

## Miscible viscous fingering involving viscosity changes of the displacing fluid by chemical reactions

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In our previous study, we experimentally studied the effects of changes in the viscosity of the displaced more-viscous liquid by instantaneous reactions on miscible viscous fingering pattern [Y. Nagatsu, K. Matsuda, Y. Kato, and Y. Tada, "Experimental study on miscible viscous fingering involving viscosity changes induced by variations in chemical species concentrations due to chemical reactions," *J. Fluid Mech.* **571**, 475 (2007)]. In the present study, experiments have been performed on the miscible viscous fingering involving changes in the viscosity of the displacing less-viscous liquid by instantaneous reactions in a radial Hele-Shaw cell. We have found that the shielding effect is suppressed and the fingers are widened when the viscosity is increased. As a result, the reaction makes the fingering pattern denser. In contrast, the shielding effect is enhanced, and the fingers are narrowed when the viscosity is decreased. As a result, the reaction makes the fingering pattern less dense. These results are essentially same as those obtained by the above-mentioned previous study. This shows that the effects of changes in the viscosity due to the instantaneous reactions are independent of whether the changes occur in the displaced liquid or in the displacing liquid. A mechanism for the independence is discussed. © 2010 American Institute of Physics. [doi:10.1063/1.3301244]

### I. INTRODUCTION

When a more-viscous fluid is displaced by a less-viscous one 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 appearance of the pioneering works on the fluid mechanics of viscous fingering, published in the 1950s,<sup>1,2</sup> many experimental and theoretical studies have been performed, and some review articles have been published.<sup>3-5</sup> This issue regarding Newtonian fluids is well understood. There are two classes of viscous fingering: fingers formed in immiscible systems 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. In both the systems, the viscosity ratio or the viscosity contrast in a form of Atwood number,  $At$ , is also an important dimensionless parameter for the dynamics. 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 neighbor fingers quickly outruns them and shields them from further growth. Spreading and splitting are the phenomena in which a finger that spreads until it reaches a certain width becomes unstable and splits.<sup>3</sup>

Since the seminal work by Nittmann *et al.*<sup>6</sup> showing that viscous fingering patterns formed in a non-Newtonian fluid are quite different from those formed in Newtonian fluids,

viscous fingering for non-Newtonian fluids has been paid special attention. Experiments in, for instance, clay slurries, colloidal fluids, and polymer solutions have revealed branched fractal or fracturelike patterns.<sup>6-9</sup> 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 within the past few years 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, showing experimentally other non-Newtonian effects to be neglected.<sup>10-12</sup>

Recently, coupling between viscous fingering and chemical reactions has been investigated. These studies can be classified into several types. One is in the case where reactions do not influence the fingering dynamics. In this case, main attention has been paid to concentration distribution of chemical species in the fingering pattern depending on the initial concentrations and the fingering velocity.<sup>13-17</sup> In the case where reactions are active to the fingering dynamics, the problems can be further divided into two categories. One category regards viscous fingering fully triggered by chemical reaction. In this problem, the displacing and displaced fluids have the same viscosity, which means that the fingering does not occur in the nonreactive case. In the reactive case, the reaction produces the more-viscous product, which leads to the fingering. This type of reactive fingering was experimentally demonstrated by Podgorski *et al.*<sup>18</sup> and numerically analyzed by Gérard and De Wit.<sup>19</sup> The other category regards viscous fingering modified by chemical reaction. In this problem, the displaced fluid is more viscous than

the displaced fluid; thus the fingering takes place even in the nonreactive case. The reactions induce changes in some properties, which results in the modification of the fingering pattern. The modifications of the fingering pattern by a decrease in interfacial tension by a reaction in the immiscible system,<sup>20</sup> by a precipitation reaction in the miscible system,<sup>21</sup> and by a reaction producing gel in the miscible system<sup>22</sup> were experimentally demonstrated. The modifications of the fingering pattern by changes in the fluid's viscosity in the miscible system first theoretically analyzed by De Wit and Homsy.<sup>23,24</sup> The chemical kinetics employed in their study produces a new type of fingering; they call it the “droplet” mechanism, which involves the formation of isolated regions of either less- or more-viscous fluids in connected domains of the other.

Nagatsu *et al.*<sup>25</sup> succeeded in the experimental demonstration of the modification of the miscible fingering pattern in a radial Hele-Shaw cell by changes in the viscosity of the displaced more-viscous liquid due to instantaneous chemical reactions. This was done by making use of a polymer solution's dependence of viscosity on  $pH$ . In that case, instantaneous reactions meant that the Damköhler number,  $D_a$ , which is defined as the ratio between a characteristic time of fluid motion and that of a chemical reaction, was significantly high or could be treated as infinity. When the viscosity was increased by the reaction, the shielding effect was suppressed, and the fingers were widened. As a result, the fingering pattern became denser by the reaction. When the viscosity was decreased by the reaction, in contrast, the shielding effect was enhanced and the fingers were narrowed. These changes led to the reactive fingering pattern being less dense. Subsequently, Nagatsu *et al.*<sup>26</sup> also succeeded in the experimental investigation of reactive miscible viscous fingering involving a decrease in the viscosity of the displaced liquid under the moderate  $D_a$  condition. This was done by employing a chemical reaction between a polymer solution and solution including metal ions. They showed that the reaction increased the area occupied by the fingering pattern around the injection hole (the experiment was performed by using a radial Hele-Shaw cell). As a result, the fingering pattern became denser in the reactive case than in the non-reactive case. This finding, interestingly, showed that the effects of the decrease in the viscosity of the more-viscous liquid due to chemical reaction for moderate  $D_a$  are opposite to those for significantly high  $D_a$  [as mentioned above, the fingering pattern became less dense by the decrease in the viscosity of the more-viscous liquid by the reaction under the significantly high  $D_a$  (Ref. 25)].

The objective of the present study is to experimentally investigate the effects of changes in the viscosity of the “displacing less-viscous liquid” due to instantaneous chemical reactions on miscible viscous fingering pattern. As mentioned above, the difference in  $D_a$  had opposite effects on the fingering pattern involving a decrease in the viscosity of the more-viscous liquid by reactions. It is interesting to examine whether the effects of changes in the viscosity of the displacing less-viscous liquid by the instantaneous reactions on fingering pattern are similar to or different from those of the displaced more-viscous liquid reported by Nagatsu *et al.*<sup>25</sup>

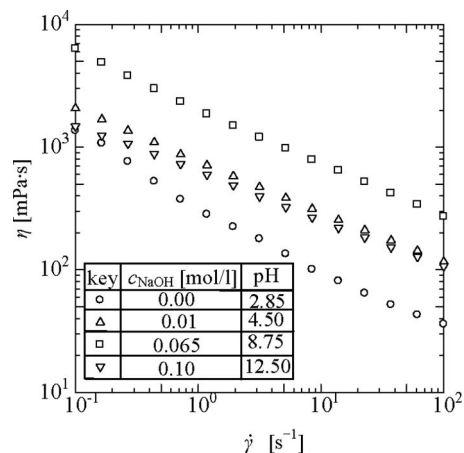
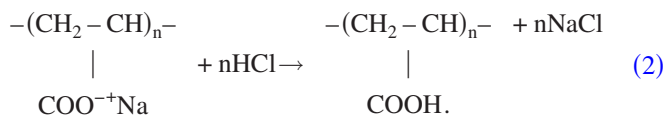
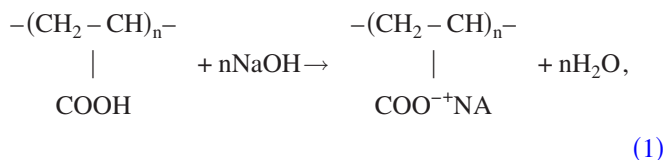


FIG. 1. Viscosity measurement of 0.5 wt % PAA solution including sodium hydroxide (NaOH) at a given concentration,  $c_{\text{NaOH}}$ .

## II. EXPERIMENTAL

### A. Liquids and chemical reactions

Nagatsu *et al.*<sup>25</sup> employed the dependence of viscosities of polyacrylic acid (PAA) solution and sodium polyacrylate (SPA) solution on  $pH$ . Note that in the work of Nagatsu *et al.*,<sup>25</sup> the SPA solution was the mixture of the PAA solution and sodium hydroxide (NaOH) solution. In the work of Nagatsu *et al.*,<sup>25</sup> in the system involving an increase in the viscosity of the displaced liquid, the PAA solution and NaOH solution were used as the more- and less-viscous liquids, respectively. In the system involving a decrease in the viscosity of the displaced liquid, the more- and less-viscous liquids were the SPA solution and hydrochloric acid (HCl) solution, respectively. The chemical reactions taking place in the systems involving an increase in the viscosity and a decrease in the viscosity were expressed as Eqs. (1) and (2), respectively. These reactions are essentially neutralization reactions and thus can be treated as instantaneous ones,



The present study made use of the dependence of the viscosities of the PAA solution and the SPA solution on  $pH$  as well as in the work of Nagatsu *et al.*<sup>25</sup> The present study used the polymer solutions as the less-viscous liquid.

In the system involving an increase in the viscosity of the displacing liquid, 0.5 wt % PAA solution (whose molecular weight is  $1 \times 10^6$  and which is manufactured by Wako, Japan) was used as the less-viscous liquid. Figure 1 shows the viscosity of the 0.5 wt % PAA solution including NaOH at a given concentration,  $c_{\text{NaOH}}$ . In this figure, the  $pH$  of each solution is also shown. This figure is the same as Fig. 1 in the

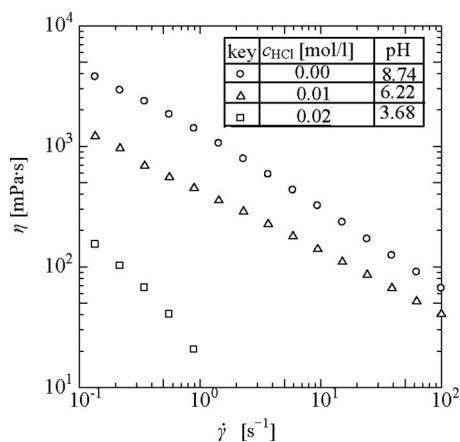


FIG. 2. Viscosity measurement of 0.3 wt % SPA solution including hydrochloric acid (HCl) at a given concentration,  $c_{\text{HCl}}$ .

work of Nagatsu *et al.*<sup>25</sup> The shear viscosity,  $\eta$ , exhibits shear-thinning behavior independent of  $c_{\text{NaOH}}$ . Regardless of shear rate,  $\dot{\gamma}$ ,  $\eta$  increases with  $c_{\text{NaOH}}$  or  $\text{pH}$  up to  $c_{\text{NaOH}}=0.065$  mol/l or  $\text{pH}=8.75$ . However,  $\eta$  decreases with an increase in  $c_{\text{NaOH}}$  when  $c_{\text{NaOH}}$  is larger than 0.065 mol/l or the  $\text{pH}$  is larger than 8.75. It is known that this is caused by an excess of addition of NaOH, which produces sodium counterions that in turn reduce the electrostatic repulsion of polymer chains,<sup>27</sup> as was already discussed in the work of Nagatsu *et al.*<sup>25</sup> In the present study, the more-viscous liquid were 99 wt% glycerin solution including NaOH at a given concentration,  $c_{m0,\text{NaOH}}$ . Here,  $c_{m0,\text{NaOH}}$  was varied up to  $c_{m0,\text{NaOH}}=0.2$  mol/l. We confirmed that the viscosity of the 99 wt % solution including NaOH was independent of  $c_{m0,\text{NaOH}}$  within the range employed here, and its value was 1 Pa·s. Note that the chemical reaction taking place in this system is that shown in Eq. (1).

In the system involving a decrease in the viscosity of the displacing liquid, 0.3 wt % SPA solution (whose molecular weight is  $2.2\sim 6.6\times 10^6$  and which is manufactured by Wako, Japan) was used as the less-viscous liquid. Figure 2 shows the viscosity of the 0.3 wt % SPA solution including HCl at a given concentration,  $c_{\text{HCl}}$ . Regardless of  $\dot{\gamma}$ ,  $\eta$  decreases with an increase in  $c_{\text{HCl}}$  or a decrease in  $\text{pH}$ . In the present study, the more-viscous liquid was 88 wt % starch syrup solution including HCl at a given concentration,  $c_{m0,\text{HCl}}$ . Here,  $c_{m0,\text{HCl}}$  was varied up to  $c_{m0,\text{NaOH}}=0.05$  mol/l. We confirmed that the viscosity of the 88 wt % starch syrup solution including HCl was independent of  $c_{m0,\text{HCl}}$  within the range employed here, and its value was 10 Pa·s. Note that the chemical reaction taking place in this system is that shown in Eq. (2).

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

System	More-viscous liquid	Less-viscous liquid	Chemical reaction
Involving a viscosity increase	99 wt % glycerin solution including NaOH at $c_{m0,\text{NaOH}}$	0.5 wt % PAA solution	Equation (1)
Involving a viscosity decrease	88 wt % starch syrup solution including HCl at $c_{m0,\text{HCl}}$	0.3 wt % SPA solution	Equation (2)

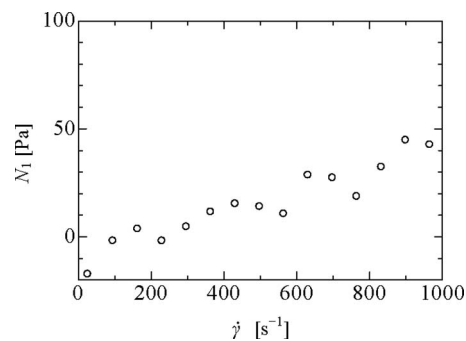


FIG. 3. Measurement of first normal stress difference,  $N_1$ , of 0.3 wt % SPA solution.

Polymer solutions, in general, simultaneously have two non-Newtonian characteristics, that is, the dependence of viscosity on shear rate and elasticity. It is therefore necessary to discuss the elastic properties of the polymer solution used. We used a rheometer (HAAKE RS600) to measure the first normal stress difference,  $N_1$ , which corresponds to the elastic property, of the 0.3 wt % SPA solution, which is expected to be the most elastic polymer solution used in the present study. The result is shown in Fig. 3. No measurable  $N_1$  was found in the range of  $\dot{\gamma} < 200$  s<sup>-1</sup>, while  $N_1$  was measurable and was seen to increase with  $\dot{\gamma}$  in the range of  $\dot{\gamma} > 200$  s<sup>-1</sup>. These results indicate that in the range of  $\dot{\gamma} < 200$  s<sup>-1</sup>, elastic effects are negligible for both polymer solutions, although elastic effects are known to influence the viscous fingering pattern, as mentioned in Sec. I. We therefore used the combination of liquids mentioned above and conducted viscous fingering experiment under the condition in which shear rate is less than 200 s<sup>-1</sup> to investigate the effects of viscosity changes due to instantaneous chemical reactions, without considering an elastic change caused by the reactions. The liquids and the reactions used in the present experiments are summarized in Table I.

For both systems,  $c_{m0,\text{NaOH}}=0$  mol/l and  $c_{m0,\text{HCl}}=0$  mol/l mean the nonreactive case. In all experiments, the less-viscous liquid was dyed blue by indigo carmine for visualization of the fingering.

## B. Viscous fingering experiment

The viscous fingering experiment was conducted using a radial Hele-Shaw cell. The experimental setup was the same as that used in our previous study.<sup>25</sup> In the present study, the gap width  $b$  was set as  $b=0.3$  mm. The bulk finger-advancement velocity,  $U$ , is defined in Eq. (3) as well as in the work of Nagatsu *et al.*<sup>25</sup> as follows:

$$U = \frac{q}{2\pi Rb}, \quad (3)$$

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 between the two liquids circular. The Péclet number,  $Pe$ , is defined in Eq. (4) as well as in the work of Nagatsu *et al.*,<sup>25</sup> as follows:

$$Pe = \frac{RU}{D} = \frac{q}{2\pi bD}, \quad (4)$$

where  $D$  is the diffusion coefficient between the more- and less-viscous liquids. In the present study,  $D$  was estimated to be  $1 \times 10^{-10}$  m<sup>2</sup>/s on the basis of the measurement of diffusion coefficient between glycerin and water by Petitjeans and Maxworthy.<sup>28</sup> From Eq. (4), we see that  $Pe$  is proportional to  $U$ , and thus in the present study it is used as a parameter indicating the bulk finger-advancement velocity. Because  $b$  is constant here,  $Pe$  is also proportional to  $q$ .

As in the work of Nagatsu *et al.*,<sup>25</sup> the shear rate in the vicinity of the fingertip,  $\dot{\gamma}_f$ , is roughly estimated in Eq. (5) as follows:

$$\dot{\gamma}_f = \frac{U}{b/2} = \frac{q}{\pi Rb^2}. \quad (5)$$

From Eq. (3),  $U$  is largest at the injection hole at  $R=2$  mm (the radius of the injection hole for liquids in the Hele-Shaw cell is 2 mm). In the present experiments, we examined the condition of  $\dot{\gamma}_f$  at  $R=2$  mm in the range of  $1.9 \times 10^{-1} \leq \dot{\gamma}_f \leq 1.9 \times 10^2$  s<sup>-1</sup>, resulting in negligible elastic effects. This condition corresponds to  $5.8 \times 10^4 \leq Pe \leq 5.6 \times 10^5$  in terms of  $Pe$ .

### III. RESULTS

#### A. Fingering pattern as affected by change in the viscosity of the displacing liquid due to the chemical reactions

Figures 4(a) and 4(b) show the typical time evolution of miscible viscous fingering (a) without the reaction and (b) with the reaction in the system involving the viscosity increase under the condition of  $Pe=5.8 \times 10^5$ . For the reactive case (b),  $c_{m0,NaOH}$  is 0.02 mol/l. Here,  $r_{max}$  is defined as the length of the longest finger in each fingering pattern. Images showing the almost same  $r_{max}$  are seen in Figs. 4(a) and 4(b). In the present study as well as in the work of Nagatsu *et al.*,<sup>25</sup> the fingering pattern area's density,  $d_a$ , which is defined as the ratio of the area occupied by the pattern within the circle with a radius  $r_{max}$  to the area of the circle,  $\pi r_{max}^2$ , is employed as a quantitative evaluation of the fingering pattern. Figure 4(c) shows the variations in  $d_a$  with  $r_{max}$  without and with the reaction for this system, where four experimental results are shown for each condition. Here, the nonreactive and reactive results are shown as open and closed plots, respectively. Note that the circle plots correspond to the results shown in Figs. 4(a) and 4(b). We can see the deviation in  $d_a$  is relatively large for small  $r_{max}$  since it is easier for the

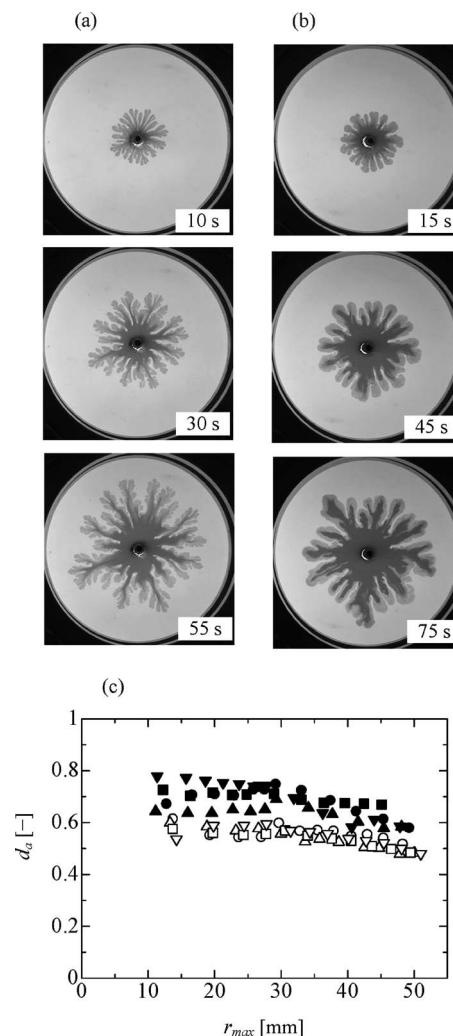


FIG. 4. Time evolutions of typical miscible viscous fingering (a) without the reaction and (b) with the reaction in the system involving an increase in the viscosity. For both (a) and (b),  $r_{max}$  increases from top to bottom:  $r_{max}=20, 33,$  and  $45$  mm. Time is shown in the lower right of each image. (c) Relationships between  $d_a$  and  $r_{max}$  of the fingering patterns with and without the reaction shown in (a) and (b). In (c), the open and closed plots represent the nonreactive and reactive cases, respectively. Different types of plots mean different experiments for each condition. The circle plots correspond to the results shown in (a) and (b).

difference in the propagation speed between some fingers to influence the values of  $d_a$  when  $r_{max}$  is small. Nevertheless, we find that  $d_a$  in the reactive case is larger for this system than that in the nonreactive case for any  $r_{max}$ . This is caused by the suppression of the shielding effect and the widening of the fingers by the reaction as is shown in Figs. 4(a) and 4(b).

Figure 5 corresponds to Fig. 4 for the system involving a decrease in the viscosity under the condition of  $Pe=5.8 \times 10^5$ . For the reactive case (b),  $c_{m0,HCl}$  is 0.05 mol/l. In Figs. 5(a) and 5(b), images showing the almost same  $r_{max}$  are also seen. Figure 5(c) shows the variation in  $d_a$  with  $r_{max}$  without and with the reaction for this system. In Fig. 5(c), four experimental results are also shown for each condition in which the nonreactive and reactive results are shown as open and closed plots, respectively. Note that the circle plots correspond to the results shown in Figs. 5(a) and 5(b). Here,



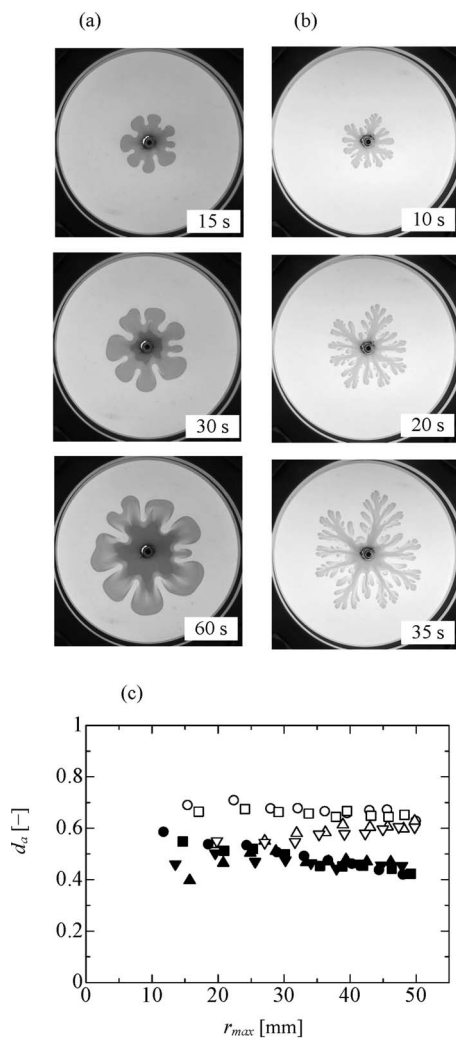


FIG. 5. Time evolutions of typical miscible viscous fingering (a) without the reaction and (b) with the reaction in the system involving the viscosity decrease. For both (a) and (b),  $r_{\max}$  increases from top to bottom:  $r_{\max} = 19$ , 29, and 40 mm. Time is shown in the lower right of each image. (c) Relationships between  $d_a$  and  $r_{\max}$  of the fingering patterns with and without the reaction shown in (a) and (b). In (c), the open and closed plots represent the nonreactive and reactive cases, respectively. Different types of plots mean different experiments for each condition. The circle plots correspond to the results shown in (a) and (b).

the deviation in  $d_a$  at small  $r_{\max}$  is larger especially for the nonreactive cases. This is because the number of the fingers in the present nonreactive case is small as shown in Fig. 5(a), which also leads to the fact that it is easier for the difference in the propagation speed between some fingers to influence the values of  $d_a$ . Nevertheless, we find  $d_a$  in the reactive case is smaller for this system than that in the nonreactive case for any  $r_{\max}$ . This is caused by the enhancement of the shielding effect and narrowing of the fingers by the reaction as is shown in Figs. 5(a) and 5(b).

In Figs. 4 and 5, we can observe that the color depth of the dye becomes light around the fingertips, which is caused by some of the displaced fluid being left along the plates of the cell during the finger formation. This phenomenon can be seen in miscible displacement of the glycerin-water system in Hele-Shaw cells at relatively low rate.<sup>14,15,17</sup> Also, the corresponding phenomenon in capillary tubes was extensively

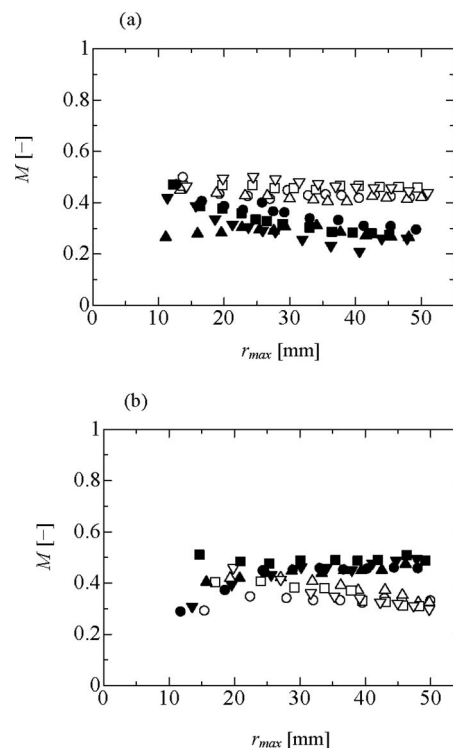


FIG. 6.  $M$  for (a) corresponding data in Fig. 4(c) and (b) corresponding data in Fig. 5(c).

examined experimentally by Petitjeans and Maxworthy<sup>28</sup> and numerically by Chen and Meiburg,<sup>29</sup> where the fraction of the displaced fluid left near the wall of the capillary was found to be affected strongly by the viscosity ratio and somehow by  $Pe$  as well. For large  $Pe$ , the fraction increases with the viscosity contrast. In the present study, this phenomenon is known as the third-dimensional effects (effects of the third dimension, i.e., in the gap). Here, we quantitatively investigate whether there are any significant influences to this third-dimensional formation when the viscosities are changed due to the reaction. To do so, we compare the actual area occupied by the fingering pattern, denoted as  $A$ , and the actual volume of the displacing fluid injected ( $=qt$ ). In other words, we measure the averaged fraction of the displaced fluid behind the wall over whole the fingering pattern,  $M$ , defined as

$$M = \frac{b - \frac{qt}{A}}{b} = 1 - \frac{qt}{bA}. \quad (6)$$

Here, if there is no third-dimensional effects,  $M=0$ . Also, as the third-dimensional effects become more significant;  $M$  is larger. In Figs. 6(a) and 6(b), we show the measured values of  $M$  for corresponding data described in Figs. 4(c) and 5(c), respectively. As shown in Fig. 6(a),  $M$  in the reactive case is smaller than that in the nonreactive case for any  $r_{\max}$  in the system involving an increase in the viscosity. In contrast, in the system involving a decrease in the viscosity as shown in Fig. 6(b),  $M$  in the reactive case is larger than that in the nonreactive case for except small  $r_{\max}$ , although the deviation is large there. In other words, the reaction suppresses the third dimension effects in the system involving an increase in the

viscosity, while it enhances in the system involving a decrease in the viscosity. These results intuitively have a good agreement with the results previously obtained results mentioned above<sup>28,29</sup> (the fraction increases with the viscosity contrast). This is because the viscosity contrast is decreased by the reaction in the system involving an increase in the viscosity, whereas it is increased by the reaction in the system involving a decrease in the viscosity.

Here we assume the cases in which only the third dimension effects are changed by the reaction without any changes in the fingering pattern in the two dimensions (in the  $r$ - $\theta$  plane). In these cases,  $d_a$  is not changed by the reaction. In this sense, we expect that the changes in the third dimension effects are independent of the observed changes in  $d_a$  by the reactions. Alternatively, we can say as follows. Under the same amount of the injected fluid, an increase in the third dimension effects leads to an increase in the area occupied the pattern. However, whether  $d_a$  is increased or decreased depends on how the area spreads.

It should be emphasized that the results obtained by Figs. 4 and 5 are essentially the same as those in the case where the viscosity of the more-viscous liquid is changed by the instantaneous reactions obtained by Nagatsu *et al.*<sup>25</sup> In other words, the shielding effect is suppressed, and fingers are widened when the viscosity is increased by the instantaneous reaction even if an increase in the viscosity occurs in the more-viscous liquid or in the less-viscous liquid; in contrast, the shielding effect is enhanced and fingers are narrowed when the viscosity is decreased by the instantaneous reaction even if a decrease in the viscosity occurs in the more-viscous liquid or in the less-viscous liquid. These results indicate that the effects of viscosity's changes due to instantaneous reactions on miscible viscous fingering pattern are independent of whether the viscosity changes occur in the more-viscous liquid or in the less-viscous liquid.

## B. Effects of reactant concentration in the more-viscous liquid on the fingering pattern

Figure 7 shows the variation in  $d_a$  at  $r_{\max}=48$  mm with  $c_{m0,\text{NaOH}}$  when  $\text{Pe}=5.8 \times 10^5$  for the system involving an increase in the viscosity along with images of the typical fingering pattern in the condition of each plot. Here, the plots show the average of four experiments for each condition. In addition, error bars are presented. It should be mentioned that similarly in Figs. 8–12, the plots show the average value of four experiments for each condition, and the error bars are presented. In the experimental conditions tested,  $d_a$  increases with  $c_{m0,\text{NaOH}}$  up to  $c_{m0,\text{NaOH}}=0.02$  mol/l. However,  $d_a$  decreases with  $c_{m0,\text{NaOH}}$  when  $c_{m0,\text{NaOH}}$  is more than 0.02 mol/l. This relationship between  $d_a$  and  $c_{m0,\text{NaOH}}$  is similar to that between the shear viscosity  $\eta$  of the 0.5 wt % PAA solution including NaOH at a concentration of  $c_{\text{NaOH}}$  and its pH as shown in Fig. 1. Figure 8 shows the correspondence to Fig. 7 for the system involving a decrease in the viscosity. As shown in Fig. 8,  $d_a$  decreases monotonically with  $c_{m0,\text{HCl}}$ . This relationship between  $d_a$  and  $c_{m0,\text{HCl}}$  is, in turn, similar to that between the shear viscosity  $\eta$  of the 0.3 wt % SPA solution including HCl at a concentration of  $c_{\text{HCl}}$  and its pH as

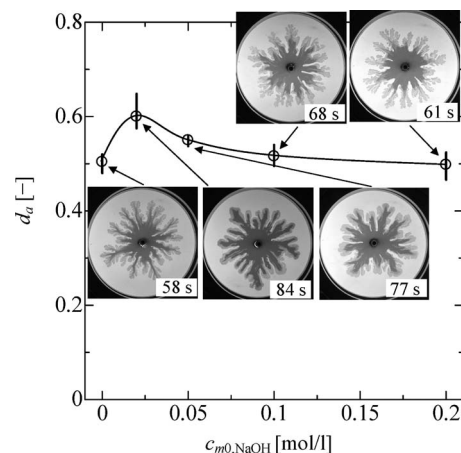


FIG. 7. Variation in  $d_a$  with  $c_{m0,\text{NaOH}}$  at  $r_{\max}=48$  mm in the system involving an increase in the viscosity along with images of the fingering pattern in the conditions corresponding to each plot. Time is shown in the lower right of each image. The plots show the average of four experiments for each condition. Error bars are also presented.

shown in Fig. 2. It should be emphasized that the results obtained in Figs. 7 and 8 are also essentially the same as those obtained when the reactant concentration in the less-viscous liquid is varied in the case where the viscosity of the more-viscous liquid is changed by the instantaneous reactions.<sup>25</sup> In the present study, we measure the fractal dimension,  $d_f$ , of the fingering pattern using the box counting method.<sup>20,30,31</sup> The measured  $d_f$  for the conditions in Figs. 7 and 8 are shown in Figs. 9(a) and 9(b), respectively. We have found that the results for  $d_f$  are qualitatively the same as those for  $d_a$  in both the systems involving an increase or a decrease in the viscosity.

## C. Effects of bulk finger-advancement velocity on the fingering pattern

Figures 10 and 11 show the variation in  $d_a$  at  $r_{\max}=48$  mm with  $\text{Pe}$  for the system involving an increase in the viscosity under the condition of  $c_{m0,\text{NaOH}}=0.02$  mol/l and for the system involving a decrease in the viscosity under the

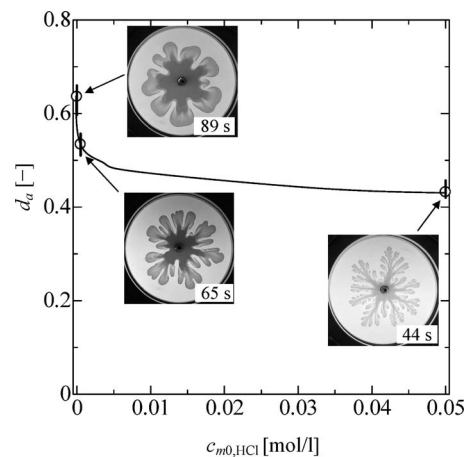


FIG. 8. Variation in  $d_a$  with  $c_{m0,\text{HCl}}$  at  $r_{\max}=48$  mm in the system involving a decrease in the viscosity along with images of the fingering pattern in the conditions corresponding to each plot. Time is shown in the lower right of each image. The plots show the average of four experiments for each condition. Error bars are also presented.

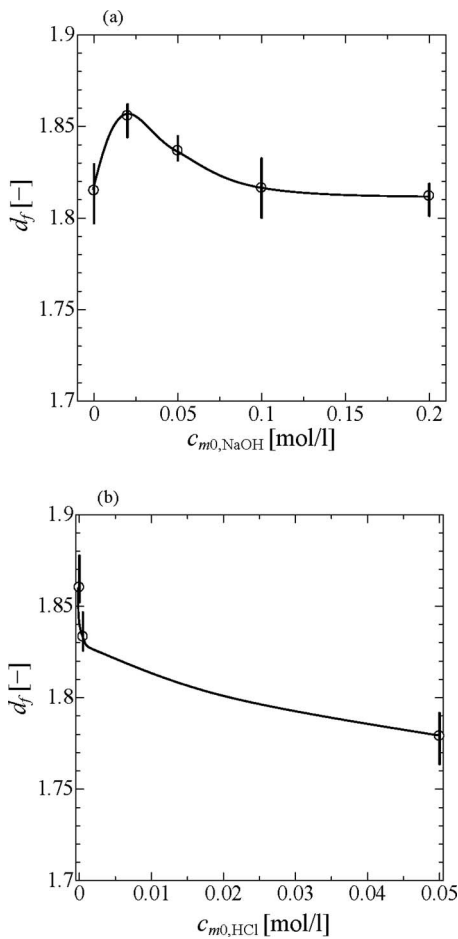


FIG. 9.  $d_f$  for (a) the condition in Fig. 7 and (b) the condition in Fig. 8. The plots show the average of four experiments for each condition. Error bars are also presented.

condition of  $c_{m0,HCl}=0.05$  mol/l, respectively. In both figures, images of the typical fingering pattern in each condition corresponding to each plot are shown. Without regard to  $Pe$ ,  $d_a$  with the reaction is larger than that without the reaction

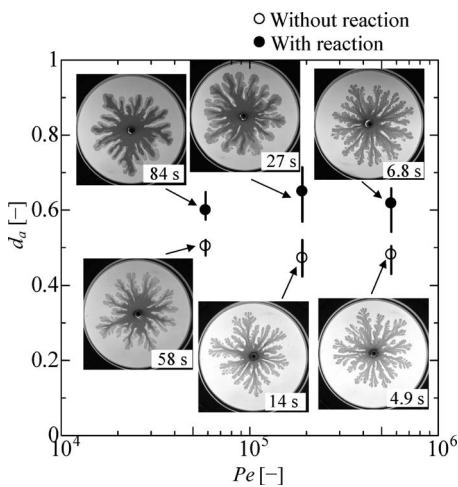


FIG. 10. Variation in  $d_a$  with  $Pe$  at  $r_{max}=48$  mm in the system involving an increase in the viscosity along with images of the fingering pattern in the conditions corresponding to each plot. Time is shown in the lower right of each image. The plots show the average of four experiments for each condition. Error bars are also presented.

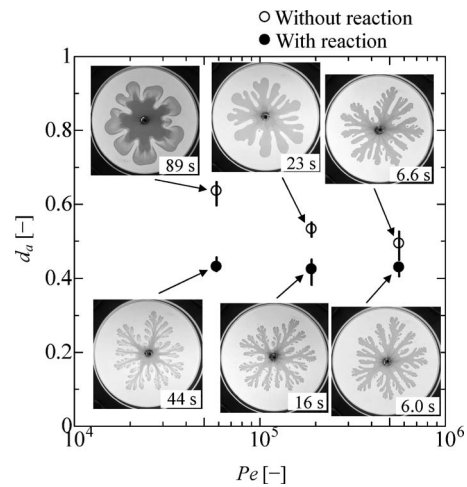


FIG. 11. Variation in  $d_a$  with  $Pe$  at  $r_{max}=48$  mm in the system involving a decrease in the viscosity along with images of the fingering pattern in the conditions corresponding to each plot. Time is shown in the lower right of each image. The plots show the average of four experiments for each condition. Error bars are also presented.

for the system involving an increase in the viscosity (Fig. 10), while  $d_a$  with the reaction is smaller than that without the reaction for the system involving a decrease in the viscosity (Fig. 11). The measured  $d_f$  for the conditions in Figs.

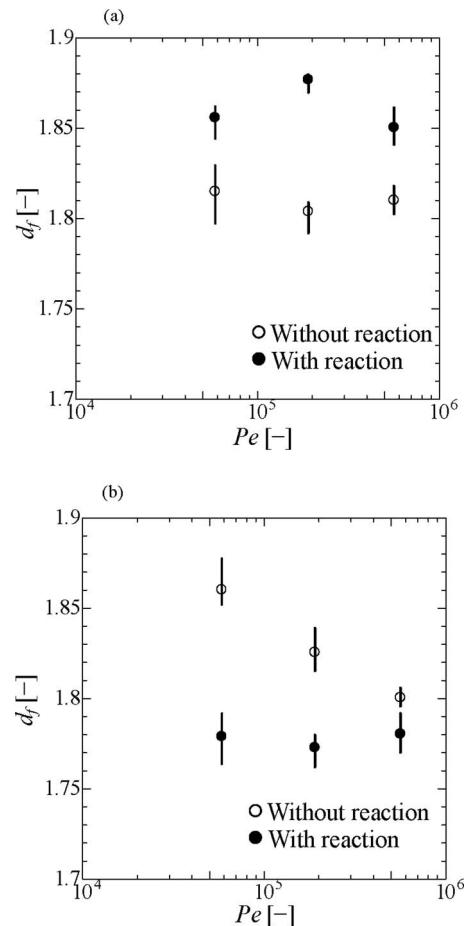


FIG. 12.  $d_f$  for (a) the condition in Fig. 10 and (b) the condition in Fig. 11. The plots show the average of four experiments for each condition. Error bars are also presented.

10 and 11 are shown in Figs. 12(a) and 12(b), respectively. Again, we have found that the results for  $d_f$  are qualitatively the same as those for  $d_a$  in both the systems involving an increase or a decrease in the viscosity. These results indicate that the reactions influence the fingering pattern even when the bulk finger-advancement velocity is increased within the present experimental conditions. This is consistent with a sufficiently large  $D_a$ . The appearance of influence of the reaction regardless of  $Pe$  under the experimental condition employed was also observed by Nagatsu *et al.*<sup>25</sup>

## IV. DISCUSSION

### A. A proposed mechanism for the obtained results

In the previous section, we showed that the effects on the fingering pattern of changes in the viscosity of the displacing liquid due to the instantaneous reactions are essentially the same as those of changes in the viscosity of the displaced liquid reported by Nagatsu *et al.*<sup>25</sup> Now we discuss the reason why the effects of the viscosity's changes on the fingering pattern are independent of whether the viscosity's changes occur in the displaced liquid or in the displacing liquid. Here, we focus on the suppression of the shielding effect by an increase in the displaced liquid's viscosity or by an increase in the displacing liquid's viscosity. In the work of Nagatsu *et al.*,<sup>25</sup> we hypothesized that the rate of chemical reaction is larger in the tip of the advancing finger than in the tips of shielded fingers. This is because in the system involving instantaneous reactions, the overall reaction rate depends on the amount of the reactants provided, and the flux of the reactant is larger in the advancing the finger than in the shielded fingers. Under this hypothesis, for the system involving an increase in the displaced liquid's viscosity, the viscosity of the more-viscous liquid will be larger in the vicinity of the tip of the advancing finger than in the vicinity of the tips of the shielded fingers. It can be considered that the displacing liquid can more easily penetrate the region with relatively lower viscosity than it can in the region with relatively higher viscosity. This results in the suppression of the shielding effects in the system involving an increase in the displaced liquid's viscosity. For the system involving an increase in the displacing liquid's viscosity, the situation under which the rate of chemical reaction is larger in the tip of the advancing finger than in the tips of shielded fingers similarly occurs. As a result, in this case, the viscosity of the less-viscous liquid is larger in the vicinity of the tip of the advancing finger than in the vicinity of the tip of the shielded fingers. The fact that the displacing liquid afterward injected can more easily penetrate the region with relatively lower viscosity also results in the suppression of the shielding effect. The enhancement of the shielding effect in the systems involving a decrease in the displaced liquid's viscosity and that in the displacing liquid's viscosity can be similarly explained.

The mechanism of the finger widening in the system involving an increase in the displaced liquid's viscosity was proposed as follows by Nagatsu *et al.*<sup>25</sup> We, in turn, hypothesized the unequal overall reaction rate along the interface of a single finger. The overall reaction rate is considered to be

higher around the tip than around the base because of larger reactant flux around the tip. In the system involving an increase in viscosity of the displaced liquid, the viscosity of the more-viscous liquid is higher around the tip than around the base. The concept that the displacing liquid can more easily penetrate the region with relatively lower viscosity than it can the region with relatively higher viscosity leads to finger widening. In the present system involving an increase in viscosity of the displacing liquid, the situation under which the overall reaction rate is higher around the tip than around the base similarly occurs. As a result, in this case the relatively higher viscosity around the tip takes place in the less-viscous liquid. The concept that the displacing liquid afterward injected can more easily penetrate the region with relatively lower viscosity also results in finger widening. Finger narrowing in the systems involving a decrease in the displaced liquid's viscosity and that in the displacing liquid's viscosity can be similarly explained.

### B. Consideration based on underlying viscosity profiles reconstructed by one-dimensional reaction-diffusion concentration profiles

The most important result in the present study is that the effects of changes in the viscosity due to the instantaneous reactions on the fingering pattern are independent of whether the changes occur in the displaced liquid or in the displacing liquid. In the system in which the changes occur in the displaced liquid,<sup>25</sup> the viscosity contrast intuitively seems to be larger when the viscosity is increased, while it seems to be smaller when the viscosity is decreased. In the present system in which the changes occur in the displacing liquid, the viscosity contrast seems to be smaller when the viscosity is increased, while it seems to be larger when the viscosity is decreased. Therefore, one would intuitively expect that the effects of changes in the viscosity of the displaced liquid on the fingering dynamics are opposite to those of the displacing liquid. The present experimental results, however, show that this expectation is not true. In this section, we discuss the independence of whether changes in the viscosity occur in the displaced liquid or in the displacing liquid in terms of the concept of underlying viscosity profiles reconstructed by one-dimensional reaction-diffusion concentration profiles. Note that to our best knowledge, the concept of underlying density profiles reconstructed one-dimensional reaction-diffusion concentration profiles was first introduced by Rongy *et al.* in which the effects of changes in density by chemical reaction on reacting fluid dynamics were theoretically investigated.<sup>32</sup>

In the previous system in which the viscosity of the displaced liquid was changed,<sup>25</sup> the acid or base solutions were the less-viscous liquids, while the polymer solutions were the more-viscous liquids. If we denote the acid or base by chemical species  $A$  and the polymers by chemical species  $B$ , the chemical reactions employed are expressed as  $A+B \rightarrow C$  (chemical species  $C$  is the product). Now for simplicity we consider that the initial concentrations of species  $A$  and  $B$  are



both equal to  $a_0$ . Three one-dimensional diffusion-reaction equations for concentrations  $a$ ,  $b$ , and  $c$  of the species  $A$ ,  $B$ , and  $C$  are written as

$$\frac{\partial a}{\partial t} = D_A \frac{\partial^2 a}{\partial x^2} - kab, \quad (7)$$

$$\frac{\partial b}{\partial t} = D_B \frac{\partial^2 b}{\partial x^2} - kab, \quad (8)$$

$$\frac{\partial c}{\partial t} = D_C \frac{\partial^2 c}{\partial x^2} + kab, \quad (9)$$

where  $D_{A,B,C}$  are the diffusion coefficients of the species  $A$ ,  $B$ , and  $C$ , respectively, and  $k$  is the kinetic constant of the chemical reaction. Here, we consider that the diffusion coefficients are equal, i.e.,  $D_A = D_B = D_C = D$ . In this system, the viscosity depends on the concentrations  $b$  and  $c$ , while it is independent of  $a$ . Thus, the viscosity is written as  $\mu = \mu(b, c)$ . We define the viscosity of the (displacing) less-viscous fluid as  $\mu_L = \mu_0$  and the viscosity of the (displaced) more-viscous fluid as  $\mu_M = \mu(a_0, 0)$ . The viscosity of the product is also defined as  $\mu_C = \mu(0, a_0)$ . Here, we define  $\mu_M$  and  $\mu_C$  as the viscosity of the solution when only one species,  $B$  or  $C$ , is present in concentration  $a_0$ . Following earlier studies,<sup>19,23,24,33</sup> an exponential dependence of the viscosity on the concentrations is adopted as follows:

$$\mu = \mu_0 \exp\left(R_M \frac{b}{a_0} + R_C \frac{c}{a_0}\right), \quad (10)$$

where  $R_M$  and  $R_C$  are the log-mobility ratios defined as

$$R_M = \ln\left(\frac{\mu_M}{\mu_0}\right) \quad \text{and} \quad R_C = \ln\left(\frac{\mu_C}{\mu_0}\right). \quad (11)$$

Here, we consider  $R_M > 0$  because  $\mu_M > \mu_0$ . An increase in the viscosity is indicated by  $R_C > R_M$ . In contrast, a decrease in the viscosity is indicated by  $R_C < R_M$ .

We then nondimensionalize the equations by the characteristic length  $L$  and diffusive time  $\tau_d = L^2/D$ , concentration  $a_0$ , and viscosity  $\mu_0$ . The nondimensional concentrations vary between 0 and 1. Nondimensional equations are obtained as follows:

$$\frac{\partial a^*}{\partial t^*} = \frac{\partial^2 a^*}{\partial x^{*2}} - D_a a^* b^*, \quad (12)$$

$$\frac{\partial b^*}{\partial t^*} = \frac{\partial^2 b^*}{\partial x^{*2}} - D_a a^* b^*, \quad (13)$$

$$\frac{\partial c^*}{\partial t^*} = \frac{\partial^2 c^*}{\partial x^{*2}} + D_a a^* b^*, \quad (14)$$

$$\mu^* = \exp(R_M b^* + R_C c^*), \quad (15)$$

where  $D_a$  is the dimensionless Damköhler number,

$$D_a = \frac{L^2 k a_0}{D}, \quad (16)$$

which corresponds to the ratio between the characteristic diffusive time  $\tau_d$  and chemical reaction time  $\tau_c = 1/k a_0$ .

In the present system in which the viscosity of the displacing liquid is changed, based on Eqs. (1) and (2), if we denote the polymers by species  $A$  and the base or acid by species  $B$ , then the  $A+B \rightarrow C$  chemical reaction takes place as well as in the previous system.<sup>25</sup> It should be noted that the displaced liquids contain glycerin or starch syrup, which we denote species  $E$  as neutral to the reaction. Now for simplicity we also consider that the initial concentrations of each species  $A$ ,  $B$ , and  $E$  take the same,  $a_0$ . In the present system, the viscosity depends on the concentrations of species  $A$ ,  $C$ , and  $E$ , denoted by  $a$ ,  $c$ , and  $e$ , respectively. In contrast, the viscosity is independent of the concentration of species  $B$  denoted by  $b$ . In other words,  $\mu = \mu(a, c, e)$ . We define the viscosity of the (displacing) less-viscous fluid,  $\mu_L = \mu(a_0, 0, 0)$ , and the viscosity of the (displaced) more-viscous fluid,  $\mu_M = \mu(0, 0, a_0)$ . We also define the viscosity of the product as  $\mu_C = \mu(0, a_0, 0)$ . If the exponential dependence of the viscosity on the concentrations is also adopted, the viscosity is written as

$$\mu = \mu_0 \exp\left(R_L \frac{a}{a_0} + R_C \frac{c}{a_0} + R_M \frac{e}{a_0}\right), \quad (17)$$

where  $R_L$ ,  $R_C$ , and  $R_M$  are the log-mobility ratios defined as

$$R_L = \ln\left(\frac{\mu_L}{\mu_0}\right), \quad R_C = \ln\left(\frac{\mu_C}{\mu_0}\right), \quad \text{and} \quad R_M = \ln\left(\frac{\mu_M}{\mu_0}\right). \quad (18)$$

Now, we consider  $R_M > R_L$  because  $\mu_M > \mu_L$ . In the present system, an increase in the viscosity is indicated by  $R_C > R_L$ . In contrast, a decrease in the viscosity is indicated by  $R_C < R_L$ . Four one-dimensional dimensionless diffusion-reaction equations for concentrations  $a$ ,  $b$ ,  $c$ , and  $e$  are similarly obtained under which all diffusion coefficients are the same and nondimensional viscosity is similarly obtained,

$$\frac{\partial a^*}{\partial t^*} = \frac{\partial^2 a^*}{\partial x^{*2}} - D_a a^* b^*, \quad (19)$$

$$\frac{\partial b^*}{\partial t^*} = \frac{\partial^2 b^*}{\partial x^{*2}} - D_a a^* b^*, \quad (20)$$

$$\frac{\partial c^*}{\partial t^*} = \frac{\partial^2 c^*}{\partial x^{*2}} + D_a a^* b^*, \quad (21)$$

$$\frac{\partial e^*}{\partial t^*} = \frac{\partial^2 e^*}{\partial x^{*2}}, \quad (22)$$

$$\mu^* = \exp(R_L a^* + R_C c^* + R_M e^*). \quad (23)$$

First we discuss the system in which the viscosity of the displaced liquid is changed. In Figs. 13(a) and 13(b), we show profiles of the dimensionless concentrations obtained by Eqs. (12)–(14) for the nonreactive case ( $D_a = 0$ ) and the

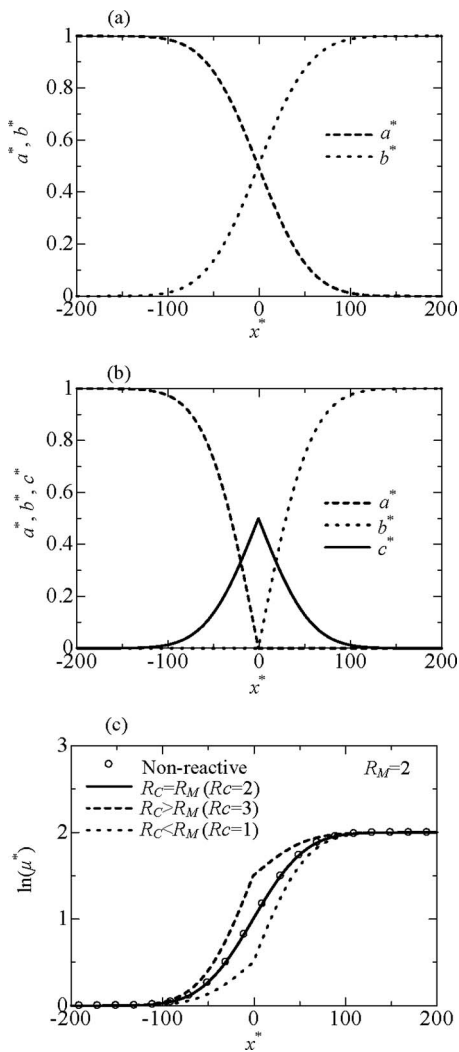


FIG. 13. Profiles of the dimensionless concentrations obtained by Eqs. (12)–(14) for (a) the nonreactive case ( $D_a=0$ ) and (b) the reactive case (infinite  $D_a$ ) are at  $t=1000$ . (c) The underlying nondimensional viscosity profiles at  $t=1000$  are reconstructed by Eq. (15). Here, the cases of  $R_M=2$  are drawn. In the reactive case, the cases of  $R_C=1, 2$ , and 3 correspond to the cases of  $R_M>R_C$ ,  $R_M=R_C$ , and  $R_M<R_C$ , respectively.

reactive case in which  $D_a$  is set as infinity (in the experiment, the reactions are effectively instantaneous), respectively, at a fixed time. In Fig. 13(c), the underlying nondimensional viscosity profiles at the fixed time reconstructed by Eq. (15) are described. Here, the cases of  $R_M=2$  are drawn. In the reactive case, the cases of  $R_C=1, 2$ , and 3 correspond to the cases of  $R_M>R_C$ ,  $R_M=R_C$ , and  $R_M<R_C$ . It should be noted again that the case of  $R_M<R_C$  corresponds to the system involving an increase in the viscosity of the displaced liquid, while the case of  $R_M>R_C$  corresponds to the system involving a decrease in the viscosity of the displaced liquid. As shown in Fig. 13(c), the viscosity profile in the case of  $R_M=R_C$  is equivalent of that in the nonreactive case. In the system involving an increase in the viscosity, the viscosity profile moves up compared to that of the nonreactive case. In contrast, in the system involving a decrease in the viscosity, the viscosity profile moves down compared to that of the nonreactive case.

Next we discuss the present system in which the viscos-

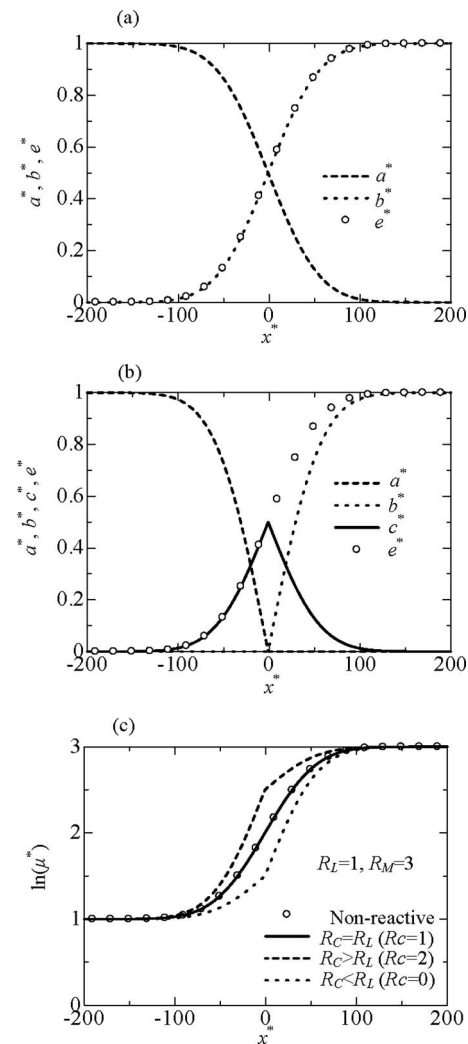


FIG. 14. Profiles of the dimensionless concentrations obtained by Eqs. (19)–(22) for (a) the nonreactive case ( $D_a=0$ ) and (b) the reactive case (infinite  $D_a$ ) are at  $t=1000$ . (c) The underlying nondimensional viscosity profiles at  $t=1000$  are reconstructed by Eq. (23). Here, the cases of  $R_L=1$  and  $R_M=3$  are drawn. In the reactive case, the cases of  $R_C=0, 1$ , and 2 correspond to the cases of  $R_L>R_C$ ,  $R_L=R_C$ , and  $R_L<R_C$ , respectively.

ity of the displacing liquid is changed. In Figs. 14(a) and 14(b), we show profiles of the dimensionless concentrations obtained by Eqs. (19)–(22) for the nonreactive case ( $D_a=0$ ) and the reactive case ( $D_a$  is infinity), respectively, at the fixed time. In Fig. 14(c), the underlying nondimensional viscosity profiles reconstructed by Eq. (23) at the fixed time are described. Here, the cases of  $R_L=1$  and  $R_M=3$  are drawn. In the reactive case, the cases of  $R_C=0, 1$ , and 2 correspond to the cases of  $R_L>R_C$ ,  $R_L=R_C$ , and  $R_L<R_C$ . It should be noted again that the case of  $R_L<R_C$  corresponds to the system involving an increase in the viscosity of the displacing liquid, while the case of  $R_L>R_C$  corresponds to the system involving a decrease in the viscosity of the displacing liquid. As shown in Fig. 14(c), the viscosity profile in the case of  $R_L=R_C$  is equivalent of that in the nonreactive case. In the system involving an increase in the viscosity, the viscosity profile moves up compared to that of the nonreactive case. In

contrast, in the system involving a decrease in the viscosity, the viscosity profile moves down compared to that of the nonreactive case.

The results obtained in Fig. 14(c) are essentially the same as those obtained in Fig. 13(c). In other words, the underlying viscosity profiles move up when the viscosity is increased by the reactions regardless of whether the increase occurs in the displaced liquid or in the displacing liquid. Reversely, the underlying viscosity profiles move down when the viscosity is decreased by the reaction regardless of whether the decrease occurs in the displaced liquid or in the displacing liquid. This discussion based on the concept of the underlying viscosity profiles reconstructed by one-dimensional diffusion-reaction concentration profiles can support the present and previous experimental results in which the effects of changes in the viscosity on the fingering dynamics are independent of whether the changes occur in the displaced liquid or in the displacing liquid.

### C. Relevance to other changes in viscous fingering induced by local changes in viscosity

As mentioned above, we have proposed the mechanism in which local changes in the viscosity due to the chemical reactions are responsible for the obtained experimental results. At the present, there are other known ways that local changes in the viscosity play a role in viscous fingering. One is by local changes in the viscosity due to non-Newtonian effects, while another is due to temperature effects. Here, we discuss the relevance of them.

First, we discuss the relevance of the present results to the changes in viscous fingering induced by local changes in the viscosity due to non-Newtonian effects. Several theoretical<sup>34</sup> and experimental<sup>10,11</sup> studies have demonstrated that the shear-thinning viscosity of non-Newtonian fluids, as the more-viscous fluid, narrows the finger width. It should be noted that the present and previous<sup>25</sup> experimental results show that the effects of changes in the viscosity by the instantaneous reactions on the fingering dynamics are independent of whether the viscosity changes occur in the less- or more-viscous fluids. In the studies involving the shear-thinning viscosity, the finger narrowing has been explained to be caused by a small viscosity in the vicinity of the finger tip due to a high shear rate there and the shear-thinning viscosity of the displaced fluid. In the system involving a decrease in the viscosity in the present and previous<sup>25</sup> studies, a small viscosity in the vicinity of the finger tip is induced by a higher rate of the reaction. In other words, in the previous<sup>25</sup> and present studies a local decrease in the viscosity near the finger tip is chemically induced, while that is mechanically induced in the studies involving the shear-thinning viscosity. Therefore, the finger narrowing observed in the present and previous<sup>25</sup> experimental systems involving a decrease in the viscosity is consistent with the finger narrowing by the shear-thinning viscosity.

In addition, we discuss the relevance of the present and previous<sup>25</sup> results to the fracturelike behavior in viscous fingering experiments using some non-Newtonian fluids as described by Maher *et al.*<sup>9,35,36</sup> They inferred that the fracture-

like instabilities are determined by the extreme shear-thinning viscosity of the non-Newtonian fluids. Now, we emphasize that the fracturelike pattern can be interpreted to arise from strong shielding effects. In the system involving a decrease in the viscosity in the previous<sup>25</sup> and present studies, the enhancement of the shielding effects is considered to be caused by a lower viscosity in the vicinity of the tip of the advancing finger than in the vicinity of the tips of the shielded fingers, which is induced by an unequal rate of the reaction. Based on the previous<sup>25</sup> and present studies, the strong shielding effects in the fracturelike pattern can be interpreted to be due to a lower viscosity in the vicinity of the tip of the advancing finger than in the vicinity of the tips of the shielded fingers, which is caused by a larger shear rate in the vicinity of the advancing finger and the extreme shear-thinning viscosity. Thus, we can mention that in the previous<sup>25</sup> and present studies, a difference in the viscosities in the vicinity of the tips of the advancing and shielded fingers is chemically induced, while the difference is mechanically induced in the experiments focusing on the fracturelike pattern. Therefore, the previous<sup>25</sup> and present results in the system involving a decrease in the viscosity support the inference by Maher and his co-workers mentioned above.

Fast *et al.*<sup>37</sup> theoretically showed the shear-thinning viscosity suppresses tip-splitting. In fact, in the previous<sup>25</sup> system the suppression of the tip-splitting seemed to occur in the system involving a decrease in the viscosity. Conversely, an enhancement of the tip-splitting seemed to occur in the system involving an increase in the viscosity. In this sense, the results in the previous<sup>25</sup> paper are consistent with the claim of Fast *et al.*<sup>37</sup> However, in the present system, the suppression of the tip-splitting seems to occur in the system involving an increase in viscosity rather than in the system involving a decrease in the viscosity. Also, the enhancement of the tip-splitting seems to occur in the system involving a decrease in the viscosity rather than in the system involving an increase in the viscosity. One of the possible reasons for this is that the suppression or enhancement of the tip-splitting may depend on whether changes in the viscosity occur in the displaced fluid or in the displacing fluid. Or, the range of changes in the viscosity may determine characteristics of the tip-splitting. Regarding this aspect, further future studies are needed.

Now, we discuss the relevance to the change in viscous fingering induced by local viscosity changes due to temperature effects.<sup>38,39</sup> We consider that the most relevant work is our recent study dealing with miscible viscous fingering in nonisothermal fields in radial Hele-Shaw cells.<sup>39</sup> In this study, we used pure glycerin at room temperature (20 °C) as the more-viscous liquid, while glycerin-water mixtures heated to 80 °C as the less-viscous liquids. We demonstrated that an increase in the viscosity of the less-viscous liquid induced by its cooling, due to heat loss to the plates of the cell, plays a major role in determining the pattern. Now we compare Figs. 5(a) and 5(f) in this paper. In Fig. 5(a), water displaces pure glycerin at 20 °C, while water displaces an 80 °C glycerin-water mixture involving 80 wt % glycerin displaces a 20 °C pure glycerin in Fig. 5(h). The viscosities of the displacing fluids at an inlet of the injection hole are

almost the same in both cases. In the nonisothermal case, the viscosity of the less-viscous liquid increases due to the temperature effect mentioned above, while it remains constant in the isothermal case. The fingering pattern in Fig. 5(h) is denser than that in Fig. 5(a). This indicates that an increase in the viscosity of the less-viscous liquid, due to the temperature effects, makes the pattern denser. Therefore, we find that both an increase in the viscosity of the less-viscous liquid by the reactions and that by the temperature effects make the pattern more dense.

## V. CONCLUSION

Experiments have been performed on the miscible viscous fingering involving changes in the viscosity of the displacing less-viscous liquid by the instantaneous reactions. We used the dependence of viscosity of the PAA solution or the SPA solution on pH as well as in the work of Nagatsu *et al.*<sup>25</sup> in which the effects of changes in the viscosity of the displaced more-viscous liquid by the instantaneous reactions on the fingering pattern were investigated. In the present study, the PAA solution or the SPA solution was used as the less-viscous liquid. We have found that the shielding effect is suppressed and the fingers are widened when the viscosity is increased. As a result, the fingering pattern becomes denser by the reaction. In contrast, the shielding effect is enhanced, and the fingers are narrowed when the viscosity is decreased. As a result, the fingering pattern becomes less dense by the reaction. These results are essentially same as those obtained by Nagatsu *et al.*<sup>25</sup> This shows that the effects of changes in viscosity due to instantaneous reactions are independent of whether the changes occur in the displaced more-viscous liquid or in the displacing less-viscous liquid. A mechanism for the independence is discussed.

Effects on the present systems of reactant concentration in the more-viscous liquid and those of bulk finger-advancement velocity have also been investigated. In the system involving an increase in the viscosity, an increase in the reactant concentration ( $c_{m0,NaOH}$ ) shows a greater effect on the change in the fingering pattern as  $c_{m0,NaOH}$  increases up to a threshold value, while over that threshold value, the effect on the change in the fingering pattern decreases with the increase in  $c_{m0,NaOH}$ . In the system involving a decrease in the viscosity, an increase in the reactant concentration ( $c_{m0,HCl}$ ) 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. Under the experimental condition of bulk finger-advancement velocity, expressed by the Péclet number, Pe, in the present study, the change in the fingering pattern due to the reaction can be observed without regard to Pe. These results are also essentially same as those obtained by Nagatsu *et al.*<sup>25</sup>

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