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Miscible viscous fingering with a chemical reaction involving precipitation

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We experimentally investigated the effects of a chemical reaction involving precipitation on the miscible viscous fingering pattern formed in a Hele-Shaw cell. The precipitation concentration, the ratio of the reactant concentrations initially included in the more- and less-viscous liquids, and the Péclet number were varied. For a Péclet number at the stoichiometric ratio the precipitation had significant effects on the fingering pattern when its concentration exceeded a threshold value. Interestingly, the type of effect of the precipitation on the pattern depended on its concentration. At moderate concentration, a straight-shaped finger was observed. At high concentration, the finger was bent in an almost perpendicular direction. The effect of precipitation on the pattern also depended on the ratio of reactant concentrations.

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When a more-viscous fluid is displaced by a less-viscous fluid in porous media and in Hele-Shaw cells, the interface or boundary of the two fluids becomes unstable and forms a fingerlike pattern. This phenomenon is referred to as viscous fingering. Since the pioneering works on the fluid mechanics of viscous fingering published in the 1950s, many experimental and theoretical studies have been performed [1]. So far, this issue regarding Newtonian fluids is well understood. Recently, the coupling between viscous fingering and chemical reactions has been the subject of study. Several studies have demonstrated how changes in the fluid properties due to chemical reactions affected the fingering pattern [2–4]. Fernandez and Homsy [2] experimentally demonstrated that a decrease in the interfacial tension due to a chemical reaction makes the immiscible viscous fingers wider. DeWit and Homsy [3] numerically showed that changes in the fluid's viscosity due to chemical reactions involving bistable chemical kinetics induced a new mechanism of miscible viscous fingering, which they referred to as the "droplet" mechanism, which involved the formation of isolated regions of either less- or more-viscous fluids in connected domains of the other. Our group [4] experimentally showed that in a miscible viscous fingering system, the increase in the displaced liquid's viscosity due to an instantaneous chemical reaction suppressed the shielding effect (a phenomenon by which a finger slightly ahead of its neighboring fingers quickly outruns them and shields them from further growth) and widened the fingers; on the contrary, a decrease in the displaced liquid's viscosity due to an instantaneous chemical reaction enhanced the shielding effect and narrowed the fingers.

It is frequently the case that solid precipitation is produced by chemical reactions in the liquid phase. Since viscous fingering generally occurs in porous media, chemical reactions involving precipitation are expected to affect the fingering pattern, even if the fluid properties are scarcely changed by the precipitation reactions, because precipitation is expected to change the permeability of porous media. However, this issue has remained unexplored experimentally or numerically. Therefore, in the present study, we have experimentally investigated viscous fingering in a Hele-Shaw cell involving a precipitation reaction.

For the precipitation reaction, a 97 wt % glycerin solution including iron(III) nitrate $[Fe(NO_3)_3]$ and a potassium hexacyanoferrate(II) ($K_4[Fe(CN)_6]$) solution were used as the more- and less-viscous liquids, respectively. Between the two liquids, the chemical reaction expressed as Eq. (1) takes place and produces a blue precipitation as follows:

$$\begin{aligned}&\mathrm{Fe}^{3+}\ (\text{yellow red}) + \mathrm{K}_4[\mathrm{Fe(CN)}_6]\ (\text{light yellow})\\&\quad\to \mathrm{KFe}[\mathrm{Fe(CN)}_6]\ (\text{blue precipitation}) + 3\mathrm{K}^+.\end{aligned} \tag{1}$$

This reaction can be treated as an instantaneous one. In the present study, a case involving a nonprecipitation reaction was also examined as a reference. In this case, a 97 wt % glycerin solution including $Fe(NO_3)_3$ and a potassium thiocyanate (KSCN) solution were used as the more- and less-viscous liquids, respectively. Between the two liquids, the chemical reaction expressed as Eq. (2) takes place and produces a blood-red product as follows:

$$\begin{aligned}&\mathrm{Fe}^{3+}\ (\text{yellowred}) + 2\mathrm{SCN}^-\ (\text{colorless})\\&\quad\to [\mathrm{Fe(SCN)}_2]^+\ (\text{bloody red}).\end{aligned} \tag{2}$$

This reaction can be treated as an instantaneous one as well. It should be emphasized that the viscosities of the more- and less-viscous liquids are identical in both the cases involving the precipitation reaction and the nonprecipitation reaction (the viscosities of the more- and less-viscous liquids in each case are 0.8 and 0.001 Pa s, respectively). From our previous studies [5,6], we know that the above-mentioned nonprecipitation reaction does not affect the hydrodynamics of the resultant fingering. In both cases, the selected liquids and chemical reactions mentioned above allow us to recognize the fingering pattern by color difference.

Viscous fingering experiments were conducted using a radial Hele-Shaw cell. This apparatus is the same as that used in our previous studies [4–6]. In the present study, the gap width b was set to be 0.2 mm. In the radial Hele-Shaw geometry, it is common to define the bulk fingering speed U, as $U=q/2\pi Rb$, where q is the volumetric flow rate of the injection of the less-viscous liquid [4–6]. This variable indicates the increase rate of the circle's radius R, when the less-viscous liquid completely displaces the more-viscous liquid, keeping the boundary circular. Since the present study

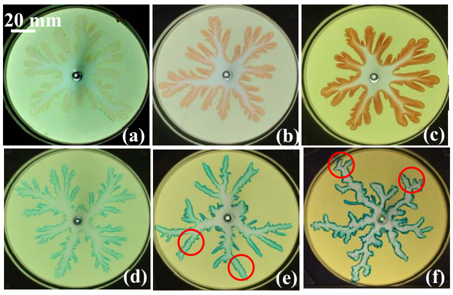

FIG. 1. (Color online) Miscible viscous fingering patterns involving the nonprecipitation reaction ($a\sim c$) and the precipitation reaction ($d\sim f$) for various values of c_{pr} under the condition of $\varphi_v=1$ when $\mathrm{Pe}_v=5.2\times 10^3$ at $t=900$ s, where t is the injection time of the less-viscous liquid. (a) $c_{pr}=0.005$ M ($c_{l0}=0.01$ M and $c_{m0}=0.005$ M), (b) $c_{pr}=0.015$ M ($c_{l0}=0.03$ M and $c_{m0}=0.015$ M), (c) $c_{pr}=0.03$ M ($c_{l0}=0.06$ M and $c_{m0}=0.03$ M), (d) $c_{pr}=0.005$ M ($c_{l0}=0.01$ M and $c_{m0}=0.01$ M), (e) $c_{pr}=0.015$ M ($c_{l0}=0.03$ M and $c_{m0}=0.03$ M), (f) $c_{pr}=0.03$ M ($c_{l0}=0.06$ M and $c_{m0}=0.06$ M). In (e), red circles show the typical straight-shaped fingers. In (f), red circles show the typical bent fingers.

treats a miscible system, the Péclet number must be defined. In this geometry, it is also common to define the Péclet number, Pe_v, (subscript v means viscous fingering) as $\mathrm{Pe}_v=RU/D=q/2\pi bD$, where D is the diffusion coefficient between the more- and less-viscous liquids [4–7]. Thus, this definition was employed in the present study. Here, D was estimated to be 1×10^{-10} m^2/s based on the measured value [8]. From the definitions, Pe_v is proportional to U; thus, Pe_v was used as a parameter indicating the bulk fingering speed.

In a previous study [5], we showed that the product distribution in miscible viscous fingers with the nonprecipitation reaction mentioned above was highly dependent on the ratio between the reactant concentrations initially included in the more- and less-viscous liquids normalized by the stoichiometric ratio of the chemical reaction φ_v, which is expressed as $\varphi_v=ac_{l0}/c_{m0}$. In this equation, c_{l0} and c_{m0} are the molar reactant concentrations initially included in the less- and more-viscous liquids, respectively, and a is the molar stoichiometric ratio of the chemical reaction. For $\varphi_v\ll 1$, the product was present in large quantities in a relatively broad area within the interior of the fingers, while for $\varphi_v\gg 1$, it was concentrated around the tips of the fingers. For $\varphi_v=1$, the product was equally distributed among the interiors and tips of the fingers. From another of our previous papers [9], under the condition of instantaneous reactions, the product's concentration at the reaction plane, c_{pr}, is expressed as $c_{pr}=c_{l0}c_{m0}/(ac_{l0}+c_{m0})$. In the present study, the experiments were conducted by varying c_{pr}, φ_v, and Pe_v. It should be noted that $\varphi_v=1$ when $a=1$ for Eq. (1) and $a=0.5$ for Eq. (2), respectively.

Experimental results for various c_{pr} under the condition of $\varphi_v=1$ are shown in Fig. 1. In the case of the nonprecipitation reaction, the pattern scarcely depended on the product's concentration. In the case of the precipitation reaction, when $c_{pr}=0.005$ M, the pattern was very similar to that in the case of nonprecipitation reaction. We found that the fingering patterns of the two cases differed when $c_{pr}=0.015$ and 0.03 M. When $c_{pr}=0.015$ M, suppression of finger splitting to form small fingers was observed in the precipitation reaction, resulting in the formation of straight-shaped fingers. We observed that the fingers bent in an almost perpendicular direction to the fingering when $c_{pr}=0.03$ M. These results show the effects of precipitation on the fingering pattern are significant when the precipitation's concentration exceeds a threshold value. Interestingly, the way precipitation affects the fingering pattern depends on the concentration of the precipitation.

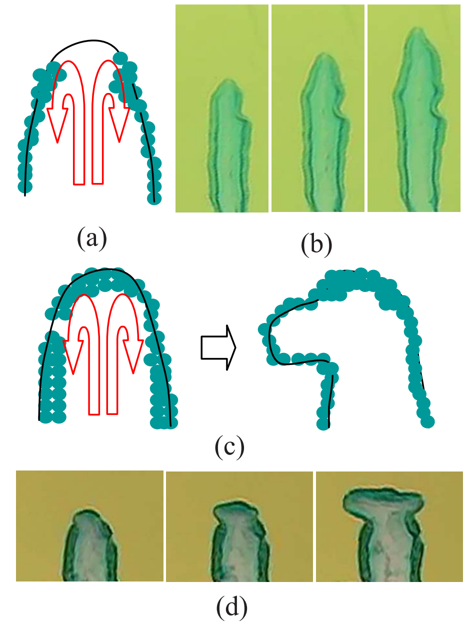

FIG. 2. (Color online) Schematics of (a) the finger for the moderate precipitation concentration and (c) formation of the bent finger for the high precipitation concentration. Actual photographs of the temporal evolution of (b) formation of the straight-shaped finger for the moderate precipitation concentration shown in Fig. 1(e) and (d) formation of the bent finger for the high precipitation concentration shown in Fig. 1(f). In (a) and (c), red arrows indicate that the less-viscous liquid's flow is stagnated around the fingertip. Blue closed circles schematically indicate the precipitation.

Figure 2 is central to our discussion of the experimental results described above. It is known that the flow of the less-viscous liquid around the viscous fingertip is stagnated when a large difference in viscosity exists between the more- and less-viscous liquids [10]. When the precipitation's concentration is moderate, the stagnated flow causes the precipitation at the fingertip to flow to the sides of the finger, which results in an accumulation of precipitation at the side of the finger. This is schematically shown in Fig. 2(a). Because of the precipitation's accumulation at the side of the finger, finger splitting to form small fingers is suppressed and straight-shaped fingers are formed. The actual photographs in Fig. 2(b) clearly show no accumulation of the precipitation at the fingertip and rather, its accumulation at the side of the finger during the formation of a straight-shaped finger. When the precipitation concentration is so high that the stagnated flow cannot completely turn the precipitation away at the tip, it accumulates there, as well. In this case, the stagnated flow tends to move the precipitation to the side part near the tip. The precipitation's accumulation at the fingertip behaves as

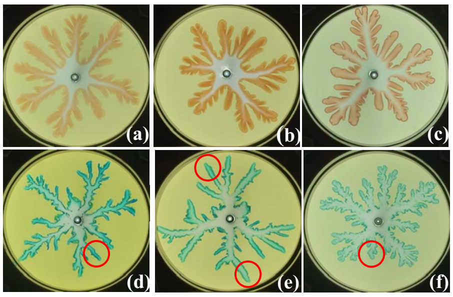

FIG. 3. (Color online) Miscible viscous fingering patterns involving the nonprecipitation reaction $(a \sim c)$ and the precipitation reaction $(d \sim f)$ for various values of φ_v under the condition of $c_{pr}=0.015$ M when $\mathrm{Pe}_v=5.2\times 10^3$ at $t=900$ s. (a) $\varphi_v=0.33$ ($c_{l0}=0.02$ M and $c_{m0}=0.03$ M), (b) $\varphi_v=1$ ($c_{l0}=0.03$ M and $c_{m0}=0.015$ M), (c) $\varphi_v=3$ ($c_{l0}=0.06$ M and $c_{m0}=0.01$ M), (d) $\varphi_v=0.33$ ($c_{l0}=0.02$ M and $c_{m0}=0.06$ M), (e) $\varphi_v=1$ ($c_{l0}=0.03$ M and $c_{m0}=0.03$ M), (f) $\varphi_v=3$ ($c_{l0}=0.06$ M and $c_{m0}=0.02$ M). In (d) and (e), red circles show the typical straight-shaped fingers. In (f), the red circle shows a typical bent finger.

an obstacle; thus, the less-viscous liquid penetrates into the region having less precipitation in the side part near the top. As a result, the finger bends almost perpendicularly. This scenario is schematically drawn in Fig. 2(c). The left photograph in Fig. 2(d) clearly shows the precipitation's accumulation at the fingertip and less accumulation at the left side near the tip. The middle and right images clearly show that the finger bends toward the left side in an almost perpendicular direction. In the right photograph, the bend of the finger to the right side is also observed.

Experimental results for various values of φ_v under the condition of $c_{pr}=0.015$ M are shown in Fig. 3. In the case of the nonprecipitation reaction, the fingering pattern scarcely changed with φ_v, although the product distribution does depend on φ_v. The product was significantly present inside the fingers for $\varphi_v=0.33$, while it concentrated at the tip of the finger for $\varphi_v=3$. In the case of the precipitation reaction, when $\varphi_v=0.33$, straight-shaped fingers were observed; the same was true for $\varphi_v=1$. [Note that Fig. 3(e) is identical to Fig. 1(e).] When $\varphi_v=3$, bent fingers formed under the conditions of $\varphi_v=1$ and $c_{pr}=0.03$ M [Fig. 1(f)] were observed. These results show that the effect of the precipitation on the fingering pattern also depends on φ_v. The photographs in Fig. 4(a), like those in Fig. 2(b), clearly show no accumulation of precipitation at the fingertip and rather, its accumulation at the side of the finger during the formation of straight-shaped fingers. In contrast, the left photograph in Fig. 4(b) clearly shows the precipitation's accumulation at the fingertip and less accumulation of the precipitation at the left side near the tip. The right one clearly shows that the finger bends toward the left side in an almost perpendicular direction. This situation is the same as the one shown in Fig. 2(d). These results also suggest that the effect of the precipitation on the fingering pattern depends on where the precipitation accumulates in the fingers. This difference in the location of accumulation is supposed to be caused by the difference in the location of the reaction plane induced by different φ_v. On the basis of our previous studies [5,9], the reaction plane is located in the less-viscous liquid when $\varphi_v<1$, and in the boundary between the two liquids when $\varphi_v>1$. Therefore, it is supposed to be more difficult for the stagnated flow to turn away the precipitation at the fingertip when $\varphi_v>1$ than when $\varphi_v<1$. It should be noted that it may be interesting to examine the case with the condition of a sufficiently small φ_v, but we were not able to examine the case with the condition of $\varphi_v<0.33$ and moderate c_{pr} because of the limits of solubility in the solutions used here.

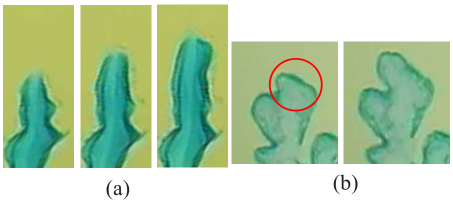

FIG. 4. (Color online) Actual photographs of temporal evolution of (a) formation of the straight-shaped finger for $\varphi_v<1$ shown in Fig. 3(d) and of (b) formation of the bent finger for $\varphi_v>1$ shown in Fig. 3(f). In (b), the fingertip indicated by a red circle should be observed closely.

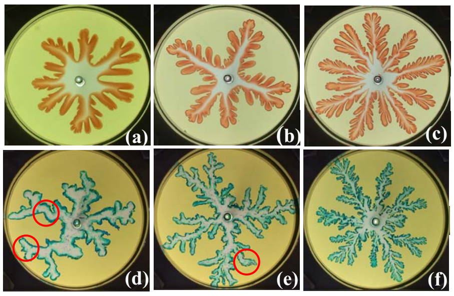

FIG. 5. (Color online) Miscible viscous fingering patterns involving the nonprecipitation reaction $(a \sim c)$ and the precipitation reaction $(d \sim f)$ for various values of Pe_v under the conditions of $\varphi_v=1$ and $c_{pr}=0.03$ M [$c_{l0}=0.06$ M and $c_{m0}=0.03$ M for (a)–(c), while $c_{l0}=0.06$ M and $c_{m0}=0.06$ M for (d)–(f)]. For (a) and (d) $\mathrm{Pe}_v=3.1\times 10^3$ at $t=2000$ s, for (b) and (e) $\mathrm{Pe}_v=9.5\times 10^3$ at $t=450$ s, for (c) and (f) $\mathrm{Pe}_v=4.3\times 10^4$ at $t=90$ s. In (e) and (f), red circles show typical bent fingers.

Experimental results for various Pe_v under the conditions of $\varphi_v=1$ and $c_{pr}=0.03$ M are shown in Fig. 5. In the case of the nonprecipitation reaction, finger splitting was enhanced with an increase in Pe_v. In the case of the precipitation reaction, small Pe_v [Figs. 5(d) and 5(e)] resulted in a bend of the fingers. For large Pe_v [Fig. 5(f)], the bend of the fingers was hardly observed and the pattern was very similar to that in the case of nonprecipitation. These results show that the effects of the precipitation reaction on the pattern decrease with an increase in Pe_v. This is considered to be because it is more difficult for the precipitation to accumulate under the condition of high Pe_v due to the convective effect. This effect of Pe_v was observed regardless of φ_v and c_{pr}.

It can be considered that the change in the fingering pattern due to the reaction involving precipitation described above originates from a decrease in the local permeability of the Hele-Shaw cell due to precipitation. In this respect, the present issue is considered to be the reverse phenomenon of the subject of so-called reactive infiltration instabilities, in which the invading fluid reacts with the solid matrix of the porous media, leading to chemical dissolution and an increase in the local permeability [11]. Indeed, the resulting fingering patterns in the present system were qualitatively different from those in the reactive infiltration instabilities [11]. In the system treated here, as mentioned above, local permeability is decreased under the condition of constant fluid viscosity, which leads to a decrease in the local fluid's mobility. In this sense, the present issue is closely related to recent experiments by the authors [4] and Podgorski *et al.* [12], in which a reaction-driven increase in viscosity was involved in viscous fingering instabilities under the condition of the constant permeability of the Hele-Shaw cell. However, there was no similarity in the resulting fingering patterns.

In summary, we have experimentally clarified the fundamental characteristics of the miscible viscous fingering patterns resulting from a precipitation reaction in a Hele-Shaw cell. Experiments were done by varying the precipitation concentration, the ratio of the reactant concentrations initially included in the more- and less-viscous liquids φ_v, and the Péclet number Pe_v. We showed that for low Pe_v under the condition of $\varphi_v=1$, the effects of the precipitation on the fingering pattern became significant when the precipitation concentration exceeded a threshold value. Interestingly, the effect of the precipitation on the pattern depends on its concentration. For moderate precipitation concentration, suppression of finger splitting to form small fingers was observed, resulting in the formation of a straight-shaped finger. For high precipitation concentration, the bend of the finger in an almost perpendicular direction was observed. We showed that for low Pe_v under the condition of moderate precipitation concentration the straight-shaped finger was observed when $\varphi_v=1$ and $\varphi_v<1$, while the bent finger was observed when $\varphi_v>1$. This shows that the effect of precipitation on the fingering pattern also depends on φ_v. The region in the finger where the precipitation accumulated depended on both the precipitation concentration and φ_v. This dependence is proposed to explain the effects of precipitation on the fingering pattern. Furthermore, we found that the effects of the precipitation on the pattern decreased with an increase in Pe_v.

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