# LOCAL STRUCTURE OF A REACTIVE FLOW FIELD ON MISCIBLE VISCOUS FINGERING WITH CHEMICAL REACTION

*Takashi Ogawa, Yuichiro Nagatsu, Yoshihito Kato, Yutaka Tada,*
*Nagoya Institute of Technology, Nagoya, Aichi, Japan*

## Introduction

When a more-viscous fluid is displaced by a less-viscous one in porous media or in Hele-Shaw cells, the interface or boundary between the two fluids becomes unstable and forms a finger-like pattern. This phenomenon is referred to as viscous fingering. Since the pioneering works on the fluid mechanics of viscous fingering was published in the 1950s (Hill 1952; Saffman and Taylor 1958), many experimental and theoretical studies have been performed and review articles have been published (Homsy 1987; McCloud & Maher 1995; Tanveer 2000). Viscous fingering is categorized into two classes: fingers formed in immiscible systems and those formed in miscible systems. Surface tension in immiscible systems plays an important role in the fingering mechanism, while in the miscible systems convective and diffusive effects are important. In both systems, the nonlinear propagation of viscous fingering is governed by different mechanisms of shielding, spreading, and splitting. Shielding is the phenomenon in which a finger slightly ahead of its neighbor fingers quickly outruns them and shields them from further growth. Spreading and splitting occur when a finger spreads until it reaches a certain width and then becomes unstable and splits (Homsy 1987).

Viscous fingering accompanied by chemical reactions is observed in processes such as petroleum recovery (Hornof and Baig 1995), chromatographic and adsorptive separation (Broyles et al. 1998), polymerization (Pojman et al. 1998), and the flow of gastric mucus (Bhaskar et al. 1992), and has been confirmed to play an important role in these processes. Therefore, the coupling of hydrodynamics and chemistry in viscous fingering with chemical reactions has recently been discussed. Jahoda and Hornof (2000) conducted a numerical investigation of a concentration field in an immiscible viscous finger involving chemical reactions. Fernandez and Homsy (2003) performed experiments on immiscible viscous fingering with a chemical reaction acting to reduce the interfacial tension in a Hele-Shaw cell, and found that the reaction makes the fingers wider. They characterized the effects of the reaction on the reactive fingering pattern using the Damköhler number, *Da*, which is defined as the ratio between a characteristic time of fluid motion and that of a chemical reaction. DeWit and Homsy (1999a, b) performed a numerical simulation on reactive miscible viscous fingering in porous media by assuming that the fluid's viscosity is a function of a chemical species concentration and by using specific chemical kinetics. They found a new mechanism of viscous fingering that they denoted as the "droplet" mechanism, which involves the formation of isolated regions of either less- or more-viscous fluids in connected domains of the other.

Nagatsu (one of the authors) and Ueda (2001) performed experiments on reactive miscible viscous fingering in a Hele-Shaw cell. In the experiments, a 99wt% glycerin solution that included potassium thiocyanate (KSCN) and iron nitrate ($Fe(NO_3)_3$) solutions were used as the more- and less-viscous liquids, respectively. The instantaneous chemical reaction expressed in Eq. (1) takes place, resulting in a blood red-colored product.

$$Fe^{3+} + 2SCN^{-} \rightarrow [Fe(SCN)_2]^{+} \text{ (blood red)} \qquad (1)$$

This reaction has no influence on the hydrodynamics of the fingering. It was shown that the product distribution is highly dependent on the ratio between the reactant concentrations initially included in the more- and less-viscous liquids normalized by a stoichiometric ratio of the chemical reaction, $\varphi_v$, which is expressed as Eq. (2),

$$\varphi_v = \frac{ac_{l0}}{c_{m0}}. \qquad (2)$$

In this equation, $c_{m0}$ and $c_{l0}$ are the molar reactant concentrations initially included in the more- and less-viscous liquids, respectively, and $a$ is the molar stoichiometric ratio of the chemical reaction, which is $a$=2 in this study, as shown in Eq. (1). For $\varphi_v$<<1, the product is present in large quantities in a relatively broad area within the interior of the fingers, while for $\varphi_v$>>1, it concentrates around the tips of the fingers. For $\varphi_v$=1, the product is equally distributed among the interiors and tips of the fingers. Nagatsu & Ueda (2001) also conducted a theoretical analysis on a concentration field of chemical species in two liquids with different viscosities using a simplified one-dimensional diffusion-reaction model. The analytical results revealed that the reaction plane is located in the less-viscous liquid far from the interface between the two liquids for $\varphi_v$<<1, but it is in the more-viscous liquid close to the interface for $\varphi_v$>>1. Therefore, it was concluded that the product distribution is caused by differences in the location of the reaction plane due to $\varphi_v$. Also, Nagatsu and Ueda (2003) showed that the dependence of the product distribution on $\varphi_v$ is diminished with an increase in the bulk finger growth velocity, i.e. the injection rate of the less-viscous liquid. In these cases, the product is present in a relatively broad area form the insides to tips of the fingers regardless of $\varphi_v$.

In the Nagatsu & Ueda (2001, 2003) experiments, one can not exactly recognize where and when the reaction takes place since the region where the product exists does not necessarily coincide with the region where the reaction takes place. This is because the region where the product exists at a given time may indicate that a previously produced product remains even though the reaction does not take place at that time. Examples are shown in Figures 1 and 2. Figure 1 shows time evolutions of the reactive miscible viscous fingering pattern when $\varphi_v$=0.1 ($c_{m0}$=0.3 mol/l and $c_{l0}$=0.015 mol/l) and $\varphi_v$=10 ($c_{m0}$=0.03 mol/l and $c_{l0}$=0.15 mol/l) under similar cell gap widths, $b$, and volumetric injection rates for the less-viscous liquid, $q$, employed in Nagatsu & Ueda (2001), namely $b$=0.3 mm and $q$=1.8 mm$^3$/s, respectively. Figure 2 shows those when $\varphi_v$=0.1 ($c_{m0}$=0.3 mol/l and $c_{l0}$=0.015 mol/l) and $\varphi_v$=10 ($c_{m0}$=0.03 mol/l and $c_{l0}$=0.15 mol/l) under similar $b$ and $q$ employed in Nagatsu & Ueda (2003), namely $b$=0.3 mm and $q$=10.8 mm$^3$/s, respectively. Figures 1 and 2 are the cases in which the product distribution significantly depends on $\varphi_v$ and in which the dependence of the product distribution on $\varphi_v$ is scarcely observed, respectively. Since variations in the distribution and the depth of the blood red color can not be observed, although sizes of the fingering patterns are different especially for $t$>120 s in Figure 1 and $t$>20 s in Figure 2, the reaction region cannot be identified. Since variations in the distribution and the depth of the blood red color can not be observed, although sizes of the fingering patterns are different as shown in Figure 1, the reaction region during the $t$=120 ~ 150 s cannot be identified.

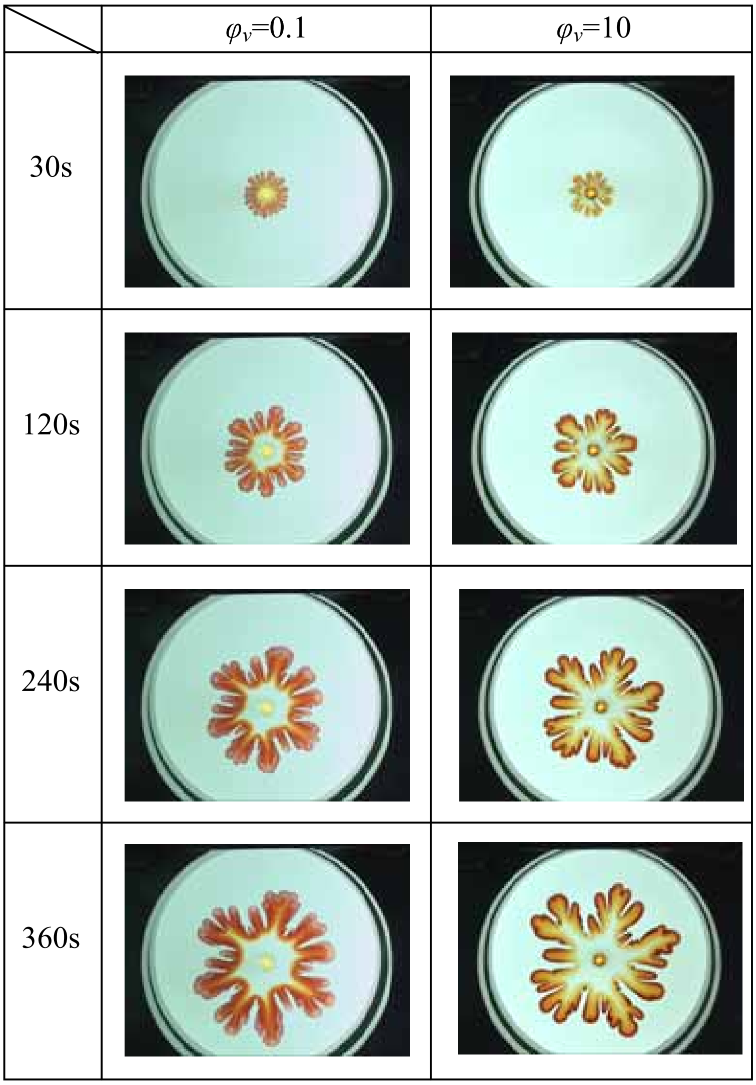



Fig.1 Time evolution of reactive viscous fingering pattern when $\varphi_v$=0.1 ($c_{l0}$=0.015 mol/l and $c_{m0}$=0.3 mol/l) and 10 ($c_{l0}$=0.15 mol/l and $c_{m0}$=0.03 mol/l) under the condition of $b$=0.3 mm and $q$=1.8 mm$^3$/s.

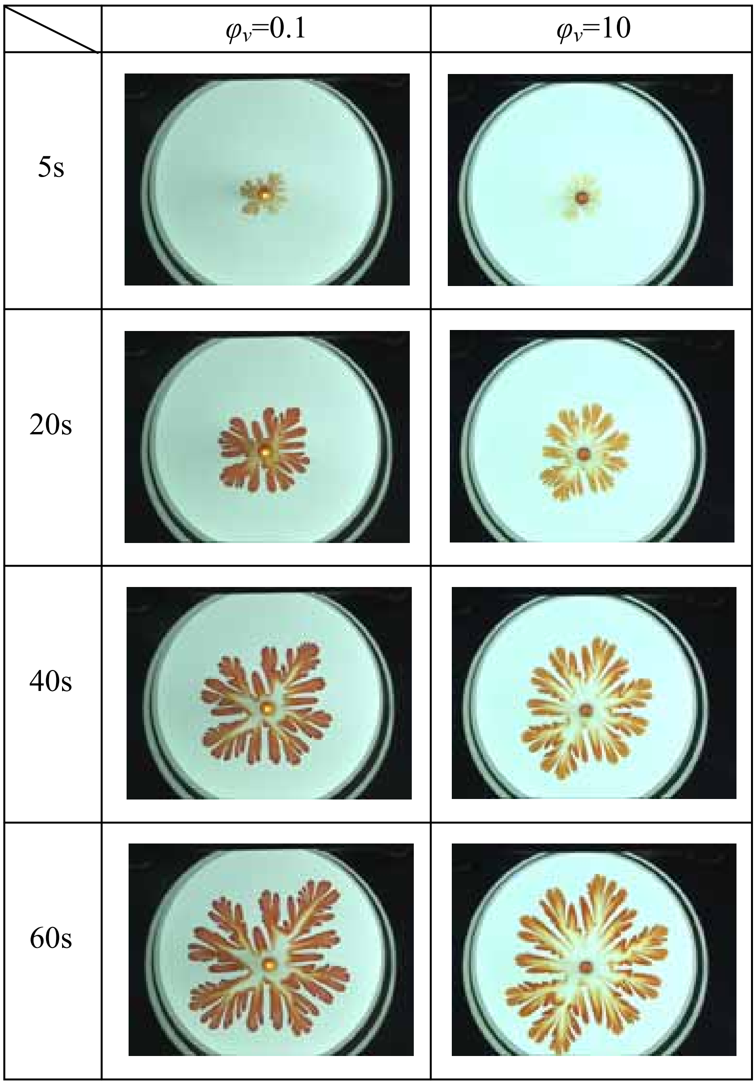



Fig.2 Time evolution of reactive viscous fingering pattern when $\varphi_v$=0.1 ($c_{l0}$=0.015 mol/l and $c_{m0}$=0.3 mol/l) and 10 ($c_{l0}$=0.15 mol/l and $c_{m0}$=0.03 mol/l) under the condition of $b$=0.3 mm and $q$=10.8 mm$^3$/s.

In Nagatsu et al. (2006), the authors have been developed a novel experimental method, which involves switching the less-viscous liquid that is injected, that allows for the identification of where and when the reaction place. The novel method is applied to the previously mentioned system, namely reactive miscible viscous fingering that forms when 99wt% glycerin solution including KSCN as a more-viscous liquid is displaced by the $Fe(NO_3)_3$ less-viscous liquid solution in a Hele-Shaw cell. Using this method, we have identified the reaction region under the reactant concentration condition of $\varphi_v$=1 at a given time. It was found that under these conditions the entire region in which the product is present in the advancing fingers in the case where the reactive less-viscous liquid is continuously injected becomes the reaction region. In contrast, the reaction does not take place in the shielded fingers although the product is present in the case where the reactive less-viscous liquid is continuously injected. This suggests that the reaction region does not necessarily coincide with the region in which the product exists in the case where the reactive less-viscous liquid is continuously injected. In the present study, we applied the method to the experimental condition described in Figures 1 and 2 to clarify how the locations of the reaction region are varied by $\varphi_v$, $q$ and $t$.

## Experiment

The experimental apparatus used was the same as that reported in Nagatsu et al. (2006). The experimental method is essentially identical to that described in Nagatsu et al. (2006). For reactive experiments, the more-viscous liquid is a colorless 99wt% glycerin solution including KSCN at a concentration of $c_{m0}$. Two solutions are used as the less-viscous liquid. One is a blue 0.1wt% indigo carmine (IC) solution that does not react with the more-viscous liquid, and the other is a $Fe(NO_3)_3$ solution at a concentration of $c_{l0}$. The second solution is light yellow but is essentially colorless in the Hele-Shaw cell due to its significantly thin gap and it reacts with the more-viscous liquid. The chemical reaction taking place is expressed as Eq. (1) and the blood red product is again produced. First, the non-reactive blue IC solution is injected until $t=t_{sw}$, and then the injected liquid is switched to the reactive $Fe(NO_3)_3$ solution. The distribution and depth of the bloody red color is noted. If the blood red color is present at $t=t_1+\Delta t$ in a region where the color does not exist at $t=t_1$, this indicates that the chemical reaction takes place in the region during the $\Delta t$ period. Also, if the blood red color is remarkably deeper at $t=t_1+\Delta t$ than at $t=t_1$ in a region, even if the blood red color is present during the $\Delta t$ period, this indicates that the chemical reaction takes place in the region during the $\Delta t$ period. If the product is not still present at $t=t_1+\Delta t$ in a region where the product does not exist at $t=t_1$, this indicates that the chemical reaction does not take place in the region during the $\Delta t$ period.

For the non-reactive experiments, a 99wt% glycerin solution is used as the more-viscous liquid. Two solutions dyed with different colors are used for the less-viscous liquid: bloody red 0.025 mol/l $[Fe(SCN)]^+$ solution and blue 0.1wt% IC solution. The blue IC solution is first injected until $t=t_{sw}$, then the blood red $[Fe(SCN)]^+$ solution is injected. Attention is focused on the flow of the secondly injected less-viscous liquid, determining to what extent the less-viscous liquid injected after $t_{sw}$ reaches in the fingering during the period, $\Delta t$. If the blood red color is present at $t=t_1+\Delta t$ in a region where the blood red color does not exist at $t=t_1$, this indicates that a part of the blood red solution injected during $t>t_{sw}$ reaches the region during the $\Delta t$ period. If the blood red color is not still present at $t=t_1+\Delta t$ in a region where the blood red color does not exist at $t=t_1$, the blood red solution injected during $t>t_{sw}$ does not reach the region during the $\Delta t$ period.

The reactive and non-reactive experiments revealed where the less-viscous liquid injected after $t=t_{sw}$ reaches and reacts with the more-viscous liquid during the $\Delta t$ period. $t_{sw}$ was varied in these experiments. The reaction region during the $\Delta t$ period for the continuously injected reactive less-viscous liquid appears to be the superimposition of the reaction regions identified in various experiments by varying $t_{sw}$.

## Results and Discussion

### *The case of small q*

Initially, the results obtained by applying the novel method to the experimental condition shown in Figure 1 are described. First, we set $t_1$=120 s and $\Delta t$=30 s, respectively. Figure 3 shows the fingering pattern without and with the reaction when $t_{sw}$=90 s and at $t$=120 s and 150 s, respectively. At $t$=120 s in the non-reactive experiments, the blood red color has spread to the troughs of the fingers (a), and at $t$=150 s the blood red color has reached the insides of the fingers near the troughs (b). In the reactive experiments, without regard to the $\varphi_v$, blood red color is barely observed at $t$=120 s (c)(e), while at $t$=150 s the blood red color can be seen in the troughs and the insides near the troughs (d)(f). These results suggest that a part of the less-viscous liquid injected after $t$=90 s reaches a region from the troughs to the insides near the troughs and reacts with the more-viscous liquid in this region during the $t$=120 ~ 150 s time period regardless of $\varphi_v$. In this figure, the blue color of the less-viscous liquid initially injected around the tips of the fingers abruptly becomes light. This was also observed in the previous experiments (Nagatsu & Ueda 2001) and is likely due to the thickness of the layer of the less-viscous liquid in the cell gap's direction becoming abruptly thin around the tips of the fingers. This structure is considered to be analogous to the "spike" observed in miscible displacements in capillary tubes (Petitjeans & Maxworthy 1996; Lajeunesse et al. 1999; Kuang et al. 2004).

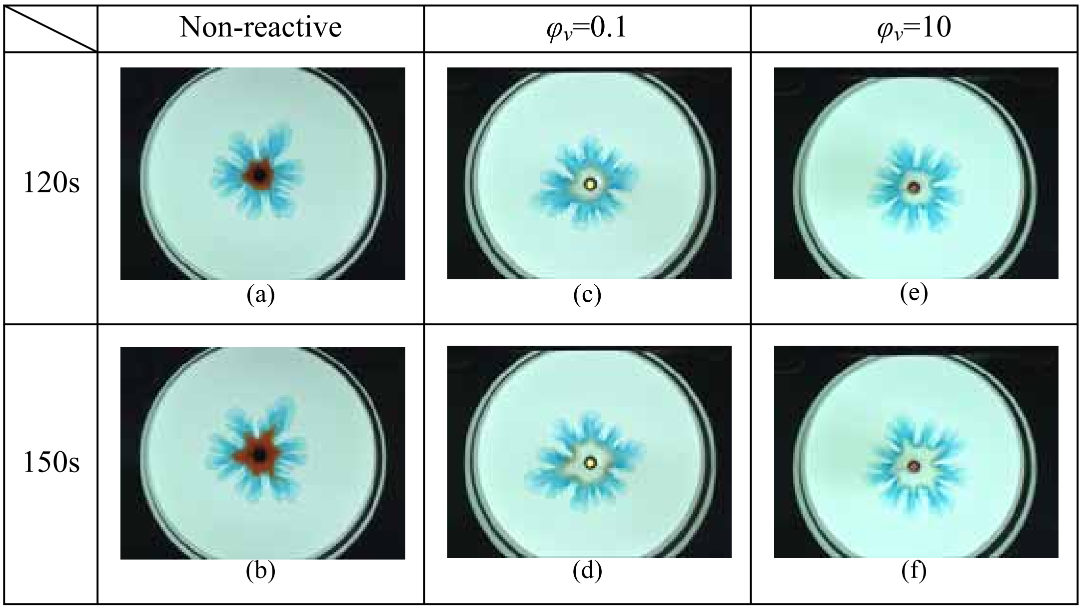



Fig.3 Viscous fingering pattern without and with the reaction when $t_{sw}$=90 s. under the condition of $b$=0.3 mm and $q$=1.8 mm$^3$/s.

Figure 4 shows the fingering pattern without and with the reaction when $t_{sw}$=60 s at $t$=120 s and 150 s, respectively. In the non-reactive experiments, the blood red color at $t$=120 s has spread to the neighborhood of the middle of the insides of the fingers (a), and at $t$=150 s the blood red color has reached the neighborhood of the front of the insides of the fingers (b). In the reactive experiments, without regard to the $\varphi_v$, the blood red color is observed in the region from the troughs to the neighborhood of middle of the insides (c)(e) at $t$=120 s. At $t$=150 s, the area exhibiting the blood red color has extended to the neighborhood of the front of the insides (d)(f). From these experimental results, it is determined that a part of the less-viscous liquid injected after $t$=60 s reaches the middle to front of the insides of the fingers, and the reaction takes place along the insides of the fingers during the $t$=120 ~ 150 s period at a minimum regardless of $\varphi_v$.

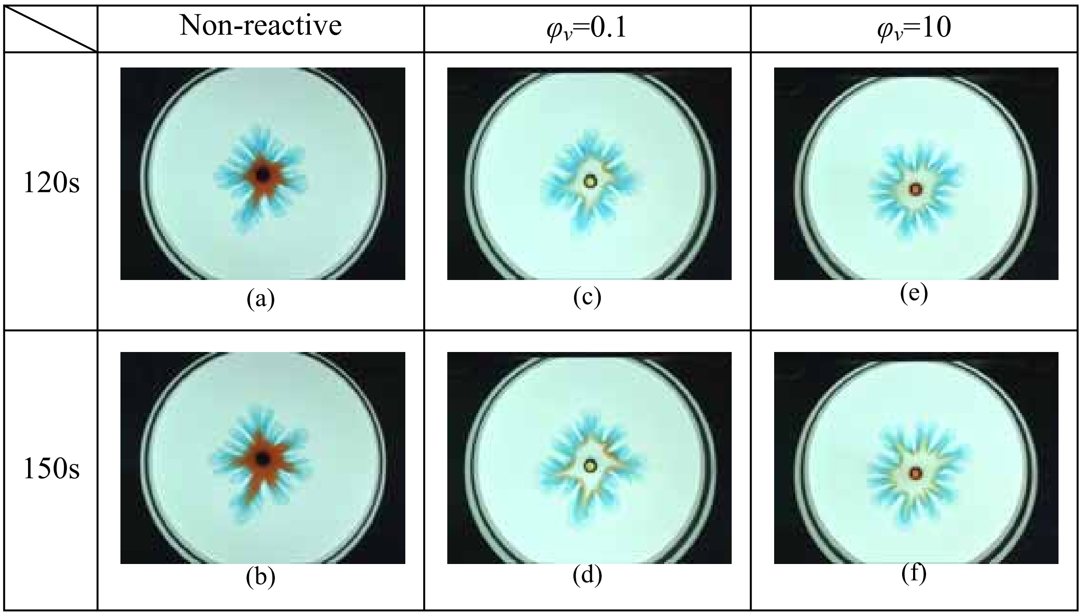



Fig.4 Viscous fingering pattern without and with the reaction when $t_{sw}$=60 s. under the condition of $b$=0.3 mm and $q$=1.8 mm$^3$/s.

Figure 5 shows the fingering pattern without and with the reaction when $t_{sw}$=30 s at $t$=120 s and 150 s, respectively. In the non-reactive experiments, the blood red color at $t$=120 s has spread to the base of the region in which the blue color of the first less-viscous liquid is abruptly light (a), and at $t$=150 s the blood red color has reached the tips of the fingers (b). This indicates that the flow of the less-viscous liquid around the fingertips is not plug flow, but a flow having an approaching velocity toward the fingertips until at least $t$=150 s. In the reactive cases, for $\varphi_v$=0.1, the blood red color is observed in the region from the troughs to the inside of the fingers at $t$=120 s (c). At $t$=150 s, the area exhibiting the blood red color has extended to the base of the light blue color region (d). These non-reactive and reactive experiments results indicate that the reaction takes place at the insides of the fingers and that although a part of the less-viscous liquid injected after $t$=30 s reaches the tips of the fingers, the reaction does not take place in the light blue region during $t$=120 ~ 150 s period. For $\varphi_v$=10, the blood red color is observed from the troughs to the base of the light blue color region around the tips of the fingers at $t$=120 s (e). At $t$=150 s the area exhibiting the blood red color has extended to the tips of the fingers. Combined with non-reactive experiments, it is found that the reaction takes place at the insides of the fingers and the light blue color region. The shielded fingers remain blue during the $t$=120 ~ 150 s period in both the non-reactive and reactive experiments. This suggests that the less-viscous liquid injected after $t$=30 s does not penetrate into the shielding fingers, indicating that the reactant included in the less-viscous liquid is not introduced into the shielding fingers. Thus, the reaction does not take place there during the $t$=120 ~ 150 s time period.

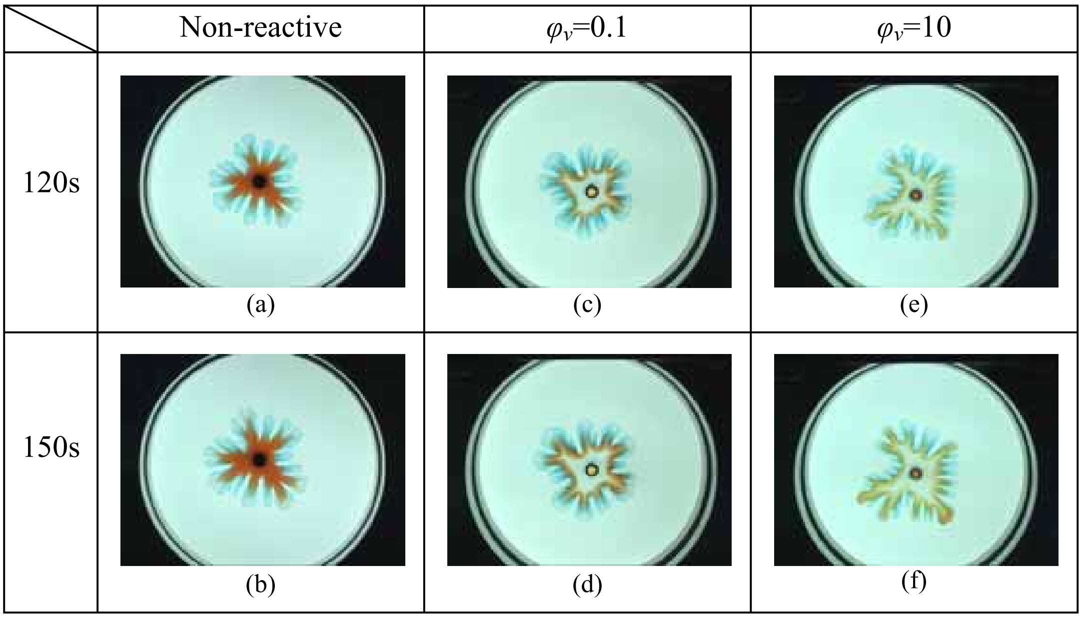



Fig.5 Viscous fingering pattern without and with the reaction when $t_{sw}$=30 s. under the condition of $b$=0.3 mm and $q$=1.8 mm$^3$/s.

The reaction region during $t$=120 ~ 150 s period when the reactive less-viscous liquid is continuously injected can be regarded as superimposition of the reaction region identified in Figures 3 ~ 5. Therefore, for $\varphi_v$=0.1, the reaction appears to take place in the troughs and insides of the advancing fingers but not to take place in the light blue color region around the tips of the advancing fingers. For $\varphi_v$=10, the reactions appears to take place in the troughs, the insides and the light blue color region of the advancing fingers. For both $\varphi_v$ conditions, the reaction does not take place in the shielded fingers during $t$=120 ~ 150 s period. The above-identified reaction region is shown in Figure 6 by using the reactive viscous fingering pattern at $t$=150 s. In Figure 6, the blood red color region, except for the region identified by the black circles, indicates the reaction region, while the black circles represent the region in which the reaction does not take place even though the product exists during the $t$=120 ~ 150 s period.

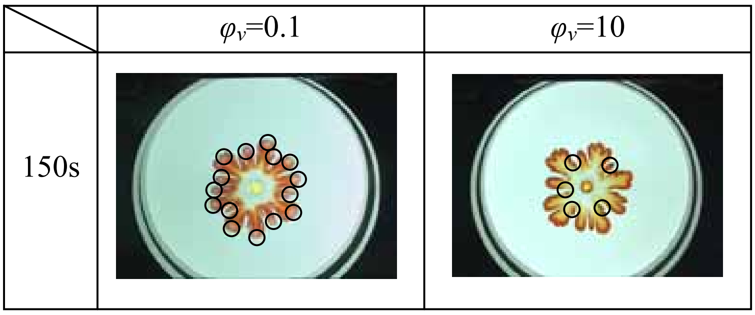



Fig.6 Reaction region in reactive miscible viscous fingering at $t$=150 s when $\varphi_v$=0.1 (a) and when $\varphi_v$=10 under the condition of $b$=0.3 mm and $q$=1.8 mm$^3$/s. Blood red color region except the region specified by black circles indicates the reaction region, while the black circles represent the region in which the reaction does not take place although the product exists.

Next, we set $t_1$=300 s and $\Delta t$=60 s, respectively. Figure 7 shows the fingering pattern without and with the reaction when $t_{sw}$=240 s at $t$=300 s and 360 s, respectively. At $t$=300 s in the non-reactive experiments, the blood red color has spread to the troughs of the fingers (a), and at $t$=360 s the blood red color has reached the insides of the fingers near the troughs (b). In the reactive experiments, without regard to the $\varphi_v$, blood red color is barely observed at $t$=300 s (c)(e), while at $t$=360 s the blood red color can be seen in the troughs and the insides near the troughs (d)(f). These results suggest that a part of the less-viscous liquid injected after $t$=240 s reaches a region from the troughs to the insides near the troughs and reacts with the more-viscous liquid in this region during the $t$=300 ~ 360 s time period regardless of $\varphi_v$.

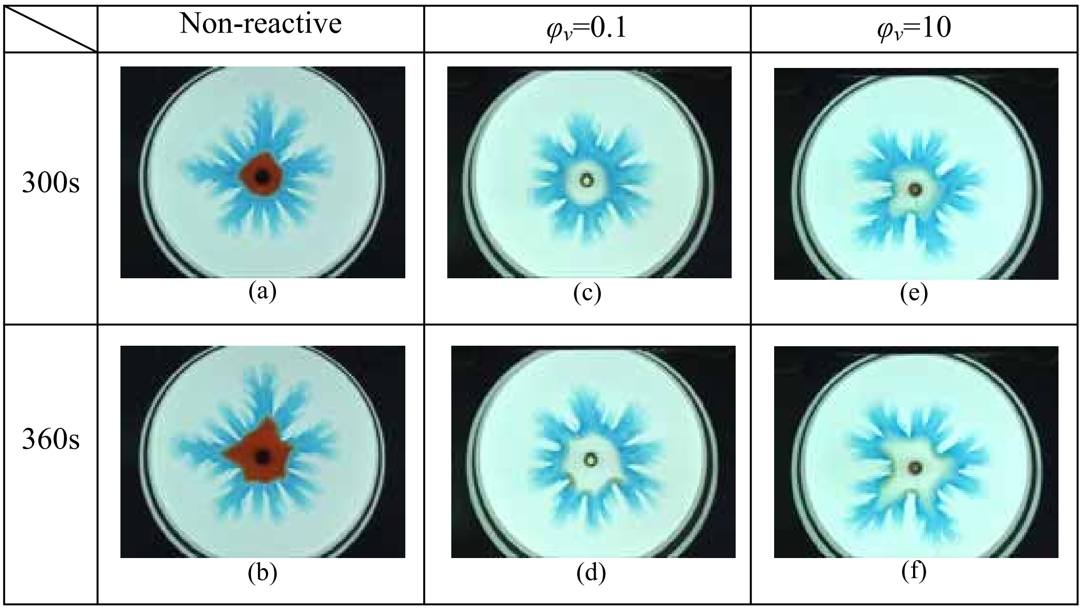



Fig.7 Viscous fingering pattern without and with the reaction when $t_{sw}$=240 s. under the condition of $b$=0.3 mm and $q$=1.8 mm$^3$/s.

Figure 8 shows the fingering pattern without and with the reaction when $t_{sw}$=180 s at $t$=300 s and 360 s, respectively. In the non-reactive experiments, the blood red color at $t$=300 s has spread to the neighborhood of the middle of the insides of the fingers (a), and at $t$=360 s the blood red color has reached the neighborhood of the front of the insides of the fingers (b). In the reactive experiments, without regard to the $\varphi_v$, the blood red color is observed in the region from the troughs to the neighborhood of middle of the insides (c)(e) at $t$=300 s. At $t$=360 s, the area exhibiting the blood red color has extended to the neighborhood of the front of the insides (d)(f). From these experimental results, it is determined that a part of the less-viscous liquid injected after $t$=180 s reaches the middle to front of the insides of the fingers, and the reaction takes place along the insides of the fingers during the $t$=300 ~ 360 s period at a minimum regardless of $\varphi_v$.

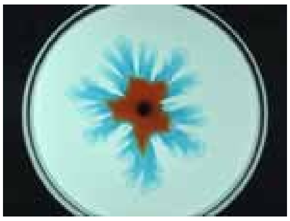
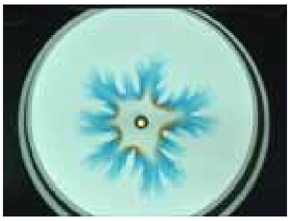
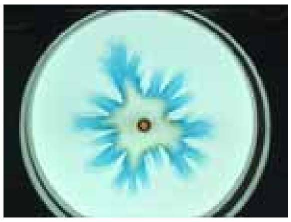
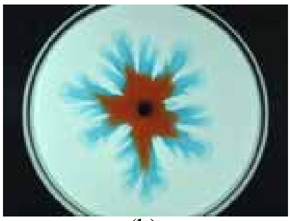
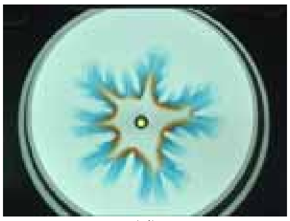
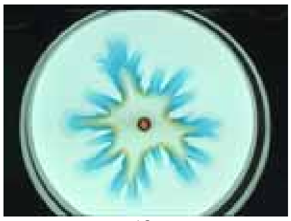
| | Non-reactive | $\varphi_v$=0.1 | $\varphi_v$=10 |
|---|---|---|---|
| 300s |  (a) |  (c) |  (e) |
| 360s |  (b) |  (d) |  (f) |

Fig. 8 Viscous fingering pattern without and with the reaction when $t_{sw}$=180 s. under the condition of $b$=0.3 mm and $q$=1.8 mm$^3$/s.

Figure 9 shows the fingering pattern without and with the reaction when $t_{sw}$=90 s at $t$=300 s and 360 s, respectively. In the non-reactive experiments, the blood red color at $t$=300 s has spread to the base of the region in which the blue color of the first less-viscous liquid is abruptly light (a), and at $t$=360 s the blood red color has reached the tips of the fingers (b). This indicates that the flow of the less-viscous liquid around the fingertips is not plug flow, but a flow having an approaching velocity toward the fingertips until at least $t$=360 s. In the reactive cases, for $\varphi_v$=0.1, the blood red color is observed in the region from the troughs to the inside of the fingers at $t$=300 s (c). At $t$=360 s, the area exhibiting the blood red color has extended to the base of the light blue color region (d). These non-reactive and reactive experiments results indicate that the reaction takes place at the insides of the fingers and that although a part of the less-viscous liquid injected after $t$=90 s reaches the tips of the fingers, the reaction does not take place in the light blue region during $t$=300 ~ 360 s period. For $\varphi_v$=10, the blood red color is observed from the troughs to the base of the light blue color region around the tips of the fingers at $t$=300 s (e). At $t$=360 s the area exhibiting the blood red color has extended to the tips of the fingers. Combined with non-reactive experiments, it is found that the reaction takes place at the insides of the fingers and the light blue color region. The shielded fingers remain blue during the $t$=300 ~ 360 s period in both the non-reactive and reactive experiments. This suggests that the less-viscous liquid injected after $t$=90 s does not penetrate into the shielding fingers, indicating that the reactant included in the less-viscous liquid is not introduced into the shielding fingers. Thus, the reaction does not take place there during the $t$=300 ~ 360 s time period.

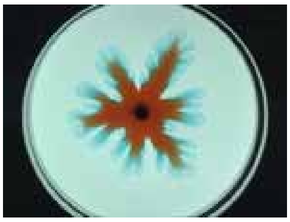
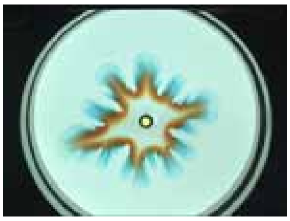
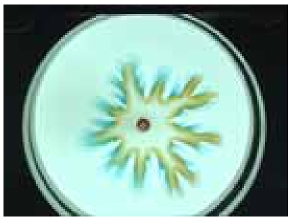
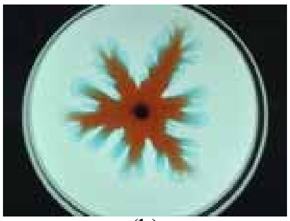
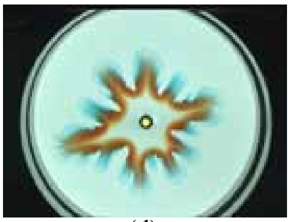
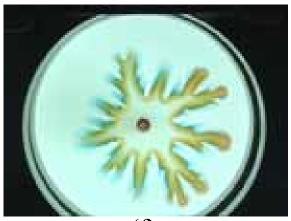
| | Non-reactive | $\varphi_v$=0.1 | $\varphi_v$=10 |
|---|---|---|---|
| 300s |  (a) |  (c) |  (e) |
| 360s |  (b) |  (d) |  (f) |

Fig. 9 Viscous fingering pattern without and with the reaction when $t_{sw}$=90 s. under the condition of $b$=0.3 mm and $q$=1.8 mm$^3$/s.

The reaction region during $t$=300 ~ 360 s period when the reactive less-viscous liquid is continuously injected can be regarded as superimposition of the reaction region identified in Figures 7 ~ 9. Therefore, for $\varphi_v$=0.1, the reaction appears to take place in the troughs and insides of the advancing fingers but not to take place in the light blue color region around the tips of the advancing fingers. For $\varphi_v$=10, the reactions appears to take place in the troughs, the insides and the light blue color region of the advancing fingers. For both $\varphi_v$ conditions, the reaction does not take place in the shielded fingers during $t$=300 ~ 360 s period. The above-identified reaction region is shown in Figure 10 by using the reactive viscous fingering pattern at $t$=360 s. In Figure 10, the blood red color region, except for the region identified by the black circles, indicates the reaction region, while the black circles represent the region in which the reaction does not take place even though the product exists during the $t$=300 ~ 360 s period.

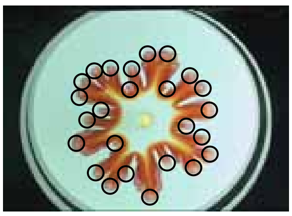
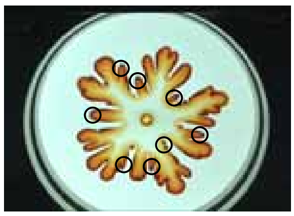
| | $\varphi_v$=0.1 | $\varphi_v$=10 |
|---|---|---|
| 360s |  |  |

Fig.10 Reaction region in reactive miscible viscous fingering at $t$=360 s when $\varphi_v$=0.1 (a) and when $\varphi_v$=10 under the condition of $b$=0.3 mm and $q$=1.8 mm$^3$/s. Blood red color region except the region specified by black circles indicates the reaction region, while the black circles represent the region in which the reaction does not take place although the product exists.

The result obtained in Figure 6 is essentially identical to those obtained in Figure 10. This indicates that the characteristics of reactive flow fields remain unchanged during $t$=120 ~ 360 s. As shown in Figure 1, at $t$=30 s the blood red color is observed around the tips of all fingers regardless of $\varphi_v$. Therefore, in the advanced fingers, for $\varphi_v$=0.1, the location of the reaction region is changed. In other words, around the fingertips at the initial stage the reaction takes place, while the reaction does not takes place as time proceeds. For $\varphi_v$=10, the reaction takes place regardless of $t$ in the present experimental condition.

***The case of large q***

From here the results obtained by applying the novel method to the experimental condition shown in Figure 2 are described. Figure 11 shows the fingering pattern without and with the reaction when $t_{sw}$=35 s at $t$=50 s and 60 s, respectively. At $t$=50 s in the non-reactive experiments, the blood red color has spread to the troughs of the fingers (a), and at $t$=60 s the blood red color has reached the insides of the fingers near the troughs (b). In the reactive experiments, without regard to the $\varphi_v$, blood red color is barely observed at $t$=50 s (c)(e), while at $t$=60 s the blood red color can be seen in the troughs and the insides near the troughs (d)(f). These results suggest that a part of the less-viscous liquid injected after $t$=35 s reaches a region from the troughs to the insides near the troughs and reacts with the more-viscous liquid in this region during the $t$=50 ~ 60 s time period regardless of $\varphi_v$.

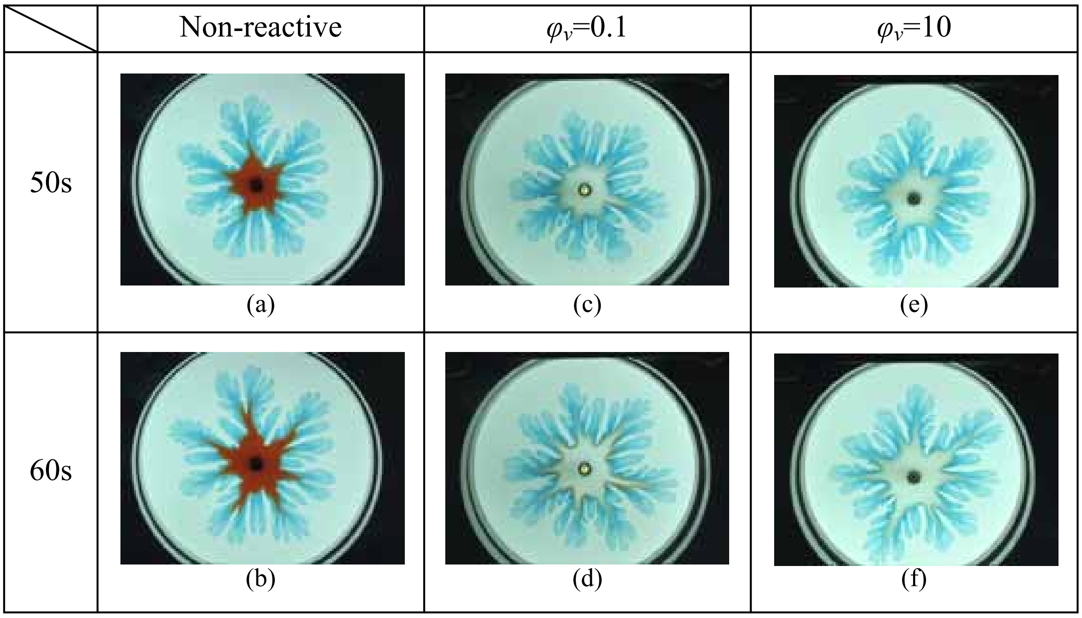



Fig. 11 Viscous fingering pattern without and with the reaction when $t_{sw}$=35 s. under the condition of $b$=0.3 mm and $q$=10.8 mm$^3$/s.

Figure 12 shows the fingering pattern without and with the reaction when $t_{sw}$=30 s at $t$=50 s and 60 s, respectively. In the non-reactive experiments, the blood red color at $t$=50 s has spread to the neighborhood of the middle of the insides of the fingers (a), and at $t$=60 s the blood red color has reached the neighborhood of the front of the insides of the fingers (b). In the reactive experiments, without regard to $\varphi_v$, the blood red color is observed in the region from the troughs to the neighborhood of middle of the insides (c)(e) at $t$=50 s. At $t$=60 s, without regard to $\varphi_v$, the area exhibiting the blood red color has extended to the neighborhood of the front of the insides (d)(f). From these experimental results, it is determined that a part of the less-viscous liquid injected after $t$=30 s reaches the middle to front of the insides of the fingers, and the reaction takes place along the insides of the fingers during the $t$=50 ~ 60 s period at a minimum regardless of $\varphi_v$.

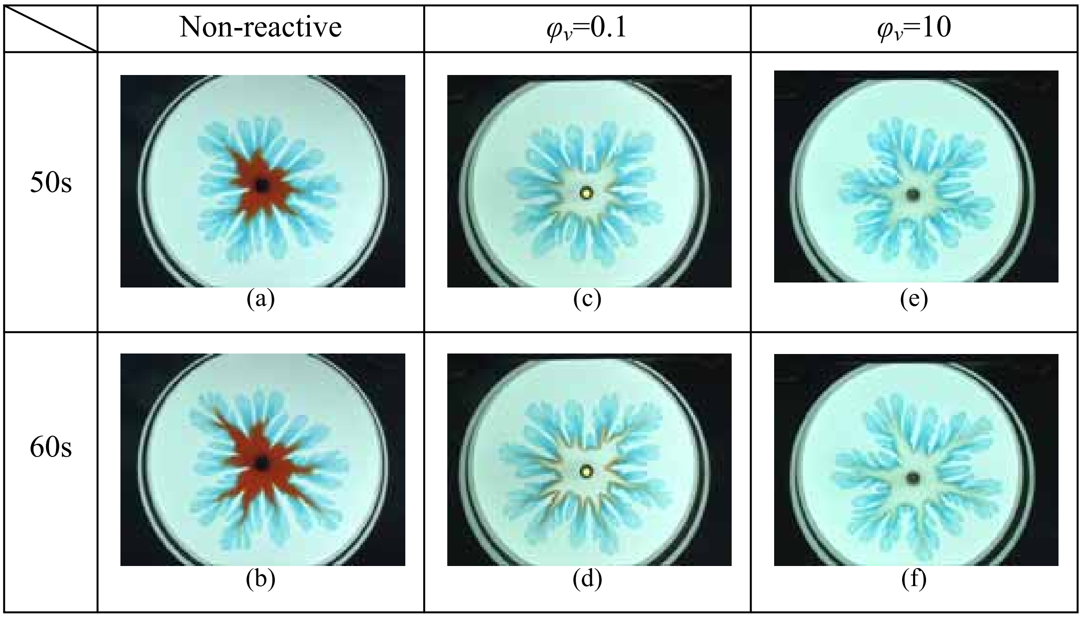



Fig.12 Viscous fingering pattern without and with the reaction when $t_{sw}$=30 s. under the condition of $b$=0.3 mm and $q$=10.8 mm$^3$/s.

Figure 13 shows the fingering pattern without and with the reaction when $t_{sw}$=20 s at $t$=50 s and 60 s, respectively. In the non-reactive experiments, the blood red color at $t$=50 s has spread in the vicinity of the fingertips (a), and at $t$=60 s the blood red color has reached the tips of the fingers (b). This indicates that the flow of the less-viscous liquid around the fingertips is not plug flow, but a flow having an approaching velocity toward the fingertips until at least $t$=60 s. In the reactive experiments, without regard to $\varphi_v$, the blood red color is observed in the region from the troughs to the vicinity of the fingertips at $t$=50 s (c)(e). At $t$=60 s without regard to $\varphi_v$, the area exhibiting the blood red color has extended to the fingertips (d)(f). These non-reactive and reactive experimental results indicate that a part of the less-viscous liquid injected after $t$=20 s reaches the tips of the fingers and the reaction takes place around the tips of the fingers during the $t$=50 ~ 60 s period at a minimum. The shielded fingers remain blue during the $t$=50 ~ 60 s period in both the non-reactive and reactive experiments. This suggests that the less-viscous liquid injected after $t$=20 s does not penetrate into the shielding fingers, indicating that the reactant included in the less-viscous liquid is not introduced into the shielding fingers. Thus, the reaction does not take place there during the $t$=50 ~ 60 s time period.

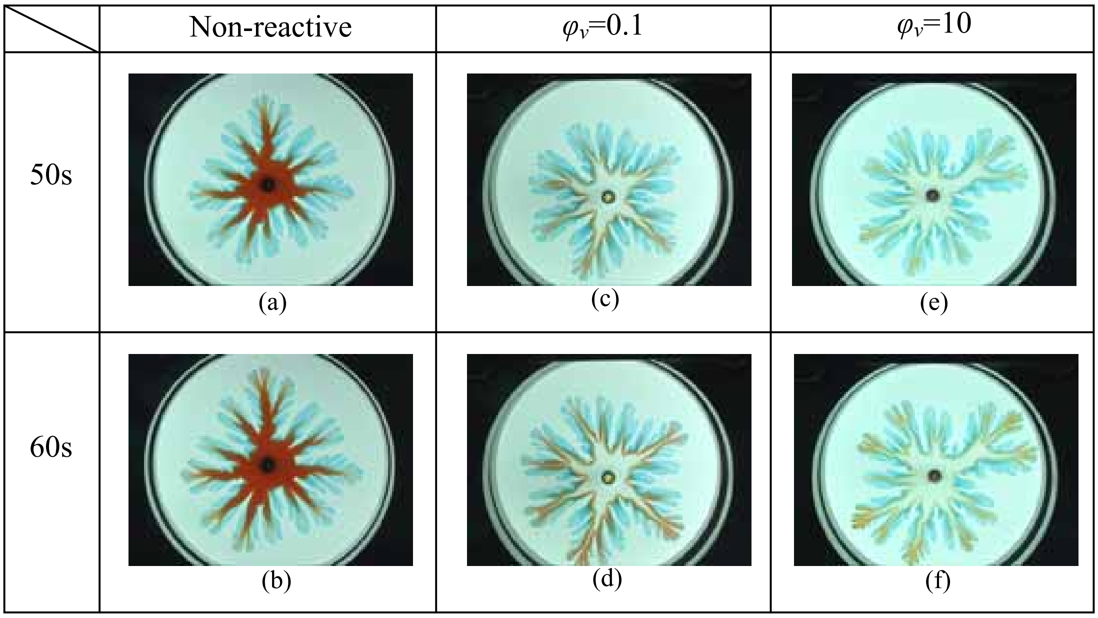



Fig.13 Viscous fingering pattern without and with the reaction when $t_{sw}$=20 s. under the condition of $b$=0.3 mm and $q$=10.8 mm$^3$/s.

The results obtained in Figures 11 ~ 13 show that in this condition the reaction takes place in the troughs, the insides and the tips of the advancing fingers regardless of $\varphi_v$. The above-identified reaction region is shown in Figure 14 by using the reactive viscous fingering pattern at $t$=60 s. In Figure 14, the blood red color region, except for the region identified by the black circles, indicates the reaction region, while the black circles represent the region in which the reaction does not take place even though the product exists during the $t$=50 ~ 60 s period. As shown in Figure 2, at $t$=10 s the blood red color is observed around the tips of all fingers regardless of $\varphi_v$. Therefore, in the advanced fingers, the reaction takes place around the finger regardless of $\varphi_v$ and $t$.

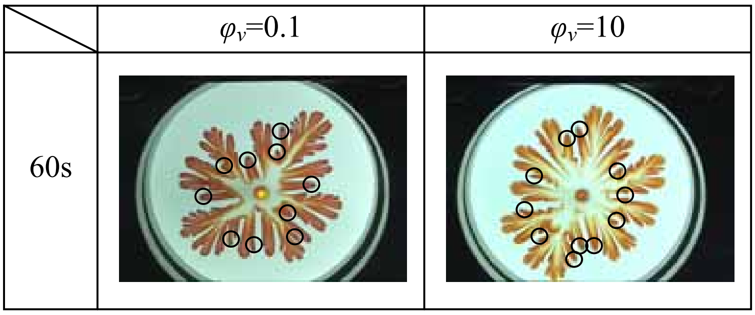



Fig.14 Reaction region in reactive miscible viscous fingering at $t$=60 s when $\varphi_v$=0.1 (a) and when $\varphi_v$=10 under the condition of $b$=0.3 mm and $q$=10.8 mm$^3$/s. Blood red color region except the region specified by black circles indicates the reaction region, while the black circles represent the region in which the reaction does not take place although the product exists.

## Conclusion

We have examined how the locations of the reaction region are varied with $\varphi_v$, $q$ and $t$ by using the novel experimental method described in detail in Nagatsu et al. (2006). The locations of the reaction region in the case of the small $q$, in which the product distribution significantly depends on $\varphi_v$, have been elucidated as follows. In early stage of fingering formation, the reaction takes place in whole the fingertips where the product is present. As time elapses, the locations of the reaction region become dependant on $\varphi_v$. When $\varphi_v$<<1, the reaction takes place from the troughs to the insides of the advanced fingers with the presence of the product. The reaction does not take place around the tips of the fingers although the product is present there. When $\varphi_v$>>1, the reaction takes place from the troughs to the tips of the advanced fingers. For both $\varphi_v$ conditions, the reaction does not take place in the shielded fingers although the product is present there. These characteristics of reactive flow field are unchanged with time in the present experimental condition. The locations of the reaction in the case of the large $q$, in which the dependence of product distribution on $\varphi_v$ is scarcely observed, have been elucidated as follows. In early stage of fingering formation, the reaction takes place in whole the fingertips where the product is present. As time elapses, the reaction takes place from the troughs to the tips of the advanced fingers regardless of $\varphi_v$. For both $\varphi_v$ conditions, the reaction does not take place in the shielded fingers although the product is present there. These characteristics of reactive flow field are unchanged with time in the present experimental condition.

## References


1. Bhaskar KR, Garik P, Turner BS, Bradley JD, Bansil R, Stanley HE, LaMont JT (1992), “Viscous fingering of HCl through gastric mucin”, *Nature*, 360, pp. 458-461.
2. Broyles BS, Shalliker RA, Cherrak DE, Guiochon G (1998), “Visualization of viscous fingering in chromatographic columns”, *J Chromatog*, A 822, pp. 173-187.
3. DeWit A, Homsy GM (1999a), “Viscous fingering in reaction-diffusion systems”, *J Chem Phys*, 110, pp. 8663-8675.
4. DeWit A, Homsy GM (1999b), “Nonlinear interaction of chemical reactions and viscous fingering in porous media”, *Phys Fluids*, 11, pp. 949-951.
5. Fernandez J, Homsy GM (2003), “Viscous fingering with chemical reaction: effect of in-situ production of surfactants”, *J Fluid Mech*, 480, pp. 267-281.
6. Hill S (1952), “Channeling in packed columns”, *Chem Eng Sci*, 1, pp. 247-253.
7. Homsy GM (1987), “Viscous fingering in porous media”, *Ann Rev Fluid Mech*, 19, pp. 271-311
8. Hornof V, Baig FU (1995), “Influence of interfacial reaction and mobility ratio on the displacement in a Hele-Shaw cell”, *Exp Fluids*, 18, pp. 448-453.
9. Jahoda M, Hornof V (2000), “Concentration profiles of reactant in a viscous finger formed during the interfacially reactive immiscible displacement in porous media”, *Powder Technol*, 110, pp. 253-257.
10. Kuang J, Petitjeans P, Maxworthy T (2004), “Velocity fields and streamline patterns of miscible displacements in cylindrical tubes”, *Exp Fluids*, 37, pp. 301-308.
11. Lajeunesse E, Martin J, Rakotomalala N, Salin D, Yortsos YC (1999), “Miscible displacement in a Hele-Shaw cell at high rates”, *J Fluid Mech*, 398, pp. 299-319.
12. McCloud KV, Maher JV (1995), “Experimental perturbations to Saffman-Taylor flow”, *Phys Rep*, 260, pp. 139-185.

13. Nagatsu Y, Ueda T (2001), “Effects of reactant concentrations on reactive miscible viscous fingering”, *AIChEJ*, 49, pp. 1711-1720.
14. Nagatsu Y, Ueda T (2003), “Effects of finger-growth velocity on reactive miscible viscous fingering”, *AIChEJ*, 49, pp. 789-792.
15. Nagatsu Y, Ogawa T, Kato Y, Tada Y, “An experimental method to identify the reaction region in reactive viscous fingering”, *2006 Annual Meeting Conference Proceedings CD-ROM*, New York, NY :AIChE.2006.
16. Petitjeans P, Maxworthy T (1996), “Miscible displacements in a capillary tube. Part 1. Experiments”, *J Fluid Mech*, 326, pp. 37-56.
17. Pojman JA, Gunn G, Patterson C, Owens J, Simmons C (1998), “Frontal dispersion polymerization”, *J Phys Chem*, B 102, pp. 3927-3929.
18. Saffman PG, Taylor GI (1958), “The penetration of a fluid into a porous medium or Hele-Shaw cell containing a more viscous liquid”, *Proc R Soc Lond*, A 245, pp. 312-308.
19. Tanveer S (2000), “Surprises in viscous fingering”, *J Fluid Mech*, 409, pp. 273-308.