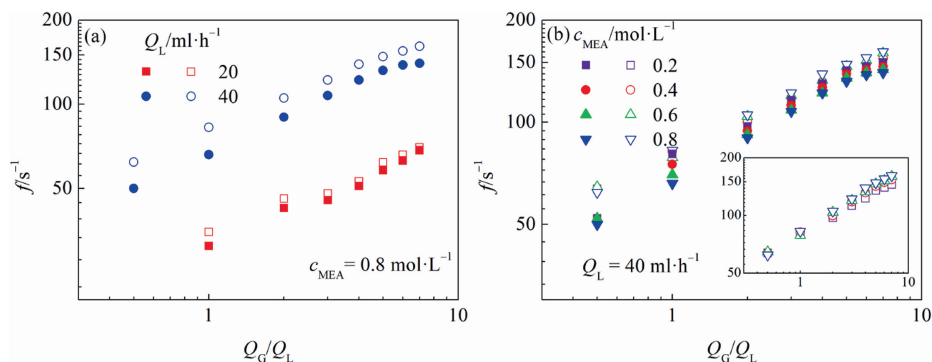


Fig. 11. Formation frequency of bubbles under different experimental conditions, solid symbols: with absorption, open symbols: without absorption.

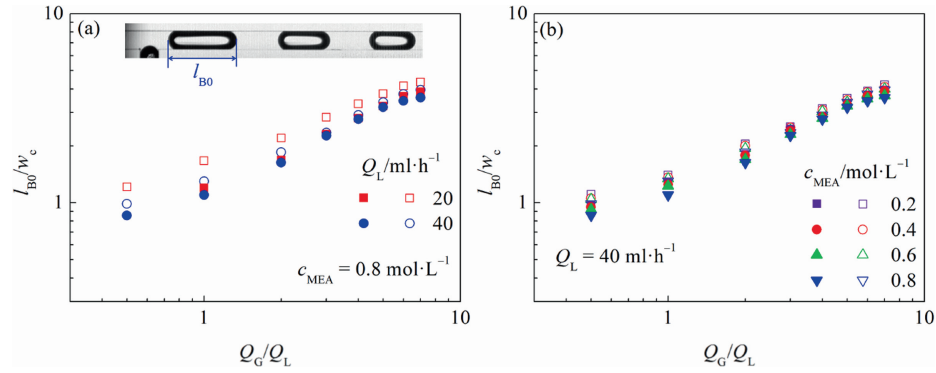


Fig. 12. The initial length of bubbles under different experimental conditions, solid symbols: with absorption, open symbols: without absorption.

(hw_c). Therefore, the final length of the bubble could be obtained as $l_{B0} \approx w_c + t_{\text{squeezing}} u_{\text{growth}} = w_c + d(Q_G/Q_L)$. The normalized length becomes $l_{B0}/w_c = 1 + \alpha(Q_G/Q_L)$, where $\alpha = d/w_c$. Practically, the length of gaseous thread at the end of expansion stage deviates from the channel width, which is related to channel geometry, size and operating conditions. Hence, the above equation is developed into a more general form, $l_{B0}/w_c = \alpha(Q_G/Q_L) + \beta$. In this study, the neck width at the end of the expansion phase and the collapse time are all related to gas and liquid two-phase rates (see Fig. 4). Xiong and Chung [21] observed a power-law scale between bubble length and gas-liquid velocity ratio, and proposed the correlation by taking into account gas-liquid rate ratio and two-phase Reynolds number to reflect the influence of two-phase rates:

$$l_{B0}/w_c = 1.724Re^{0.173} \left(\frac{Q_G}{Q_L} \right)^{0.797} + 1 \quad (1)$$

As shown in Fig. 12(a), the bubble length exhibits a power-law scale with gas-liquid rate ratio and decreases with the increase of liquid rate. To establish an operation guideline for the bubble size prediction in microchannels, the bubble length data are correlated using the ratio of gas/liquid rates and two-phase Reynolds number for bubbles generated without chemical absorption based on the general form of the equation proposed by Xiong and Chung [21], as follows:

$$l_{B0}/w_c = 1.88Re^{-0.14} \left(\frac{Q_G}{Q_L} \right)^{0.76} + 0.36 \quad (2)$$

As discussed above, for the chemical absorption process, the length and neck width of gaseous thread at the end of expansion stage, and the neck squeezing velocity have no obvious difference

compared to those in non-absorption process. In addition, the gaseous thread length satisfies the power-law scale over time. The exponent is identical to that without absorption, but the pre-exponential coefficient is smaller. Therefore, for chemical absorption process, there remains the constant term and the exponent term of $\left(\frac{Q_G}{Q_L} \right)$ in Eq. (2), however the coefficient term ($1.88 Re^{-0.14}$) needs to be modified. To extend the modified equation to non-absorption process, the parameter $(1 + Ha)^b$ is introduced. Through data regression, the following correlation is achieved:

$$l_{B0}/w_c = 1.88Re^{-0.14} (1 + Ha)^{-0.09} \left(\frac{Q_G}{Q_L} \right)^{0.76} + 0.36 \quad (3)$$

As shown in Fig. 13, the correlation shows excellent predictive performance with the relative deviation of most experimental data within 10%. The influences of gas-liquid flow rate ratio, liquid rate and chemical reaction on bubble length can be judged by these exponents. The parameters obtained in the above formula applies to the square microchannel with a width of 0.4 mm, and variables of entry conditions of the MEA concentration of 0.2–0.8 $\text{mol}\cdot\text{L}^{-1}$, Q_G/Q_L of 0.5–8, Re of 42–111 and Ha of 1.8–5.8, which can be adjusted according to the geometry and size of the microchannel and operating condition. The correlation of initial bubble length can identify the relative importance of operating parameters and provide guidance for optimizing the process operation. As discussed, the bubble length is highly related to the gas-liquid flow rate but less related to reaction rate, unless the chemical reaction rate and formation time are large enough. Therefore, it is no wonder that there exists diversity about the contribution of bubble absorption in the formation stage. The fast reaction of CO_2 -NaOH and long formation time (0.2–0.4 s) contribute 30%–40% of mass transfer amount [9], whereas the physical absorption of CO_2 -ethanol and short time (2–14 ms) contribute only 2%–10% [10].

4. Conclusions

This study aims at the effect of chemical absorption on bubble formation dynamics and initial length in a T-shaped microchannel. The temporal evolutions of neck width and extension length, as well as formation frequency and initial bubble length were investigated with and without chemical absorption. The results show that the bubble formation goes through typical three stages: expansion, squeezing and pinch off for both two processes. Chemical absorption reduces gas dynamic pressure, which increases the time proportion of expansion stage in the overall bubble formation process and total bubble formation time. The enhanced leakage flow in the expansion stage with chemical absorption results in a decrease in the liquid squeezing force during neck shrinking, nevertheless, the neck shrinking velocity is almost unaffected. Addi-

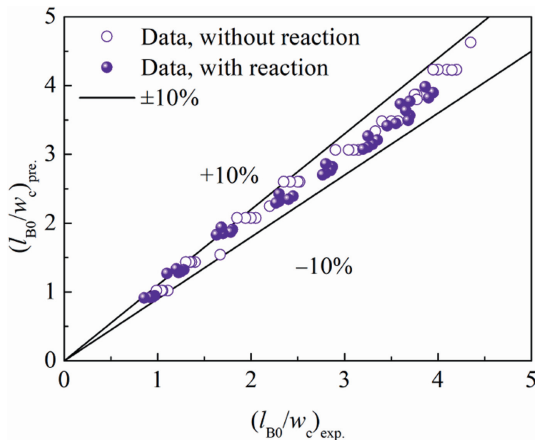


Fig. 13. Prediction performance of the model for initial bubble length.

tionally, the gaseous thread length satisfies a power-law scale over time with the same exponent but smaller pre-exponential factor than that in the non-absorption process. The correlations of bubble neck width (for stage transition) and initial length with Hatta number reveal that the increase of reaction rate or/and generation time (for small gas and liquid velocities) can enhance the effects of chemical absorption on bubble formation dynamic and initial length. The findings in this study provide deep insights into the effect of chemical absorption on bubble formation in microchannels, which would be helpful for regulating and designing microfluidic devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

A	the cross section of emerging bubble, m^2
C_{MEA}	MEA concentration, $\text{mol}\cdot\text{m}^{-3}$
D	diffusion coefficient of CO_2 in the liquid bulk, $\text{m}^2\cdot\text{s}^{-1}$
D_h	hydraulic diameter, m
f	frequency of bubble formation, s^{-1}
h	height, m
k_p	physical mass transfer coefficient, $\text{m}\cdot\text{s}^{-1}$
k_1	pseudo-first-order reaction rate constant, s^{-1}
l	length, m
p_G	inlet pressure of gas phase, Pa
Δp_s	squeezing pressure, Pa
Δp_t	shear stress, Pa
Q	flow rate, $\text{m}^3\cdot\text{s}^{-1}$
T	bubble formation period, s
t	time, s
U	superficial velocity, $\text{m}\cdot\text{s}^{-1}$
w	width, m
w_m	minimum neck width, m
X_l	proportion of bubble extension length in each stage
X_t	proportion of duration in each stage, dimensionless
ε	width of the gap between bubble head and channel wall, m
θ	angle, ($^\circ$)
μ	dynamic viscosity, $\text{Pa}\cdot\text{s}$
ρ	density, $\text{kg}\cdot\text{m}^{-3}$
σ	surface tension, $\text{N}\cdot\text{m}^{-1}$
φ	the ratio of gas rate to liquid rate

Subscripts

BO	initial bubble
c	channel
G	gas phase
h	bubble head
L	liquid phase
f	formation
e	expansion
s	squeezing
p	pinch off

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