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Experimental study on miscible viscous fingering involving viscosity changes induced by variations in chemical species concentrations due to chemical reactions

By YUICHIRO NAGATSU, KENJI MATSUDA,
YOSHIHITO KATO AND YUTAKA TADA

Department of Material Engineering, Graduate School of Engineering, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya, Aichi, 466-8555, Japan

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When a reactive and miscible less-viscous liquid displaces a more-viscous liquid in a Hele-Shaw cell, reactive miscible viscous fingering takes place. We succeed in showing experimentally how a reactive miscible viscous fingering pattern in a radial Hele-Shaw cell changes when the viscosity of the more-viscous liquid is varied owing to variation in chemical species concentration induced by an instantaneous chemical reaction. This is done by making use of a polymer solution's dependence of viscosity on pH. When the viscosity is increased by the chemical reaction, the shielding effect is suppressed and the fingers are widened. As a result, the ratio of the area occupied by the fingering pattern in a circle whose radius is the length of the longest finger is larger in the reactive case than in the non-reactive case. When the viscosity is decreased by the chemical reaction, in contrast, the shielding effect is enhanced and the fingers are narrowed. These lead to the area ratio being smaller in the reactive case than in the non-reactive case. A physical model to explain this change in the fingering pattern caused by the chemical reaction is proposed.

1. Introduction

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 finger-like pattern. This phenomenon is referred to as viscous fingering. Since the pioneering works on the fluid mechanics of viscous fingering published in the 1950s (Hill 1952; Saffman & Taylor 1958), many experimental and theoretical studies have been performed and some review articles have been published (Homsy 1987; McCloud & Maher 1995; Tanveer 2000). This issue regarding Newtonian fluids is well understood. There are two classes of viscous fingering: fingers formed in immiscible and those formed in miscible systems. The dimensionless number that controls the fingering dynamics in immiscible systems is the capillary number, *Ca*, which is defined as the ratio between viscous and interface-tension forces. In miscible systems, the dimensionless number is the Péclet number, *Pe*, which is defined as the ratio between convective and diffusive transport rates of mass. For both systems, 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 neighbouring fingers quickly outruns them and shields them from further growth. Spreading and splitting are the phenomena in which a finger which spreads until it reaches a certain width becomes unstable and splits (Homsy 1987).

Since the seminal work of Nittmann, Daccord & Stanley (1985) showing that viscous fingering patterns formed in a non-Newtonian fluid are quite different from those formed in Newtonian fluids, special attention has been paid to viscous fingering for non-Newtonian fluids. Experiments in, for instance, clay slurries, colloidal fluids and polymer solutions reveal branched fractal or fracture-like patterns (Nittmann *et al.* 1985; van Damme *et al.* 1986; Lemaire *et al.* 1991; Zhao & Maher 1993). The physical origin of the very different structures is so far unclear, mainly because these fluids can simultaneously display many non-Newtonian properties, such as shear thinning or thickening, viscoelasticity, yield stress, etc. Experiments have been performed to disentangle the influence that different non-Newtonian flow properties have on the instability by using fluids that each exhibit only one non-Newtonian property, allowing other non-Newtonian effects to be neglected (Lindner, Bonn & Meunier 2000; Lindner *et al.* 2002; Vlad & Maher 2000).

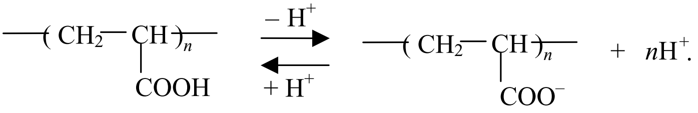
Viscous fingering accompanied by chemical reactions is observed in processes such as petroleum recovery (Hornof & Baig 1995), chromatographic and adsorptive separation (Broyles *et al.* 1998), polymerization (Pojman *et al.* 1998), and the flow of gastric mucus (Bhaskar *et al.* 1992) and is confirmed as playing an important role to these processes. Therefore, the coupling between hydrodynamics and chemistry in viscous fingering with chemical reactions has been studied. Jahoda & Hornof (2000) conducted a numerical investigation of a concentration field in an immiscble viscous finger involving chemical reactions. Fernandez & Homsy (2003) performed experiments on immiscible viscous fingering with a chemical reaction acting to reduce interfacial tension in a Hele-Shaw cell, finding that the reaction makes the fingers wider. They characterized the effects of the reaction on the reactive fingering pattern by the Damköhler number, *Da*, which is defined as the ratio between a characteristic time of fluid motion and that of a chemical reaction. DeWit & Homsy (1999*a*, *b*) performed a numerical simulation on reactive miscible viscous fingering in porous media by assuming that the fluid's viscosity is given as a function of a chemical species concentration and by using a specific chemical kinetics. They found a new mechanism of viscous fingering that they call the 'droplet' mechanism, which involves the formation of isolated regions of either less- or more-viscous fluids in connected domains of the other. Nagatsu & Ueda (2001, 2003, 2004) have experimentally investigated miscible viscous fingering involving an instantaneous chemical reaction which does not have any influence on the fingering pattern in a Hele-Shaw cell, and performed a theoretical analysis in terms of a convection–diffusion-reaction in two fluids with different viscosities. They focused on the effects of reactant concentrations and the effects of bulk finger-growth velocity on the product distribution in the fingers.

The present study is especially motivated by the numerical simulation by DeWit & Homsy (1999*a*, *b*) mentioned above. Experiments regarding this issue, that is, miscible viscous fingering involving viscosity changes due to variation in chemical species concentrations caused by chemical reaction, however, have, as mentioned in the subsequent papers (DeWit *et al.* 2003; DeWit 2004), not yet been performed. This is mainly because it is difficult to find a combination of liquids and chemical reaction which induces significant viscosity changes due to variation in chemical species concentrations. The possibility of finding the required combination of liquids and chemical reaction by using a dependence of viscosity of polymer solutions on pH has been pointed out by DeWit *et al.* (2003). In the present study, we attempt to investigate experimentally viscous fingering of the type described above by focusing on the dependence of viscosity of polymer solutions on pH.

2. Experimental

2.1. *Liquids and chemical reactions*

We focus on the dependence of an aqueous polyacrylic acid (PAA) solution's viscosity on pH. It is well known that an ionization equilibrium, which depends on pH as shown in (1), is present in the PAA solution



$$-\left(\mathrm{CH_2-\underset{\displaystyle COOH}{CH}}\right)_n- \;\underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftarrows}}\; -\left(\mathrm{CH_2-\underset{\displaystyle COO^-}{CH}}\right)_n- \;+\; n\mathrm{H}^+. \tag{1}$$

When PAA is dissolved in water, the equilibrium is inclined to the left-hand side and carboxyl groups are dominant. From this condition, pH is increased (the concentration of H^+ is decreased), the equilibrium state is shifted to the right-hand side, and then finally carboxylate ions are dominant. From this condition, pH is decreased (the concentration of H^+ is increased), the equilibrium state is again shifted to the left-hand side, and then finally carboxyl groups are dominant again. The solution's viscosity in the case in which the carboxylate ion is dominant (right-hand side) is significantly larger than that in the case where the carboxyl group is dominant (left-hand side) owing to the extension of the polymer chain induced by electrostatic repulsion.

We measured the viscosity of the PAA solution at various pH by adding sodium hydroxide (NaOH) and hydrochloric acid (HCl) in order to confirm the dependence of its viscosity on pH. We used PAA whose molecular weight is 1 million (Wako, Japan). Viscosity measurements were performed using a rheometer (HAAKE RS600) and a rotational viscometer (HAAKE VT550). Also, the pH of the polymer solutions was measured using a pH meter (TOA DDK HM-30G). Figure 1 shows the results of viscosity measurement of 0.5 wt % PAA solution including NaOH at a given concentration, c_{NaOH}. The shear viscosity of the polymer solutions, η, exhibits shear-shinning behaviorour independent of c_{NaOH}. It is confirmed that η increases with c_{NaOH} or pH regardless of the shear rate, $\dot{\gamma}$, up to $c_{\mathrm{NaOH}} = 0.065\,\mathrm{mol\,l^{-1}}$ or $\mathrm{pH} = 8.75$. However, η decreases with an increase in c_{NaOH} regardless of $\dot{\gamma}$ when c_{NaOH} is larger than $0.065\,\mathrm{mol\,l^{-1}}$ or pH is larger than 8.75. It is known that this is caused by an excess of NaOH which produces sodium counter ions which in turn reduces the electrostatic repulsion of polymer chains (Nakamura 1981). Subsequently, the viscosity of the 0.5 wt % PAA solution which included NaOH at $c_{\mathrm{NaOH}} = 0.065\,\mathrm{mol\,l^{-1}}$ and HCl at a given concentration, c_{HCl}, was measured. Figure 2 shows that η decreases with an increase in c_{HCl} or a decrease in pH regardless of $\dot{\gamma}$. A satisfactory description of most of the data shown in figures 1 and 2 can be obtained using the Ostwald de Waele power law model for the viscosity; $\eta = k\dot{\gamma}^{n-1}$; the viscosity shows a power-law dependence on the shear rate. The range of validity of this model is limited to a certain range of shear rates, depending on c_{NaOH} or c_{HCl}. The constants k and n for a given polymer solution can be obtained by fitting the rheological data. The values obtained for k and n for the polymer solutions presented in figures 1 and 2 are given in tables 1 and 2, respectively. As shown in tables 1 and 2, the power-law index is about the same for all of these fluids, so the leading constant k is a good indicator of the level of the viscosity at a given shear rate.

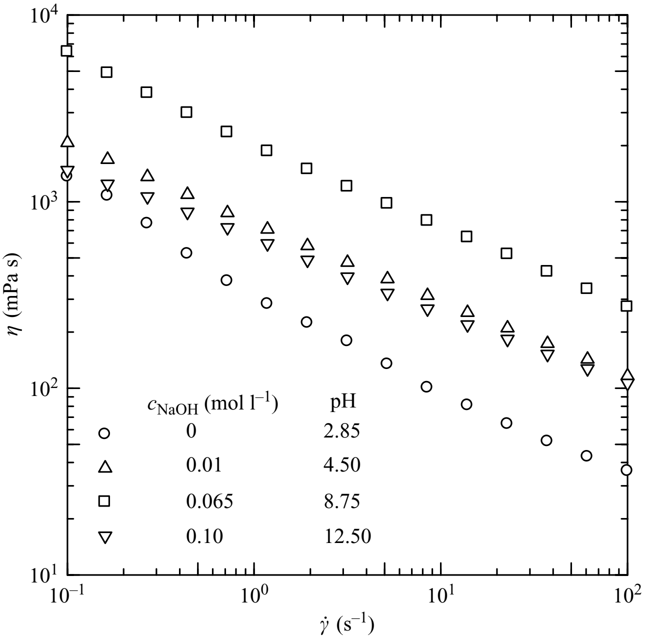


FIGURE 1. Viscosity measurement of 0.5 wt % PAA solution including sodium hydroxide (NaOH) at a given concentration, c_{NaOH}.

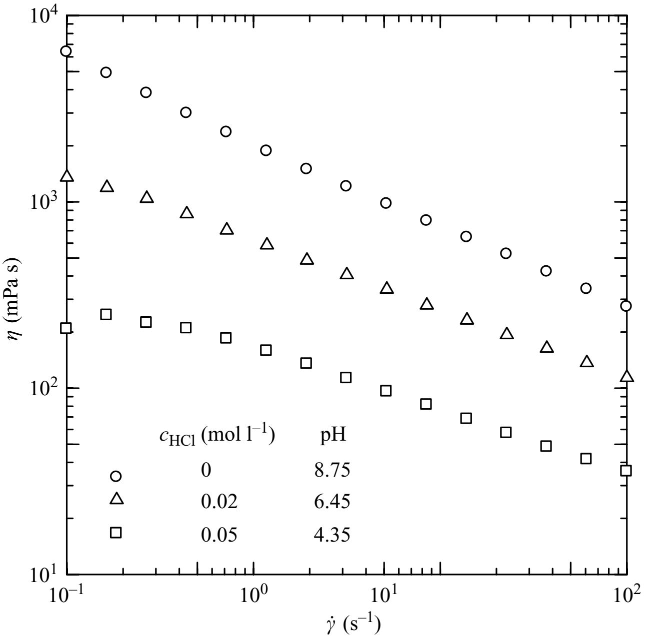


FIGURE 2. Viscosity measurement of 0.5 wt % PAA solution including NaOH at $c_{NaOH} = 0.065\,\text{mol}\,l^{-1}$ and hydrochloric acid (HCl) at a given concentration, c_{HCl}.

The results of the two viscosity measurements mentioned above are shown in figure 3 in terms of the relationship between k and pH. The solid line indicates a variation in k against pH when c_{NaOH} is varied, while the dashed line means when c_{HCl} is

c_{NaOH} ($mol\,l^{-1}$)	pH	k ($m\,Pa\,s^n$)	n
0	2.85	305	0.52
0.01	4.50	773	0.58
0.065	8.75	2101	0.55
0.10	12.50	626	0.61

TABLE 1. Parameters determined from the rhelogogical measurements described in figure 1 using the power-law model discussed in the text.

c_{HCl} ($mol\,l^{-1}$)	pH	k ($m\,Pa\,s^n$)	n
0	8.75	2101	0.55
0.02	6.45	620	0.63
0.05	4.35	166	0.66

TABLE 2. Parameters determined from the rheological measurements described in figure 2 using the power-law model disussed in the text.

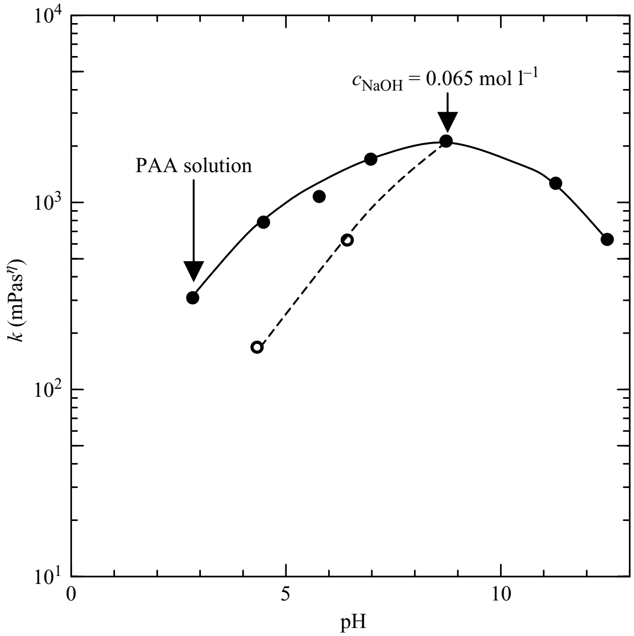


FIGURE 3. Dependence on pH of k (an indicator of the level of the viscosity at a given shear rate) of 0.5 wt % PAA solution including NaOH at c_{NaOH} (solid line) and that including NaOH at $c_{NaOH} = 0.065\,mol\,l^{-1}$ and HCl at c_{HCl} (dashed line).

varied at $c_{NaOH} = 0.065\,mol\,l^{-1}$. The solid line at pH $\leqslant 8.75$ and the dashed line do not coincide because the existence of sodium chloride (NaCl) acts to reduce the viscosity of the polymer solutions. Based on figure 3, the combination of the use of the 0.5 wt % PAA solution as the more-viscous liquid and the use of the NaOH solution as the less-viscous liquid is expected to permit the experimental investigation of reactive miscible viscous fingering involving a increase in viscosity induced by a variation in chemical species concentration due to a chemical reaction, expressed by (2). Furthermore, it is also expected that we can examine experimentally reactive

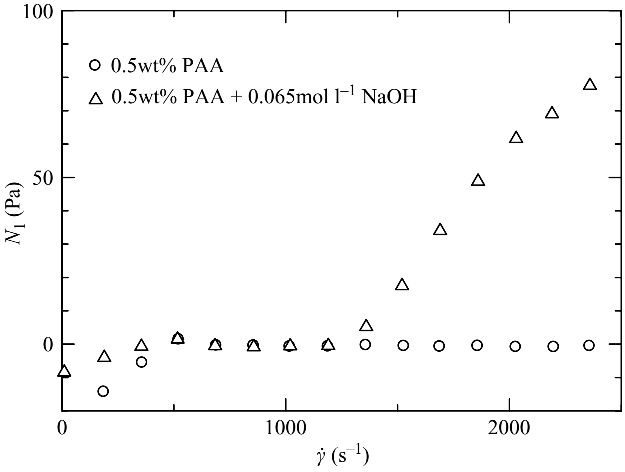
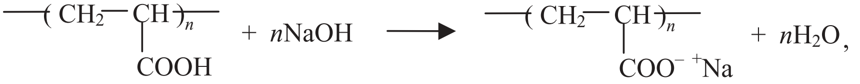
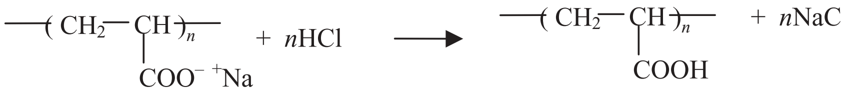


FIGURE 4. Measurement of first normal stress difference, N_1, of ○, 0.5 wt % PAA solution and △, 0.5 wt % PAA solution including NaOH at $c_{\mathrm{NaOH}} = 0.065\,\mathrm{mol\,l^{-1}}$.

miscible viscous fingering involving a decrease in viscosity induced by variation in chemical species concentration due to a chemical reaction expressed by (3) by using a 0.5 wt % PAA solution including NaOH at a concentration of $c_{\mathrm{NaOH}} = 0.065\,\mathrm{mol\,l^{-1}}$ as the more viscous liquid and an HCl solution as the less-viscous liquid. The chemical reactions expressed by (2) and (3) are essentially neutralization reactions, and thus the reactions can be treated as instantaneous ones.



$$-\!\left(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}}\right)_n\!- + n\mathrm{NaOH} \longrightarrow -\!\left(\mathrm{CH_2}-\underset{\mathrm{COO^-\,{}^+Na}}{\mathrm{CH}}\right)_n\!- + n\mathrm{H_2O}, \tag{2}$$



$$-\!\left(\mathrm{CH_2}-\underset{\mathrm{COO^-\,{}^+Na}}{\mathrm{CH}}\right)_n\!- + n\mathrm{HCl} \longrightarrow -\!\left(\mathrm{CH_2}-\underset{\mathrm{COOH}}{\mathrm{CH}}\right)_n\!- + n\mathrm{NaCl}. \tag{3}$$

Polymer solutions, in general, have two non-Newtonian characteristics simultaneously, that is, dependence of viscosity on shear rate and elasticity. It is therefore necessary to discuss the elastic properties of the polymer solution used. We used the RS600 to measure the first normal stress difference, N_1, which corresponds to the elastic property of the 0.5 wt % PAA solution and the 0.5 wt % PAA solution including NaOH at a concentration of $c_{\mathrm{NaOH}} = 0.065\,\mathrm{mol\,l^{-1}}$ which is expected to be the most elastic of the polymer solutions used in the present study. The results are shown in figure 4. No measurable N_1 was found in the range of $\dot{\gamma}$ studied for the 0.5 wt % PAA solution. For the 0.5 wt % PAA solution including NaOH at a concentration of $c_{\mathrm{NaOH}} = 0.065\,\mathrm{mol\,l^{-1}}$, no measurable N_1 was found in the range of $\dot{\gamma} < 1000\,\mathrm{s^{-1}}$, whereas N_1 was measurable and was seen to increase with $\dot{\gamma}$ in the range of $\dot{\gamma} > 1000\,\mathrm{s^{-1}}$. These results indicate that in the range of $\dot{\gamma} < 1000\,\mathrm{s^{-1}}$, elastic effects are negligible for both liquids. We, therefore, used the combination of liquids mentioned above and conducted viscous fingering experiment under the condition in which the shear rate is less than $1000\,\mathrm{s^{-1}}$ to investigate the effects of viscosity changes induced by chemical species concentrations due to an instantaneous chemical reaction, without considering an elastic change caused by the chemical reaction. The liquids

System	More-viscous liquid	Less-viscous liquid	Chemical reaction
Involving a viscosity increase	0.5 wt % PAA solution	NaOH solution	Equation (2)
Involving a viscosity decrease	0.5 wt % PAA solution including 0.065 mol l^{-1} NaOH	HCl solution	Equation (3)

TABLE 3. Summary of the liquids and chemical reactions used.

and the reaction used in the experiments are summarized in table 3. In this paper, the systems in which the viscosity of the more-viscous liquid is increased or decreased by variations in chemical species concentrations due to the chemical reactions are referred to as 'the system involving a viscosity increase' or 'the system involving a viscosity decrease', respectively.

In both systems, for control experiments without the chemical reactions, deionized water is used as the less-viscous liquid. In all experiments, the less-viscous liquids are dyed by tripan blue for visualization of the fingering. We confirmed that tripan blue has no influence on the dependence of the viscosity of the PAA solutions on pH.

2.2. *On viscous fingering experiments*

In the present study, viscous fingering experiments were conducted by using a radial Hele-Shaw cell. This apparatus is the same as that used in our previous study (Nagatsu & Ueda 2001). Our Hele-Shaw cell is formed by two transparent glass plates of 140 mm × 140 mm × 10 mm thickness with a constant gap width b. The gap width b is set as $b = 0.3$ mm by placing four metal triangular plates (30 mm × 30 mm) at four corners between the two glass plates. For liquid injection, the upper glass plate has a small hole of 4 mm in diameter in the centre. A syringe pump was used to inject the liquids. The viscous fingering formed in the Hele-Shaw cell was videotaped by a CCD camera mounted below the cell.

The bulk finger-growth velocity, U, is as defined by Nagatsu & Ueda (2001, 2003, 2004), which is expressed as

$$U = \frac{q}{2\pi R b}, \tag{4}$$

where q is the volumetric flow rate of the injection of the less-viscous liquid. This 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. The Péclet number, Pe_v, is as defined by Petitjeans *et al.* (1999) and Nagatsu & Ueda (2001, 2003, 2004) as follows:

$$Pe_v = \frac{RU}{D_v} = \frac{q}{2\pi b D_v}, \tag{5}$$

where D_v is the diffusion coefficient between the more- and less-viscous liquids. In the present study, D_v can be regarded as the diffusion coefficient of the polymer at small concentrations in water because the more-viscous liquid is 0.5 wt % PAA solution and the less-viscous liquid is water, and so D_v is estimated to be 1×10^{-9} m^2 s^{-1}. From (5), Pe_v is proportional to U, thus in the present study, it is used as a parameter indicating the bulk finger-growth velocity. Because b is constant here, Pe_v is also proportional to q.

In order to remove the elastic effects of the polymer solutions, we had to conduct the viscous fingering experiments under the condition in which the shear rate in the

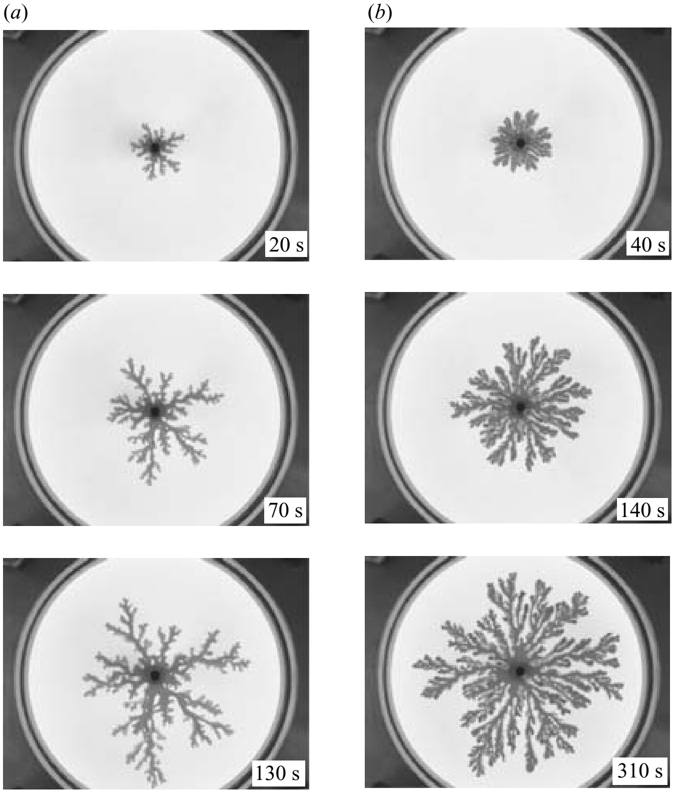


FIGURE 5. Time evolutions of miscible viscous fingering (*a*) without the reaction and (*b*) with the reaction in the system involving a viscosity increase. For both (*a*) and (*b*), r_{max} increases from top to bottom: $r_{max} = 11$, 23, 37 mm. The time of each image is shown.

vicinity of the fingertip, denoted as $\dot{\gamma}_f$, is less than $1000\,\mathrm{s}^{-1}$, as mentioned above. We roughly estimate $\dot{\gamma}_f$ as (6) based on the argument by Vlad & Maher (2000),

$$\dot{\gamma}_f = \frac{U}{\frac{1}{2}b} = \frac{q}{\pi R b^2}. \tag{6}$$

From (4), U is greatest at the injection hole, at $R = 2$ mm. In the present experiments, the condition of $\dot{\gamma}_f$ at $R = 2$ mm is examined in the range of $5\,\mathrm{s}^{-1} \leqslant \dot{\gamma}_f \leqslant 200\,\mathrm{s}^{-1}$, resulting in negligible elastic effects. This condition corresponds to $1.6 \times 10^4 \leqslant Pe_v \leqslant 64 \times 10^4$ in terms of Pe_v. The reaction employed here is a neutralization reaction and thus can be treated as an instantaneous one. Therefore, the Damköhler number, Da, is supposed to be sufficiently large.

3. Results

3.1. *Fingering pattern as affected by the change in viscosity due to the chemical reaction*

Figure 5 shows the time evolution of typical miscible viscous fingering (*a*) without the reaction and (*b*) with the reaction in the system involving a viscosity increase at $Pe_v = 1.6 \times 10^4$. In this figure, for the reactive case, the concentration of NaOH included in the less-viscous liquid, $c_{l0,\mathrm{NaOH}}$, is $0.02\,\mathrm{mol\,l}^{-1}$. Figure 6 shows the time

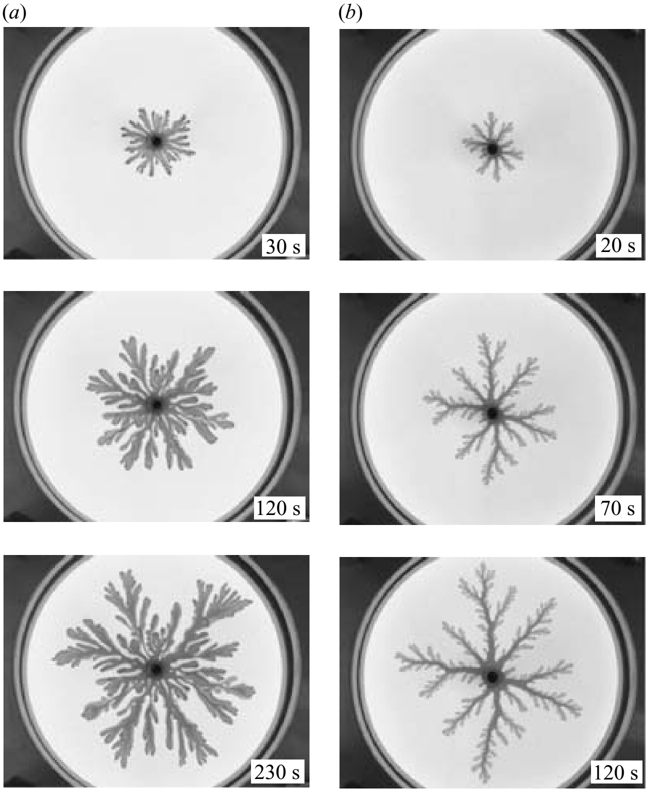


FIGURE 6. Time evolutions of miscible viscous fingering (*a*) without the reaction and (*b*) with the reaction in the system involving a viscosity decrease. For both (*a*) and (*b*), r_{max} increases from top to bottom: $r_{max} = 12$, 26, 37 mm. The time of each image is shown.

evolution of that in the system involving a viscosity decrease at $Pe_v = 1.6 \times 10^4$, in which, the concentration of HCl included in the less-viscous liquid, $c_{l0,\mathrm{HCl}}$, is $0.05\,\mathrm{mol\,l^{-1}}$ for the reactive case. Here, r_{max} is defined as the length of the longest finger in each fingering pattern. Images showing the same r_{max} are seen in figures 5 and 6. As shown in figure 5, for the system involving a viscosity increase, we find that the area occupied by the fingering pattern in the circle of a radius of r_{max} with the chemical reaction is larger than that without the reaction regardless of r_{max}. In contrast, for the system involving a viscosity decrease, the area occupied by the fingering in the circle of radius r_{max} with the reaction is smaller than that without the reaction regardless of r_{max}, as shown in figure 6. These phenomena are caused by the suppression of the shielding effect (i.e. a finger slightly ahead of its neighbouring fingers quickly outruns them and shields them from further growth) and widening of the fingers by the reaction in the system involving a viscosity increase. In contrast, the shielding effect is enhanced and the fingers are narrowed by the reaction in the system involving a viscosity decrease. Note that the non-reactive experiments shown in figures 5(*a*) and 6(*a*) feature different patterns. This difference arises from the difference in the rheological properties of the more-viscous liquids used in each non-reactive experiment.

In the present study, the fingering pattern area's density, d_a, which is defined as the ratio of the area occupied by the pattern within the circle of radius r_{max} to the area

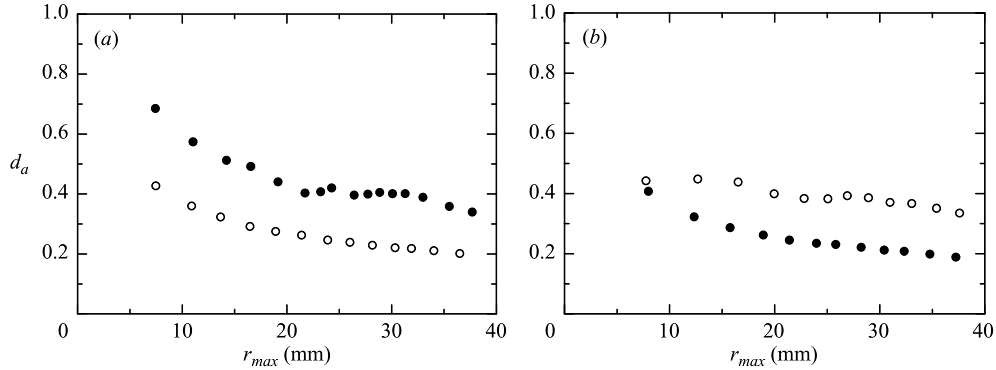


FIGURE 7. Relationships between r_{max} and d_a of the fingering pattern ●, with and ○, without the reaction (*a*) in the system involving a viscosity increase and (*b*) in the system involving a viscosity decrease.

of the circle, πr_{max}^2, is employed as a quantitative evaluation of the fingering pattern. This is because d_a is supposed to be consistent with the qualitative estimation of the experimental results discussed above. Figures 7(*a*) and 7(*b*) show the variation in d_a with r_{max} with and without the reaction for the system involving a viscosity increase and for the system involving a viscosity decrease, respectively. As shown in figure 7, d_a in the reactive case is larger for the system involving a viscosity increase and is smaller for the system involving a viscosity decrease than that in the non-reactive case for any r_{max}, respectively. These results indicate that the qualitative estimation of the fingering pattern mentioned above can be quantitatively confirmed by using d_a.

3.2. *Effects of bulk finger-growth velocity on the fingering pattern*

Figures 8 and 9 show the variation in d_a at $r_{max} = 37$ mm with Pe_v for the system involving a viscosity increase under the condition of $c_{l0,\mathrm{NaOH}} = 0.005\,\mathrm{mol\,l^{-1}}$ and for the system involving a viscosity decrease under the condition of $c_{l0,\mathrm{HCl}} = 0.005\,\mathrm{mol\,l^{-1}}$, respectively. In both figures, images of the fingering pattern in each condition corresponding to each plot are shown. Without regard to Pe_v, d_a with the chemical reaction is larger than that without the reaction for the system involving a viscosity increase, and d_a with the chemical reaction is smaller than that without the reaction for the system involving a viscosity decrease. These results indicate that the reactions influence the fingering pattern even when the bulk finger-growth velocity is increased within the present experimental conditions. This is consistent with a sufficiently large *Da*.

Further analysis is performed with regard to the effects of Pe_v on the fingering pattern with reaction. Figure 10(*a*) shows the ratio between d_a with and without reaction obtained in figures 8 and 9 plotted with respect to Pe_v. The ratio is defined as d_a with reaction divided by d_a without reaction in the system involving a viscosity increase, and is defined inversely as d_a without reaction divided by d_a with reaction in the system involving a viscosity decrease, so that the ratio is always larger than unity. Figure 10(*b*) shows the difference between d_a with and without reaction obtained in figures 8 and 9 plotted with respect to Pe_v. The difference is defined as d_a with reaction subtracted by d_a without reaction in the system involving a viscosity increase, and is defined inversely as d_a without reaction subtracted by d_a with reaction in the system involving a viscosity decrease, so that the difference is always positive. We have found that the ratio and the difference increase with Pe_v in the system involving a viscosity increase,

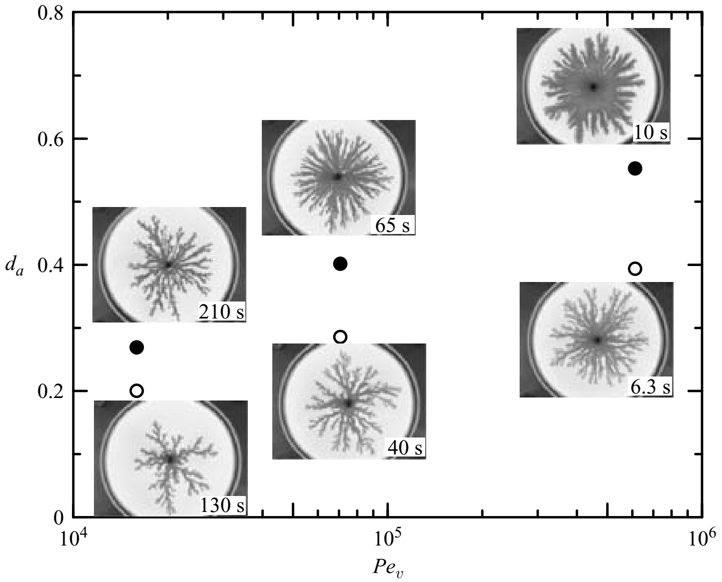


FIGURE 8. Variation in d_a with Pe_v at $r_{max} = 37$ mm in the system involving a viscosity increase along with images of the fingering pattern ●, with and ○, without reaction in the conditions corresponding to each plot. The time of each image is shown.

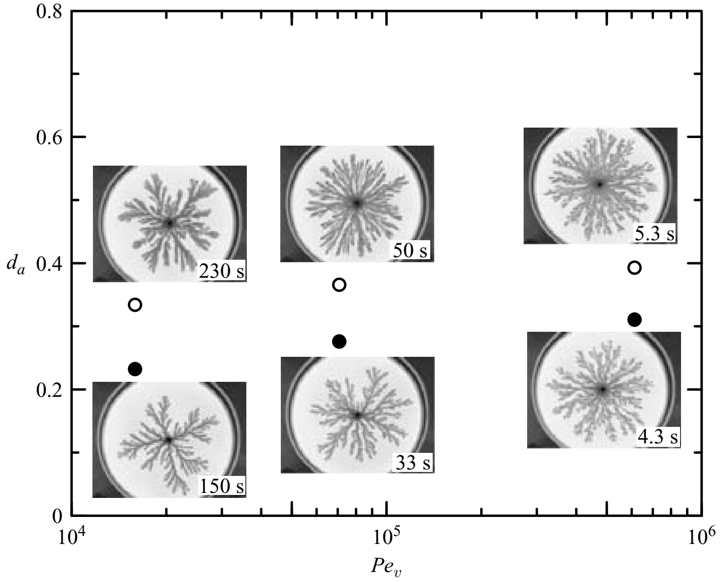


FIGURE 9. Variation in d_a with Pe_v at $r_{max} = 37$ mm in the system involving a viscosity decrease along with images of the fingering pattern ●, with and ○, without reaction in the conditions corresponding to each plot. The time of each image is shown.

but decrease with Pe_v in the system involving a viscosity decrease. These results are supposed to reveal that the effect of the reaction on the fingering pattern increases with Pe_v in the system involving a viscosity increase, but decreases with Pe_v in the system involving a viscosity decrease. This trend in the effects of Pe_v on the fingering

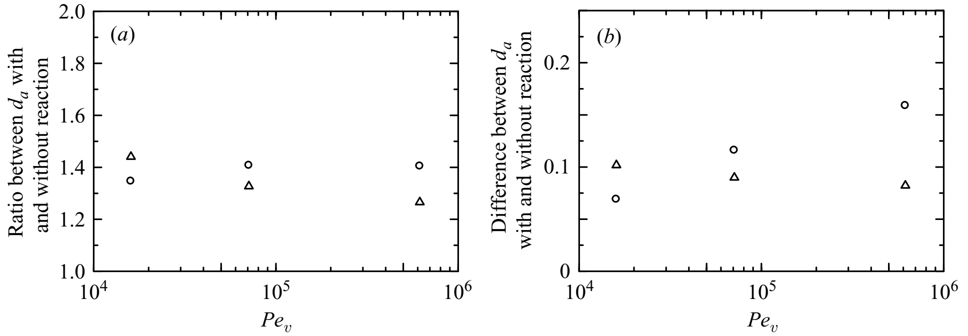


FIGURE 10. (*a*) Ratio and (*b*) difference between d_a with and without the reaction obtained in figures 8 and 9 plotted with respect to Pe_v. The ratio is defined as d_a with the reaction divided by d_a without reaction in ○, the system involving a viscosity increase, and is defined inversely as d_a without reaction divided by d_a with reaction in △, the system involving a viscosity decrease. The difference is defined as d_a with reaction subtracted by d_a without reaction in ○, the system involving a viscosity increase, and is defined inversely as d_a without reaction subtracted by d_a with reaction in △, the system involving a viscosity decrease.

pattern may be interpreted as follows. In the non-reactive experiments in the systems involving either a viscosity increase or a viscosity decrease, d_a increased with Pe_v for the same r_{max}, as shown in figures 8 and 9, which indicates that the shielding effect is suppressed with an increase in Pe_v. As for the effects of the reaction on the fingering pattern, as mentioned above, the reaction suppresses the shielding effect in the system involving a viscosity increase, whereas the reaction enhances the shielding effects in the system involving a viscosity decrease. Combining the effects of the reaction and Pe_v results in a suppression of the shielding effect by the reaction being further enhanced by an increase in Pe_v in the system involving a viscosity increase. In contrast, this combination results in an enhancement of the shielding effect by the reaction being suppressed by an increase in Pe_v in the system involving a viscosity decrease.

These results shown in figures 8–10 are observed under all experimental conditions in the range of $0.005\,\mathrm{mol\,l^{-1}} \leqslant c_{l0,\mathrm{NaOH}} \leqslant 0.20\,\mathrm{mol\,l^{-1}}$, and $0.005\,\mathrm{mol\,l^{-1}} \leqslant c_{l0,\mathrm{HCl}} \leqslant 0.05\,\mathrm{mol\,l^{-1}}$. In addition, these results in figures 8–10 are observed without regard to r_{max} when r_{max} is large enough to measure d_a with high accuracy, i.e. r_{max} is larger than about 10 mm, as is expected in figures 5–7 in which the reactions used here have an influence on the fingering pattern regardless of r_{max}. We selected $r_{max} = 37$ mm as the radius at which the largest entire fingering pattern is seen in the present experimental setting.

3.3. *Effects of reactant concentration in the less-viscous liquid on the fingering pattern*

Figure 11 shows the variation in d_a at $r_{max} = 37$ mm with $c_{l0,\mathrm{NaOH}}$ at $Pe_v = 1.6 \times 10^4$ for the system involving a viscosity increase along with images of the fingering pattern in the condition of each plot. In the experimental conditions tested, d_a increases with $c_{l0,\mathrm{NaOH}}$ when $c_{l0,\mathrm{NaOH}}$ is less than $0.02\,\mathrm{mol\,l^{-1}}$. However, d_a decreases with $c_{l0,\mathrm{NaOH}}$ when $c_{l0,\mathrm{NaOH}}$ is more than $0.02\,\mathrm{mol\,l^{-1}}$. This relationship between d_a and $c_{l0,\mathrm{NaOH}}$ is similar to that between the shear viscosity η of the 0.5 wt % PAA solution including NaOH containing a concentration of c_{NaOH} and its pH as shown in the solid line in figure 3. Figure 12 shows the variation in d_a at $r_{max} = 37$ mm with $c_{l0,\mathrm{HCl}}$ for the system involving a viscosity decrease at $Pe_v = 1.6 \times 10^4$ along with images of the fingering pattern in the condition of each plot. As shown in figure 12, d_a decreases monotonically with $c_{l0,\mathrm{HCl}}$, which corresponds to the dashed line in figure 3. These

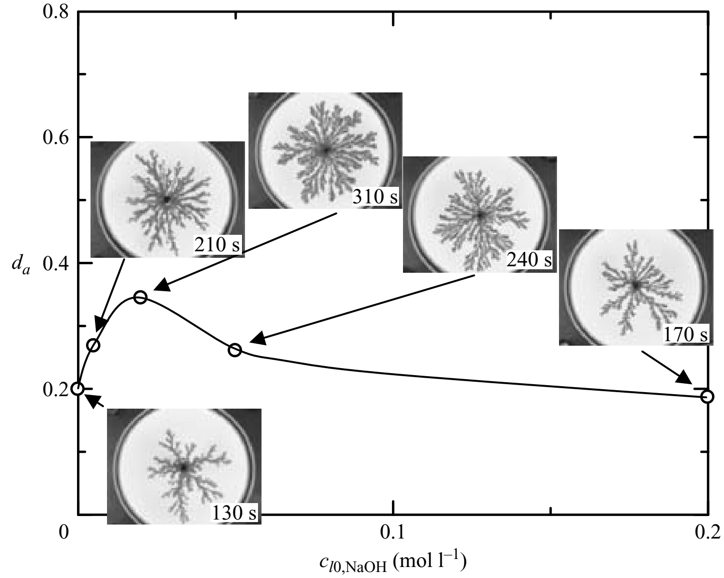


FIGURE 11. Variation in d_a with $c_{l0,\mathrm{NaOH}}$ at $r_{max} = 37$ mm in the system involving a viscosity increase along with images of the fingering pattern in the conditions corresponding to each plot. The time of each image is shown.

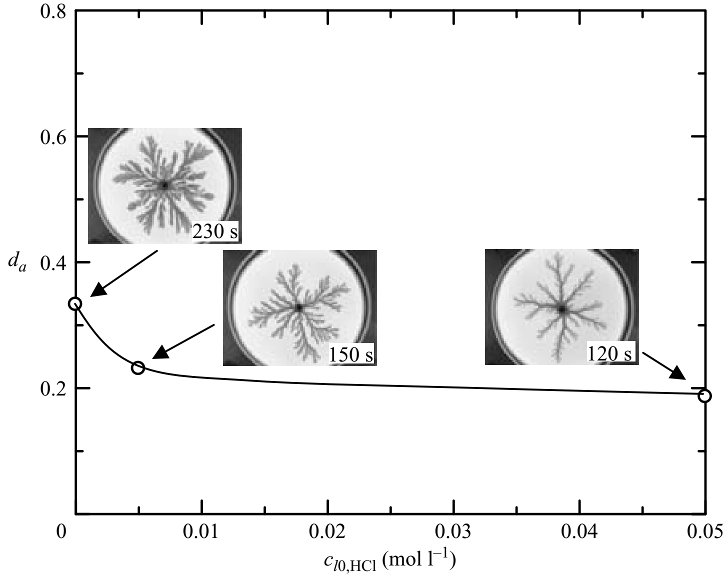


FIGURE 12. Variation in d_a with $c_{l0,\mathrm{HCl}}$ at $r_{max} = 37$ mm in the system involving a viscosity decrease along with images of the fingering pattern in the conditions corresponding to each plot. The time of each image is shown.

similarities confirm that the change in the fingering pattern is caused by the change in the viscosity of the displaced liquid induced by the variation in chemical species concentrations due to the reaction. These results are observed under all experimental conditions in the range of $1.6 \times 10^4 \leqslant Pe_v \leqslant 64 \times 10^4$. In addition, these results are

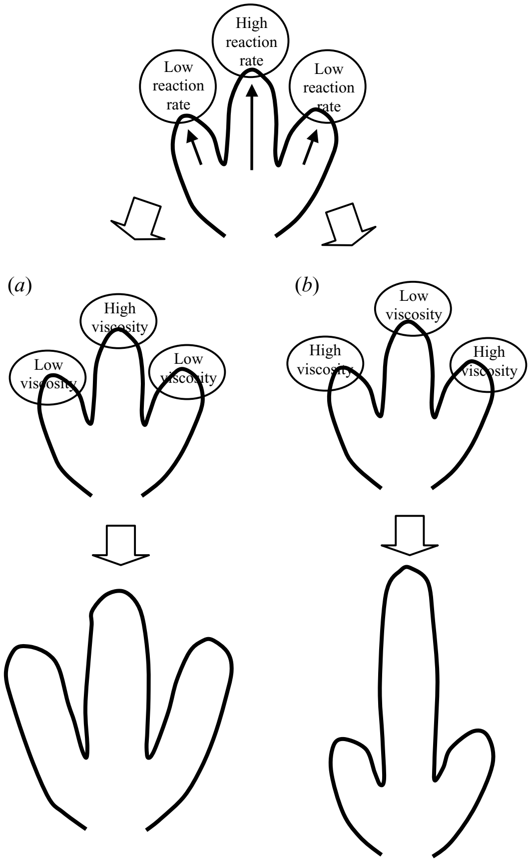


FIGURE 13. A physical model to explain (*a*) the suppression of the shielding effect by the chemical reaction for the system involving a viscosity increase and (*b*) the enhancement of the shielding effect by the chemical reaction for the system involving a viscosity decrease. The length of the arrows corresponds to the amount of reactant flux provided.

observed without regard to r_{max}. The reason for the choice of $r_{max} = 37\,\text{mm}$ is the same as that mentioned earlier.

4. Discussion

Here we discuss a physical model to explain the changes in the fingering pattern mentioned above. Fernandez & Homsy (2003) have proposed an unequal rate of the chemical reaction at different places on the interface. They hypothesize that, because of the diffusional limitations of the fingers in the troughs, the reaction attains a higher level of completion near the tips of the fingers than in the troughs, leading to a lower interfacial tension at the tips. The Marangoni stress so produced will cause flow from regions of low tension to high, i.e. from the tip to the trough. Such a flow will then act to spread the finger laterally, thus forming a wider finger. We propose a similar model in a slightly different way to explain the suppression and enhancement of the shielding effect. We hypothesize that the rate of chemical reaction is larger in the tip of the advancing finger than in the tips of shielded fingers (figure 13), owing to the larger amount of reactant flux provided in the tip of the advancing finger. The rate of the reaction in the fingers' troughs are smaller than in the tips of the shielded fingers owing

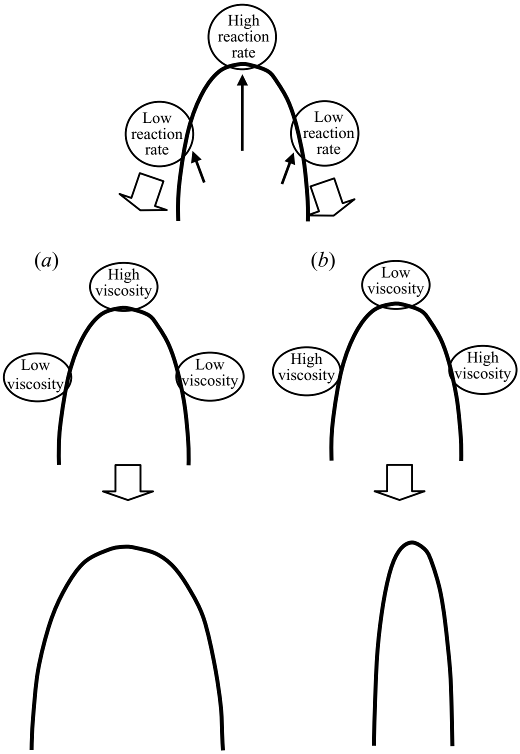


FIGURE 14. A physical model to explain (*a*) the finger widening by the chemical reaction for the system involving a viscosity increase and (*b*) the finger narrowing by the chemical reaction for the system involving a viscosity decrease. The length of the arrows corresponds to the amount of reactant flux provided.

to diffusional limitations (Fernandez & Homsy 2003) and/or the larger amount of reactant flux provided in the tips of the shielded fingers. Under this hypothesis, for the system involving a viscosity increase, the pH of the displaced liquid will be larger in the vicinity of the tip of the advancing fingers than in the vicinity of the tips of the shielded fingers, leading to a higher viscosity of the displaced liquid in the vicinity of the tip of the advancing finger. In contrast, for the system involving a viscosity decrease, the pH of the displaced liquid will be smaller in the vicinity of the tip of the advancing finger than in the vicinity of the tips of the shielded fingers, leading to a lower viscosity of the displaced liquid in the vicinity of the tip of the advancing finger. It can be considered that the displacing liquid can more easily penetrate the region with relatively lower viscosity than it can the region with relatively higher viscosity. This results in the suppression of the shielding effects in the system involving a viscosity increase and that, in contrast, the shielding effect is enhanced in the system involving a viscosity decrease (figure 13). We can also explain the mechanisms of the finger widening by the reaction for the system involving a viscosity increase and the finger narrowing by the reaction for the system involving a viscosity decrease by an unequal rate of chemical reaction at different places on the boundary between the less- and more-viscous liquids. We, in turn, hypothesize that the rate of chemical reaction is larger in the tip of the finger than in the rear of the finger (figure 14), owing to the larger amount of reactant flux provided in the tip of the finger. Under this hypothesis, for the system involving a viscosity increase, the viscosity of the displaced liquid will be larger in the vicinity of the tip of the finger than in the vicinity of the rear of the finger, which leads to widening of the finger. In contrast, for the system involving a viscosity decrease, the viscosity of the displaced liquid will be smaller in the vicinity of the tip of the finger than in the vicinity of the rear of the finger, which leads to narrowing of the finger.

In the experiments reported by Fernandez & Homsy (2003), at high *Da*, the chemical reaction has no influence on the fingering pattern. They mention that this is because the reaction has reached completion very quickly in the experiment. This is different from our results which show that the chemical reaction influences the fingering pattern for sufficiently high *Da*. We interpret our results as being due to the reaction successively taking place even for high *Da* because fresh reactant continues to be provided to the boundary between the less- and more-viscous liquids. The chemical reaction's lack of influence on the fingering pattern described by Fernandez & Homsy (2003) may be interpreted as resulting from the continuing reaction in which interfacial tension has been reduced early and the interfacial tension is no longer reduced by the reaction, which leads to a lack of gradient of interfacial tension on the interface. Also the fingering pattern is independent of the capillary number, *Ca*, in their experiments.

We discuss a relationship between the present results and the fracture-like behaviour in viscous fingering experiments using associating polymer solutions as described by Maher and colleagues (Zhao & Maher 1993; Ignés-Mullol, Zhao & Maher 1995; Vlad, Ignés-Mullol & Maher 1999). They inferred that the fracture-like instabilities are determined by the extreme shear thinning viscosity of the more-viscous liquid. The fracture-like pattern is interpreted to arise from strong shielding effects. In the system involving a viscosity decrease in the present study, the enhancement of the shielding effects is considered to be caused by the lower viscosity of the displaced liquid in the vicinity of the tips of the advancing fingers than that in the vicinity of the tips of the shielded fingers which is induced by an unequal rate of chemical reaction. Based on the present study, the strong shielding effects in the fracture-like pattern can be interpreted as being due to the lower viscosity of the displaced liquid in the vicinity of the tips of the advancing fingers than that in the vicinity of the tips of the shielded fingers, which is caused by the displaced liquid in the vicinity of the advancing fingers' subjection to a larger shear rate and the extreme shear-thinning viscosity of the displaced liquid. In other words, in the present study the difference in the viscosities of the displaced liquid in the vicinity of the tips of the advancing and shielded fingers is chemically induced, while this difference is mechanically induced in the experiments focusing on the fracture-like pattern. Therefore, the present results in the system involving a viscosity decrease support the inference by Maher and his coworkers mentioned above. Our results also can be interpreted as having a good agreement with the experimental results obtained by Lindner *et al.* (2000, 2002) showing that shear-thinning viscosity of the displaced liquids makes a finger narrow. They explained that the finger narrowing is caused by a small viscosity in front of the finger tip owing to a high shear rate there and the shear-thinning viscosity of the displaced liquid. In the system involving a viscosity decrease in the present study, a small viscosity in front of the finger is induced by a high rate of chemical reaction. The finger narrowing by the reaction for the system involving a viscosity decrease, therefore, is consistent with the results of Lindner *et al.* (2000, 2002).

The present experimental findings in the large-Péclet-number limit may relate to experimental observations on the extreme sensitivity of the immiscible interfacial shapes to local flow inhomogeneities such as a little bubble (Couder, Gérard & Rabaud 1986) near the tip of a finger, a needle (Zocchi *et al.* 1987) piercing the interface, or anisotropy (Ben-Jacob *et al.* 1985) introduced by etching the glass plates. Such a local perturbation leads to narrower and more stable fingers than the regular ones. When instability does set in for these fingers, it is dendritic rather than the usual tip splitting. However, we find it difficult to reconcile our experimental findings to their experimental results at present. The primary reason for this difficulty is that our results were obtained for two contrasting situations, i.e. finger widening and finger narrowing, whereas immiscible cases have only one situation, i.e. finger narrowing, without regard to the origin of the small perturbation.

Finally, the present results should be compared with those of the numerical simulation reported by DeWit & Homsy (1999*a*, *b*), because the present study is especially motivated by their study. The present results do not show droplet formation. This is because the chemical kinetics in DeWit & Homsy's study are strikingly different from those in ours.

5. Conclusion

We have succeeded in selecting liquids and a chemical reaction which permits the experimental investigation of miscible viscous fingering involving changes in the viscosity of a more-viscous liquid, this change is due to variation in chemical species concentrations caused by an instantaneous chemical reaction. We have also shown how the fingering pattern changes with an increase or decrease in viscosity. We used the viscosity of the aqueous PAA solution's dependence on pH. When the viscosity is increased by the chemical reaction, the shielding effect is suppressed and the fingers are widened. As a result, the density of the area of the fingering pattern, d_a, with the reaction is larger than that without the reaction. In contrast, when the viscosity is decreased by the chemical reaction, the shielding effect is enhanced and the fingers are narrowed. As a result, d_a with the reaction is smaller than that without the reaction. Under the experimental condition of bulk finger-growth velocity, expressed by the Péclet number, Pe_v, as employed in the present study, the change in the fingering pattern owing to the reaction can be observed without regard to Pe_v. This is because the Damköhler number, Da, is sufficiently large under the present Pe_v condition. The effects of reactant concentration included in the less-viscous liquid on the change in the fingering pattern are also investigated. In the system involving a viscosity increase, an increase in $c_{l0,\mathrm{NaOH}}$ shows a greater effect on the change in the fingering pattern as $c_{l0,\mathrm{NaOH}}$ increases up to a threshold value, whereas over that threshold value, the effect on the change in the fingering pattern decreases with the increase in $c_{l0,\mathrm{NaOH}}$. In the system involving a viscosity decrease, an increase in $c_{l0,\mathrm{HCl}}$ causes a monotonic increase in the effect on the change in the fingering pattern. These tendencies are consistent with the relationships between the shear viscosity of the polymer solution used and its pH. These results confirm that the change in the fingering pattern is caused by the change in viscosity caused by variation in chemical species concentrations induced by the chemical reaction. A physical model to explain the change in the fingering pattern caused by the reaction is proposed in which the rate of chemical reaction is unequal at different places on the boundary between the less- and more- viscous liquids.

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