AN EXPERIMENTAL METHOD TO IDENTIFY THE REACTION REGION IN REACTIVE VISCOUS FINGERING

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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, φ_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 φ_v<<1, the product is present in large quantities in a relatively broad area within the interior of the fingers, while for φ_v>>1, it concentrates around the tips of the fingers. For φ_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 φ_v<<1, but it is in the more-viscous liquid close to the interface for φ_v>>1. Therefore, it was concluded that the product distribution is caused by differences in the location of the reaction plane due to φ_v.

In the Nagatsu & Ueda (2001) 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. An example is shown in Figure 1. In this figure, the reaction region can not exactly be identified for a given time. Figure 1 shows the reactive miscible viscous fingering pattern when φ_v=1 (c_{m0}=0.08 mol/l and c_{l0}=0.04 mol/l) at (a) t=120 s and (b) t=150 s 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. 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. It is worth noting that a clear understanding of the reaction region was not obtained in other reactive immiscible viscous fingering experiments performed by Fernandez & Homsy (2003) and by Hornof and his coworkers (Hornof & Baig 1995; Hornof et al. 1995, 2000).

Figure 1. Reactive viscous fingering pattern when φ_v=1 (c_{l0}=0.04 mol/l and c_{m0}=0.08 mol/l) under the condition of b=0.3 mm and q=1.8 mm^3/s (a) at t=120 s and (b) at t=150 s.

In the present article, a novel experimental method that allows for the identification of where and when the reaction in reactive viscous fingering takes place is described. 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. This method detects when the reaction takes place during the t=120 ~ 150 s period in the experimental conditions shown in Figure 1. As discussed in the Results and Discussion section, the novel method is not only valid for the present system, but can be applied to other systems that satisfy some basic requirements.

Experiment

The experimental apparatuses used in this study were the same as those previously reported (Nagatsu & Ueda 2001), except for the configuration of the syringe pump. The Hele-Shaw cell is formed by two transparent glass plates measuring 140 mm × 140 mm × 10 mm thick with a constant gap width b. The gap width was set to b=0.3 mm, as mentioned in the Introduction, by placing four metal triangular plates (30 mm × 30 mm) at the four corners between the two glass plates. The upper glass plate has a small 4 mm diameter hole in the center for liquid injection. A syringe pump was used to inject the liquids. In the present study, a syringe pump carrying two syringes was employed for the novel method. The volumetric injection rate of the less-viscous liquid, q, was set as q=1.8 mm^3/s, as mentioned in Introduction. The viscous fingering formed in the Hele-Shaw cell was videotaped by a CCD camera mounted below the cell.

The novel experimental method employs two kinds of experiments, i.e., reactive experiments and non-reactive experiments. For reactive experiments, the more-viscous liquid is a colorless 99wt% glycerin solution including KSCN at a concentration of c_{m0}=0.08 mol/l. 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}=0.04 mol/l. 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. As mentioned in the Introduction, this reaction can be regarded as instantaneous and does not influence the fluid dynamics of the fingering. 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=150 s in a region where the color does not exist at t=120s, this indicates that the chemical reaction takes place in the region during the t=120 ~ 150 s period. Also, if the blood red color is remarkably deeper at t=150 s than at t=120 s in a region, even if the blood red color is present during the t=120 ~ 150 s period, this indicates that the chemical reaction takes place in the region during the t=120 ~ 150 s period. If the product is not still present at t=150 s in a region where the product does not exist at t=120 s, this indicates that the chemical reaction does not take place in the region during the t=120 ~ 150 s period.

The following non-reactive experiments were conducted in order to investigate the flow field of the less-viscous liquid injected in the fingering. This is important because understanding the flow field helps identify the reaction region in reactive experiments and provides a physical means for identifying the reaction region. 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, t=120 ~ 150 s. If the blood red color is present at t=150 s in a region where the blood red color does not exist at t=120 s, this indicates that a part of the blood red solution injected during $t>t_{sw}$ reaches the region during the t=120 ~ 150 s period. If the blood red color is not still present at t=150 s in a region where the blood red color does not exist at t=120 s, the blood red solution injected during $t>t_{sw}$ does not reach the region during the t=120 ~ 150 s period. The liquids used in the reactive and non-reactive experiments are summarized in Table 1.

Table 1. Summary of the liquids used

System	More-viscous liquid	Less-viscous liquid first injected	Less-viscous liquid secondly injected
Reactive	99wt% glycerin solution including 0.08 mol/l KSCN	IC solution	0.04 mol/l $Fe(NO_3)_3$ solution
Non-reactive	99wt% glycerin solution	IC solution	0.025 mol/l $[Fe(SCN)]^+$ solution

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 t=120 ~ 150 s period. t_{sw} was varied in these experiments. The reaction region during the t=120 ~ 150 s 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

Figure 2 shows the fingering pattern without and with the reaction when t_{sw} =90 s 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, the blood red color is barely observed at t=120 s (c), while at t=150 s the blood red color can be seen in the troughs and the insides near the troughs (d). 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. 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).

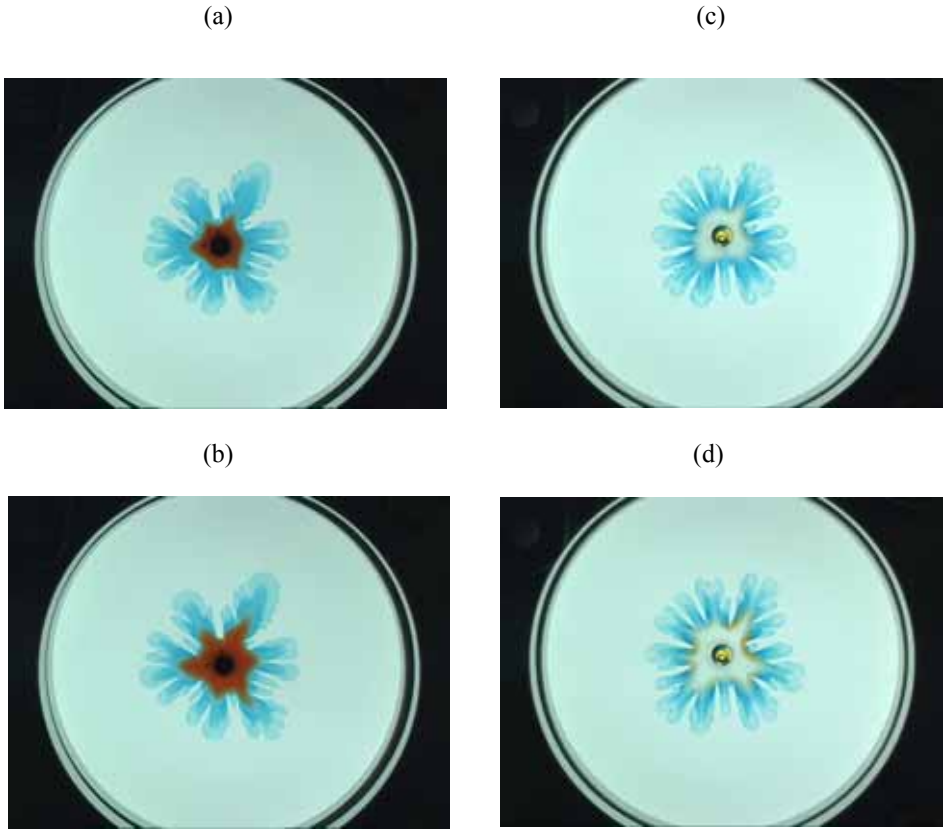

Figure 2. Viscous fingering pattern without and with the reaction when t_{sw}=90 s. (a) without reaction at t=120 s; (b) without reaction at t=150 s; (c) with reaction at t=120 s; (d) with reaction at t=150 s.

Figure 3 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, the blood red color is observed in the region from the troughs to the neighborhood of middle of the insides (c) 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, and the depth of the blood red color particularly in the insides of the fingers is obviously deeper than at t=120 s (d). 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.

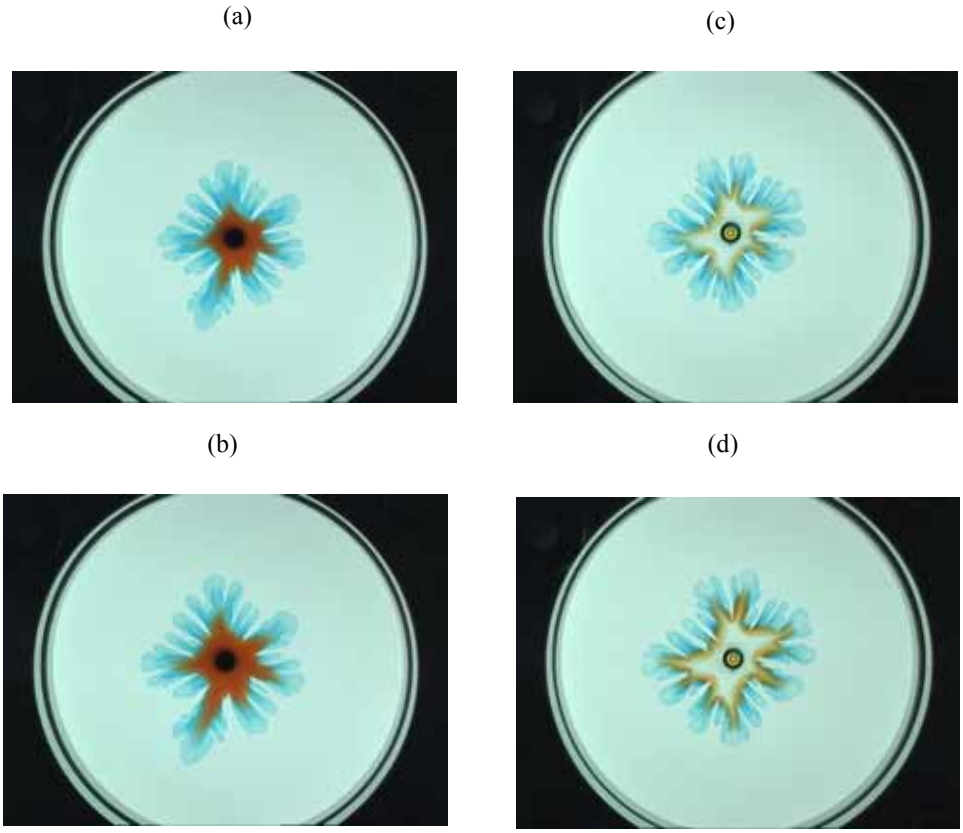

Figure 3. Viscous fingering pattern without and with the reaction when t_{sw}=60 s. (a) without reaction at t=120 s; (b) without reaction at t=150 s; (c) with reaction at t=120 s; (d) with reaction at t=150 s.

Figure 4 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 experiments, the blood red color is significantly observed in the region from the troughs to the insides of the fingers and is slightly observed at the bases of the light blue color region around the tips of the fingers at t=120 s (c). At t=150s the deep blood red color is observed in the light blue region as well as in the region from the troughs to the insides (d). These non-reactive and reactive experimental results indicate that a part of the less-viscous liquid injected after t=30 s reaches the tips of the fingers and the reaction takes place in the light blue region around the tips of the fingers during the t=120 ~ 150 s period at a minimum. 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.

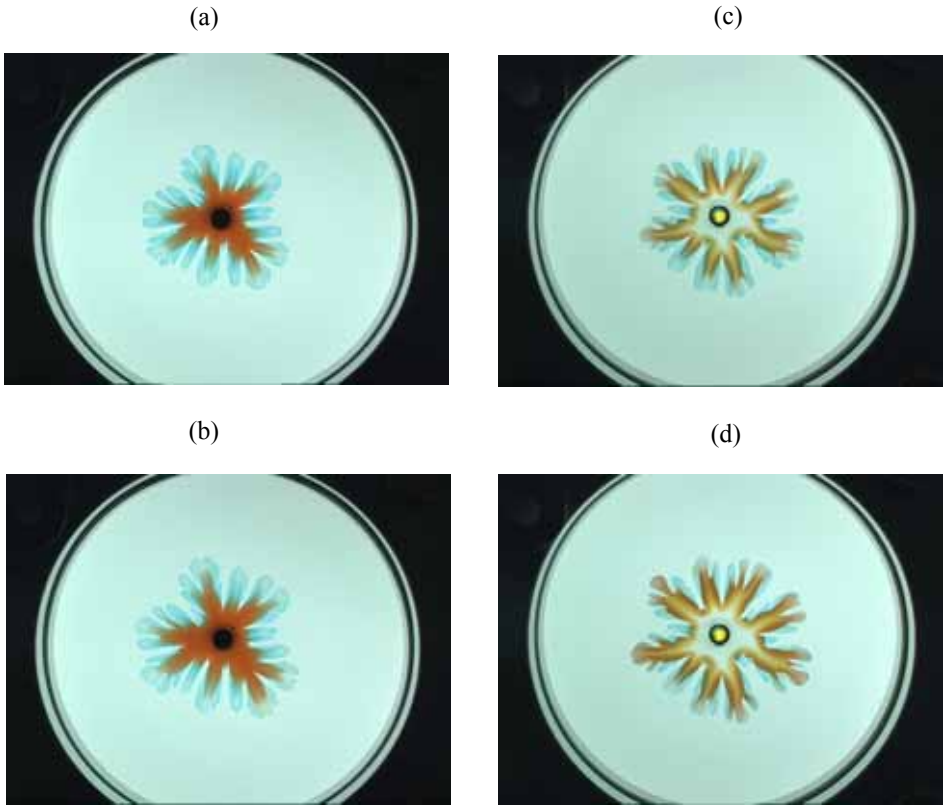

Figure 4. Viscous fingering pattern without and with the reaction when t_{sw} =30 s. (a) without reaction at t=120 s; (b) without reaction at t=150 s; (c) with reaction at t=120 s; (d) with reaction at t=150 s.

As mentioned in the Experiment section, the reaction region during the t=120 ~ 150 s period when the reactive less-viscous liquid is continuously injected, as shown in Figure 1, can be regarded as superimposition of the reaction region identified in Figures 2 ~ 4. Therefore, the reaction for this case appears to take place in the troughs and insides of the advancing fingers. This means that the entire blood red color region in the advancing finger in Figure 1 is verified to be the reaction region. On the other hand, the reaction does not take place in the shielded fingers during the t=120 ~ 150 s period. The above-identified reaction region is shown in Figure 5 by using the reactive viscous fingering pattern at t=150 s, which is the same image as Figure 1(b). In Figure 5, 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. These results show that the reaction region does not exactly coincide with the blood red color region in Figure 1.

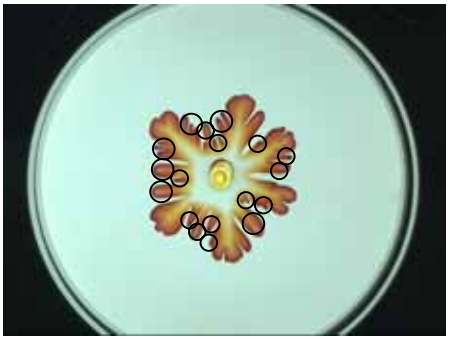

Figure 5. Reaction region in reactive miscible viscous fingering at t=150 s at φ_v=1 (c_{l0}=0.04 mol/l and c_{m0}=0.08 mol/l) under the condition of b=0.3 mm and q=1.8 mm^3/s. Blood red color region except the region specified by black circles indicates the reaction region, while the black circles represent the region in which the reaction does not take place although the product exists.

Here, attention was focused on the reaction region during the t=120 ~ 150 s time period. If similar experiments are performed in which the period is varied, it will become evident how the location of the reaction region is affected by time.

The application of the novel method described here is not restricted to the present systems of liquids and stated chemical reactions; this method can be applied to other systems that satisfy the following three conditions: (1) the product is visibly recognized, (2) the reaction rate is sufficiently fast compared to the growth rate of viscous fingering, and (3) the reaction does not influence the fluid dynamics of the viscous fingering.

As mentioned in the Introduction, the product distribution significantly depends on φ_v. Furthermore, it was found that the dependence of the product distribution is reduced with an increase in the finger-growth velocity (Nagatsu & Ueda 2003). Future works include investigating how the location of the reaction region is affected by time, φ_v, and the finger-growth velocity by means of the novel method presented here.

Conclusion

A novel experimental method has been developed to identify the reaction region in viscous fingering by switching the less-viscous liquid that is injected into the system. The method is applied to reactive miscible viscous fingering that is formed in a Hele-Shaw cell by using previously employed liquids and chemical reactions (Nagatsu & Ueda 2001). The reaction region at a specific condition of reactant concentrations, φ_v=1, at a cell gap width of b=0.3 mm and a volumetric injection rate for the less-viscous liquid of q=1.8 mm^3/s is identified in a given period: t=120 ~ 150 s. 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. This method can be applied to other systems that satisfy the following three conditions: (1) the product is visibly recognized, (2) the reaction rate is sufficiently fast compared to the growth rate of the viscous fingering, and (3) the reaction does not influence the fluid dynamics of the viscous fingering.

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