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Miscible viscous fingering involving viscosity increase by a chemical reaction with moderate Damköhler number

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In our previous study, we experimentally studied the effects of increased or decreased viscosity of the more-viscous liquid caused by chemical reactions at a very high Damköhler number, Da (defined as the ratio between a characteristic time of fluid motion and that of a chemical reaction), on miscible viscous fingering [Y. Nagatsu *et al.*, "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 another study, we experimentally studied the effects of decreased viscosity caused by chemical reaction at a moderate Da on the fingering [Y. Nagatsu *et al.*, "Effects of moderate Damköhler number on miscible viscous fingering involving viscosity decrease due to a chemical reaction," J. Fluid Mech. **625**, 97 (2009)]. In the present study, we investigated the effects of increased viscosity caused by chemical reaction at a moderate Da on the fingering in a radial Hele-Shaw cell. We observed that the present reaction decreased the area occupied by the fingering pattern around the injection hole. As a result, the fingering pattern became less dense following the reaction. The smaller the Da, the less significant the influence of the reaction on the fingering pattern. The present experimental results provide a coherent link between the results of earlier studies of miscible viscous fingering involving changes in the viscosity caused by chemical reactions. © *2011 American Institute of Physics*. [doi:10.1063/1.3549844]

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.[1–5] Recently, coupling between viscous fingering and chemical reactions has been investigated in several types of studies. One type of study examines reactions that do not influence the fingering dynamics. In this case, attention has mainly been paid to the concentration distribution of chemical species in the fingering pattern depending on the initial concentrations and the fingering velocity.[6–10] In studies that examine reactions that do influence the viscous fingering dynamics, the problems can be further divided into two categories. One category regards viscous fingering fully triggered by a chemical reaction. In this situation, the displacing and displaced fluids have the same viscosity, which means 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.*[11] and numerically analyzed by Gérard and De Wit.[12] The other category regards viscous fingering modified as a result of chemical reaction. In this situation, the displaced fluid is more viscous than the displacing fluid, and thus the fingering takes place even in the nonreactive case. The reactions induce changes in some properties, which results in modification of the fingering pattern. To date, modifications of the fingering pattern in response to a decrease in interfacial tension following a reaction in immiscible systems,[13] a precipitation reaction in miscible systems,[14] and a reaction producing gel in miscible systems[15] have been demonstrated experimentally. Modifications of the fingering pattern caused by changes in the fluid viscosity in a miscible system were first analyzed by De Wit and Homsy.[16,17] The bistable chemical kinetics employed in their study produced a new type of fingering that they called the "droplet" mechanism, which involves the formation of isolated regions of either less- or more-viscous fluids in connected domains of the other level of viscosity. More recently, Hejazi *et al.*[18] set up a reaction-diffusion-convection model to analyze the linear stability properties of miscible fingering with simple $A+B\rightarrow C$ reactions, where the viscosity of the solution is a function of all species concentrations.

Nagatsu *et al.*[19] demonstrated the modification of a miscible viscous fingering pattern in a radial Hele-Shaw cell caused by changes in viscosity of the more-viscous liquid due to instantaneous chemical reactions. This was done by using the dependence of polymer viscosity on *p*H. In that case, instantaneous reactions meant that the Damköhler number, Da, which is defined as the ratio between a characteristic time of fluid motion and that of a chemical reaction, was very high or could be treated as infinity. When the viscosity was increased as a result of the reaction, the shielding effect (the phenomenon in which a finger slightly ahead of its neighbor fingers quickly outruns them and shields them from further growth) was suppressed and the fingers were widened. As a result, the fingering pattern became more dense. When the viscosity was decreased as a result of the reaction, in contrast, the shielding effect was enhanced and the fingers were narrowed. These changes led to the reactive fingering

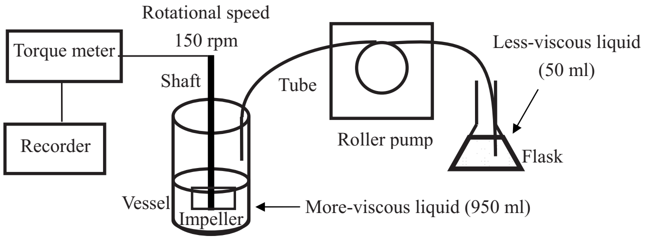

FIG. 1. Experimental apparatus to measure the rate of the increase in viscosity due to the reaction.

pattern being less dense. Subsequently, Nagatsu *et al.*[20] also investigated reactive miscible viscous fingering involving a decrease in the viscosity of the more-viscous liquid under the moderate Da condition. This was done by employing a chemical reaction between a polymer solution and a solution that included 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 more dense in the reactive cases than in the nonreactive cases. This finding, interestingly, showed that the effects of decreased viscosity due to a chemical reaction for moderate Da are the opposite of those for a very high Da (as mentioned above, the fingering pattern became less dense with the viscosity decrease due to the reaction under the very high Da condition[19]).

To date, there has been no published study about the investigation of miscible viscous fingering involving increased viscosity of the more-viscous liquid caused by a chemical reaction under moderate Da. This is mainly because it is not yet known what chemical reaction(s) will increase solution viscosity at a moderate rate. If we obtained experimental results in which the reaction increasing the viscosity at moderate Da decreased the area occupied by the radial fingering around the injection hole, these results would be consistent with previously reported results.[20] In the present study, we found a chemical system in which a solution's viscosity increased due to a chemical reaction at a moderate rate. We investigated reactive miscible viscous fingering in such a system by using the chemical recipe developed in the present study.

II. EXPERIMENTAL PROCEDURE

A. Liquids and chemical reactions

In the present study, we found that a chemical reaction between a starch syrup solution and a high-concentration sodium hydroxide (NaOH) solution increased the viscosity of the mixture solution at a moderate rate (that is, the rate of the reaction was moderate). We used the experimental apparatus shown in Fig. 1 to measure the rate of the viscosity increase due to the reaction. It should be noted that this measurement method was essentially the same as that employed to measure the rate of viscosity decrease in our previous study.[20] We regard the torque imposed on a shaft involving an impeller required to agitate a solution in a vessel at a constant rotational speed as the indicator of the viscosity of the solution in the vessel. We used a cylindrical acrylic vessel with 130 mm inner diameter and a six-blade paddle impeller, 100 mm in diameter and 60 mm tall. A total of 50 ml of the less-viscous 20M NaOH solution was added for 8 s by a roller pump to the vessel in which the more-viscous 52.5 wt % starch syrup solution with 950 ml was agitated by an impeller at 150 rpm. After the addition of the NaOH solution, the concentration of the starch syrup in the solution in the vessel became 50.3 wt % and that of NaOH became 1M (see the Appendix). Agitation was kept constant at 150 rpm during and after the addition of the NaOH solution. We measured the torque during and after the injection of the NaOH solution using a torque meter. As a reference, the nonreactive case was examined. In the nonreactive case, de-ionized water was used as the less-viscous liquid. In addition, the torque measurement was performed for the system involving an increase in viscosity caused by an instantaneous (or a very fast) chemical reaction to clearly show that the rate of the present reaction was moderate. To serve as the system involving the viscosity increase caused by an instantaneous reaction, we used the chemical recipe presented in our previous study.[19] The experimental conditions of the torque measurements employed in the present study are summarized in Table I. Here, case (I) is the reactive case at a moderate rate. Case (II) is the nonreactive case, and case (III) is the reactive case at a fast rate, both included as references by which to judge case (I).

Time evolutions of the measured torque, T, in the three cases are shown in Fig. 2, in which $t=0$ s is taken to be the time when the less-viscous solution begins to be added to the more-viscous solution. The measured torques for cases (I) and (II) are described on the left vertical axis, while that for case (III) is on the right vertical axis. In case (II), the nonreactive case, the torque decreased very slightly in response to the addition of the less-viscous liquid. After the slight decrease, the torque remained constant with time. In contrast, in case (I), the reactive case, the torque gradually increased until $t=60$ s. After $t=60$ s, the torque remained constant. In case (III), the instantaneous reaction, the torque rapidly increased until $t=20$ s. After $t=20$ s, the torque remained constant. The comparison between cases (I) and (III) shows that the rate of viscosity increase by the reaction we tested in this study was moderate. It was not possible to measure the viscosity increase rate for a higher concentration of NaOH in the vessel after the addition of the NaOH solution than that employed in the present study. The concentration of 20M for NaOH is close to the solubility limit, and thus if we wish to measure for a higher concentration of NaOH in the vessel after the addition of the NaOH solution, we would need to change the amount of NaOH solution added to the vessel. For example, if a total of 100 ml of 20M NaOH solution was added to the vessel in which 900 ml of 54.9 wt % starch syrup solution was being agitated, the concentrations of starch syrup and NaOH after the addition of the NaOH solution would be 50.3 wt % and 2M, respectively. In this case, however, the effect of a decrease in the viscosity due to a decrease in the concentration of starch syrup would change the effect of an increase in the viscosity due to the chemical reaction.

We normalized the increase in the torque in case (I) by

TABLE I. Liquids used for the measurement of the rate of increase in viscosity due to the reaction and the obtained first-order rate constant of the decrease κ.

	More-viscous liquid	Less-viscous liquid	κ (s^{-1})
Case (I)	52.5 wt % starch syrup solution	20M NaOH solution	0.052
Case (II)	52.5 wt % starch syrup solution	De-ionized water	0
Case (III)	0.53 wt % polyacrylic acid solution	1.3M NaOH solution	⋯

the difference between the initial value, T_0, and the final value, T_∞, which is denoted as T^*, as follows:

$$T^* = \frac{T - T_\infty}{T_0 - T_\infty}. \tag{1}$$

As shown in Fig. 3, the decrease in the reduced torque approximately exhibits a single exponential decay. Note that T^* decreases with time, although T increases with time. In general, in first-order reactions where the reaction rate is proportional to the reactant concentration, the reactant concentration shows a single exponential decay, as shown in Fig. 3 (in this case, the slope becomes $-k \log_{10} e$, where k is the reaction rate constant). Based on this fact, the slope in Fig. 3 gives the first-order rate constant of the viscosity increase due to the reaction, κ. The obtained value of κ is 0.052 s^{-1}. This procedure is essentially the same as that employed in previous studies.[13,20]

B. Viscous fingering experiment

The reactive viscous fingering experiment was performed by using 87 wt % starch syrup solution and 2M or 4M NaOH solution as the more- and less-viscous liquids, respectively. In the fingering experiment, it would be reasonable to regard the average concentrations of starch syrup and NaOH in the boundary region between the less- and more-viscous liquids as those that would be obtained if equal volumes of the less- and more-viscous liquids were mixed. The concentrations of the starch syrup solution and the lower concentration of NaOH solution (2M) used in the fingering experiment were determined to be the average concentrations of starch syrup and NaOH in the boundary region in the fingering experiment being the same as the concentration of starch syrup and NaOH in the vessel after the addition of the NaOH solution in the experiment where we measured the rate of increasing viscosity due to the reaction. In other words, the average concentrations of starch syrup and NaOH in the boundary region in the fingering experiment are 50.3 wt % and 1M, respectively, in this case (see the Appendix). Thus, the value of κ obtained in the torque measurement was used as the rate of viscosity increase due to the reaction in the fingering experiment. Note that the viscosity of 87 wt % starch syrup solution is 4 Pa s. Also note that we measured the viscosities of 50.3 wt % starch syrup solutions with 1M NaOH and without NaOH and the obtained values were 33 and 15 mPa s, respectively. Thus, we confirmed that NaOH increases the solution's viscosity. We performed the experiment with the higher concentration of NaOH, so this would be a useful parametric study. As mentioned above, unfortunately, under the high concentration of NaOH, we were not able to measure the reaction rate because of the limitation of the solubility of NaOH, a point that we will discuss again in Sec. III. In the nonreactive fingering experiment, de-ionized water was used as the less-viscous liquid. In both the reactive and the nonreactive cases, the less-viscous liquid was dyed by 0.06 wt % trypan blue for visualization of the fingering.

The viscous fingering experiment was conducted using a radial Hele-Shaw cell. The experimental setup was the same as that used in our previous studies.[19,20] In the present study, the gap width $b = 0.5$ mm. The Péclet number, Pe, is defined in Eq. (2) as well as in our previous studies[19,20] as follows:

$$\mathrm{Pe} = \frac{RU}{D} = \frac{q}{2\pi b D}, \tag{2}$$

where q is the volumetric flow rate of the injection of the less-viscous liquid. In Eq. (2), D is the diffusion coefficient between the more- and less-viscous liquids. To the best of our knowledge, there is no available data about a diffusion coefficient between starch syrup solution and water. Thus, in the present study, we regard the diffusion coefficient as that between glycerin and water, which was measured by Petitjeans and Maxworthy.[21] Based on the measurement, we estimated D as 1×10^{-10} m^2/s. Because b was constant here, Pe was also proportional to q.

We defined the characteristic time as the nominal residence time of fluid, t_r, and the Damköhler number, Da,

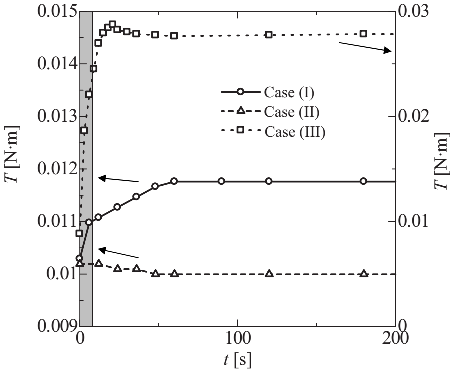

FIG. 2. Time evolutions of the measured torque during the increase in viscosity due to the chemical reaction. The measured torques for cases (I) and (II) are described on the left vertical axis, while that for case (III) is on the right vertical axis. The gray region indicates the period of the addition of the less-viscous liquid.

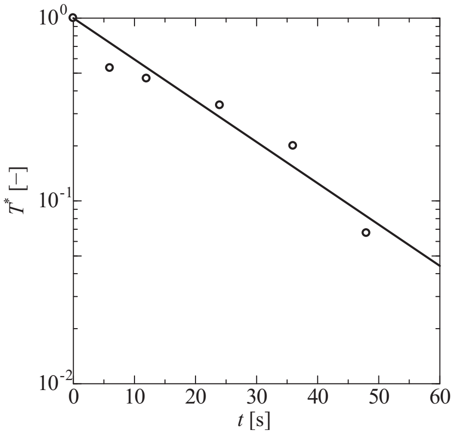

FIG. 3. Time evolution of the normalized torque in case (I) in a semilogarithmic plot.

which is the ratio of the residence time of fluid to the characteristic time of the reaction in Eqs. (3) and (4) as well as in the previous studies,[13,20] as follows:

$$t_r = \frac{b{R_0}^2}{2q}. \tag{3}$$

$$\mathrm{Da} = \frac{\kappa b{R_0}^2}{2q}. \tag{4}$$

Although Fernandez and Homsy[13] set R_0 as the radius of the cell, we set $R_0 = 58$ mm because our cell was not formed by circular plates but by square plates, as in our previous study.[20] The reason for our choice of 58 mm is explained later. Note that Da=0 is the nonreactive case. As mentioned above, we were not able to determine κ in the fingering experiments for the higher concentration of NaOH. However, if we accept that the reaction rates increase with the reactant concentration, we can consider that Da in the higher concentrations of NaOH is larger than that in the lower concentrations for a fixed condition of Pe.

III. RESULTS AND DISCUSSION

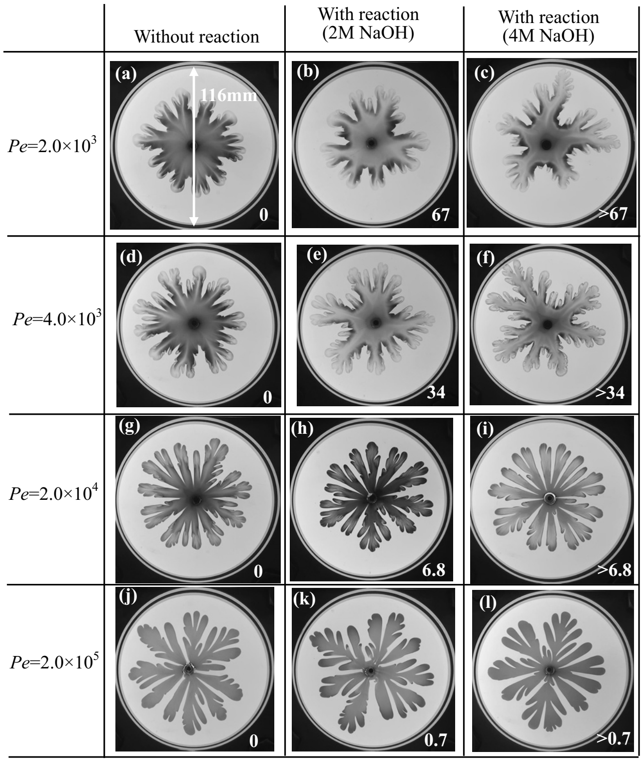

FIG. 4. Miscible viscous fingering patterns without and with the reaction for various Pe when the amount of injected less-viscous liquid is constant ($qt = 1.2 \times 10^{-6}$ m^3, where t is an injection time of the less-viscous liquid). The value of Da is shown in the lower right of each image. The injection times, t, are t=1800, 900, 180, and 18 s for Pe=2.0×10^3, Pe=4.0×10^3, Pe=2.0×10^4, and Pe=2.0×10^5, respectively.

Figure 4 shows the fingering patterns with and without the reaction for various Pe in which the total amount of the injected less-viscous liquid is always the same ($qt = 1.2 \times 10^{-6}$ m^3, where t is the injection time of the less-viscous liquid). The value of Da is shown in the lower right corner of each image. As noted above, Da in the higher concentrations of NaOH cannot be defined but can be considered to be larger than that in the lower concentration for a fixed condition of Pe. In the nonreactive cases, fingering takes place at a smaller radius as Pe is larger. Note that for smaller Pe cases the color depth of the dye becomes abruptly light around the fingertips, which is caused by the less-viscous liquid's layer in the cell's gap direction becoming abruptly thin around the fingertips. This phenomenon can be seen in miscible displacement of the glycerin-water system at a relatively low rate.[7,8,10] When Pe is small (Pe=2.0×10^3–2.0×10^4), comparison between the nonreactive and reactive cases for each Pe shows that fingering takes place at a smaller radius in the reactive case than in the nonreactive case, although no clear difference between the reactive and nonreactive patterns can be seen around the fingertips. This trend becomes more significant as the concentration of NaOH is larger for each Pe. In other words, the area occupied by the pattern around the injection hole is decreased by the reaction. Furthermore, this trend becomes more significant as Da is larger for each Pe. When Pe is large (Pe=2.0×10^5), however, no clear difference between the reactive and nonreactive fingering patterns can be seen. This means that the influence of the reaction on the fingering pattern becomes insignificant as Da becomes small. Note that R_0 is set to 58 mm in the present study because the inner diameter of the flange is 116 mm (and thus the radius is 58 mm), as shown in Fig. 4(a). We emphasize that the effects of the present reaction increasing the viscosity at a moderate Da on the fingering pattern are opposed to those of the previous reaction decreasing the viscosity at a moderate Da.[20] This means that the present results are consistent with the previous results presented by Nagatsu *et al.*[20]

In the present study as well as in Ref. 20, the concept of area density proposed by Chen[22] was used to quantitatively evaluate the fingering patterns. We measured the area density of the fingering pattern, d, which is defined as the ratio of the area occupied by the fingering pattern within an arbitrary radius r, $A(r)$, to the area of the circle of the radius, $A_0(r) = \pi r^2$. We plotted d versus r. Figure 5 shows the d-r curves of the fingering pattern with and without the reaction for several Pe shown in Fig. 4. The d-r curves in Fig. 5 are the

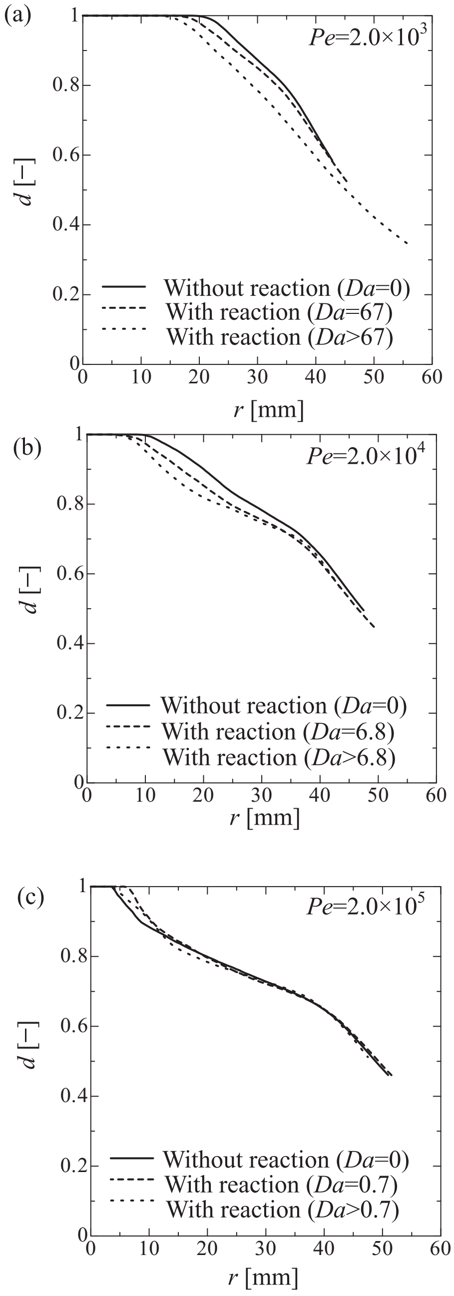

FIG. 5. The d-r curve of the fingering patterns without and with the reaction for the various Pe shown in Fig. 4. The value of Da is also shown.

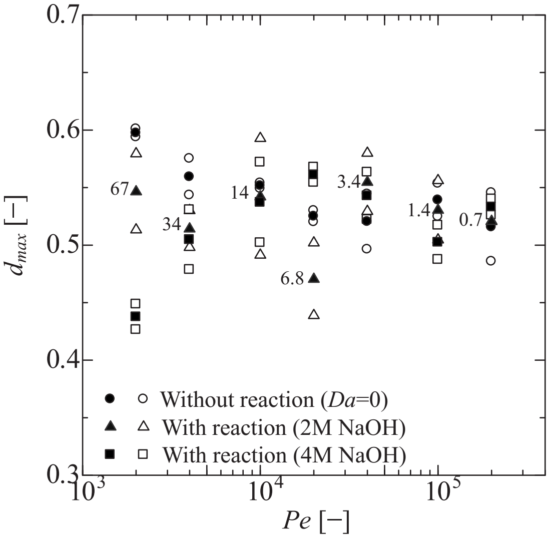

FIG. 6. Relationship between d_{max} and Pe under the condition of $r_{\mathrm{max}}=40$ mm. Open symbols indicate the individual data of the two experiments for each condition, while the closed symbols indicate their average. The values of Da corresponding to each symbol indicating the average in the reactive cases with 2M NaOH (closed triangles) are also shown. Da in the reactive case with 4M NaOH can be considered to be larger than that in the reactive case with 2M NaOH.

average of the data obtained in the two experiments under each condition. When $\mathrm{Pe}=2.0\times10^3$ and $\mathrm{Pe}=2.0\times10^4$ [(a) and (b), respectively] at smaller r, d in the reactive case is smaller than that in the case without the reaction. This trend becomes more significant as Da is larger for each Pe. In the d-r curves, if the coordinate of the end of the curve is denoted as $(r_{\mathrm{end}},d_{\mathrm{end}})$, then the total area of the pattern can be calculated as $d_{\mathrm{end}}\pi r_{\mathrm{end}}{}^2$. We found that the total area of the pattern with the reaction was almost the same as that without the reaction under these conditions of Pe. This is reasonable because the total amount of the injected liquid was the same in Fig. 5 as that shown in Fig. 4. These results quantitatively show that the area occupied by the fingering pattern around the injection hole was decreased by the reaction even though the total area of the pattern is independent of the reaction. When $\mathrm{Pe}=2.0\times10^5$, the d-r curve of the pattern with the reaction almost coincided with that without the reaction for any r. We confirmed that the total area with the reaction was also almost the same as that without the reaction in this Pe condition. These findings indicate that the insignificant influence of the reaction on the fingering pattern in this Pe condition is confirmed by the d-r curve. In brief, the results shown in Fig. 5 indicate that the observation results shown in Fig. 4 can be quantitatively confirmed by the d-r curves.

In our previous studies,[19,20] the area density of the fingering pattern, d_{max}, defined as the ratio of the area occupied by the pattern within the circle with a radius r_{max} (r_{max} is defined as the length of the longest finger in each fingering pattern) to the area of the circle, $\pi r_{\mathrm{max}}{}^2$, was also employed as a quantitative evaluation of the fingering pattern. Note that d_{max} was denoted as d_a in Ref. 19. Figure 6 shows the relationship between d_{max} and Pe in which $r_{\mathrm{max}}=40$ mm. Note that in this case the injection volume of the less-viscous liquid was not the same in each case. Here, the individual data obtained by the two experiments (open plots) and their average (closed plots) are shown to enable us to discuss the accuracy of the data because there is some influence of the symmetry of the radial fingering pattern on the characterization. When a finger or fingers advance much more quickly than other fingers (in this case the pattern is less symmetric), d_{max} tends to be smaller. In contrast, when all fingers advance equivalently (in this case the pattern is more symmetric), d_{max} tends to be larger. For the smallest Pe ($\mathrm{Pe}=2.0\times10^3$) case in which Da is the largest, i.e., the influence of the reaction is most significant, the individual data of d_{max} and also their average decrease with an increase in Da. For the second-smallest Pe ($\mathrm{Pe}=4.0\times10^3$) in which Da is at its second-largest value, the average value of d_{max} decreases with an increase in Da. When Pe is larger than 2.0×10^4, where Da is relatively small, clear dependence of Da on $d_{\max}$ cannot be observed; in other words, the influence of Da on $d_{\max}$ becomes insignificant. These results show that the present reaction decreases $d_{\max}$ even if the experimental error margin is considered when Da is larger (Pe is smaller). In our previous study,[19] we showed that increased viscosity induced by the reaction at a very high Da increased $d_{\max}$. This means that the effects of increased viscosity due to chemical reaction on the fingering pattern for moderate Da are the opposite of those for a very high Da. The opposite effect due to Da was also observed in the system involving decreased viscosity caused by chemical reactions. The present experimental results, together with previous results, form a coherent series of findings regarding miscible viscous fingering involving changes in the viscosity in a radial Hele-Shaw cell.

The fingering dynamics were independent of Pe and depended only on Da, and thus the characteristics were scaled only with Da in the previous study.[20] However, in the present system, the fingering dynamics depended on both Pe and Da. As shown in Fig. 4, the nonreactive fingering patterns depended on Pe for Da=0. Here, we emphasize that the influence of the reaction on the fingering dynamics (the present reaction resulted in a decreased area occupied by the fingering pattern around the injection hole) directly appears as Da. To clearly demonstrate this, we have shown the reactive experiments with two different NaOH concentrations, although the reaction rate could not be measured for the higher NaOH concentration case. By doing so, we could independently change Da at a fixed Pe. The results described in the smallest Pe case in Fig. 4 clearly show that the decrease in the area occupied by the fingering pattern became more significant as the influence of the reaction (that is, Da) grew. In the present reactive case, an increase in Pe could be interpreted as a decrease in Da.

In our previous paper,[20] we discussed the mechanism for the opposite effects of the viscosity decrease by the reactions on the fingering pattern depending on Da. In the case of a very high Da,[19] we hypothesized that an overall reaction rate would be larger near the finger's tip than near the finger's base due to the larger amount of reactant flux provided near the tip. Thus, the viscosity of the more-viscous liquid would be relatively smaller near the tip than near the base. Since the displacing liquid can more easily penetrate the region with relatively lower viscosity, the finger is narrowed. To discuss the case of a moderate Da,[20] we introduced a local Damköhler number (Da*) based on the local fluid residence time, $t_{r,l}$, or the local finger advancement velocity, V, as follows:

$$\mathrm{Da}^* = \kappa t_{r,l} = \frac{\kappa R_0}{V}, \tag{5}$$

where $t_{r,l}=R_0/V$.[13] We considered that V would be higher near the tip than near the base or that $t_{r,l}$ would be larger near the base than near the tip. This leads to Da* being higher near the base than near the tip. Higher Da* means higher completion of the reaction, resulting in the viscosity of the more-viscous liquid being relatively lower near the base than near the tip. This situation is contrary to that in the case of a very high Da described above. The fact that the displacing liquid can more easily penetrate the region with relatively lower viscosity would make the finger wider. Note that we considered that the finger would be widened mainly near the base in terms of a single finger in the previous study.[20] This means that the area occupied by the radial fingering pattern around the injection hole would be increased. It should be noted that there would be a difference between V or $t_{r,l}$ near the tip and that near the base, even in the case of a very high Da. In this case, however, there would be no difference between Da* near the tip and that near the base since κ can be treated as infinity.

We can likewise explain the opposite effects of the viscosity increase caused by the reactions on the fingering pattern depending on Da shown in the present and previous[19] studies. In the case of a very high Da, the overall reaction rate being larger near the tip than near the base, in this case, results in the viscosity of the more-viscous liquid being relatively larger near the tip than near the base, leading to finger widening. In the case of moderate Da, with Da* being higher near the base than near the tip, the viscosity of the more-viscous liquid is relatively higher near the base than near the tip, leading to the finger being narrowed. This situation is contrary to that in the case of a very significantly high Da mentioned above. Note that we consider the finger to be narrowed mainly near the base in terms of a single finger in the present study. This results in a decrease in the area occupied by the radial fingering pattern around the injection hole.

IV. CONCLUSION

In the present study, we found that a chemical reaction between a starch syrup solution and a high-concentration sodium hydroxide (NaOH) solution increased the viscosity of the mixture solution at a moderate rate. We investigated the effects on the miscible viscous fingering pattern in a radial Hele-Shaw cell of an increase in the more-viscous liquid's viscosity due to a chemical reaction under the condition of moderate Da by using a starch syrup solution and a high-concentration NaOH solution as the more- and less-viscous liquids, respectively. We have shown that the present reaction decreases the area occupied by the fingering pattern around the injection hole. As a result, the fingering pattern becomes less dense in response to the reaction. As Pe is larger, meaning that Da is smaller, the influence of the reaction on the fingering pattern becomes insignificant. The present experimental results, together with the previous results, form a coherent series of findings regarding miscible viscous fingering in a radial Hele-Shaw cell involving changes in the viscosity of the more-viscous liquid. Under very high Da, the reaction increasing the viscosity makes the fingering pattern more dense, and in contrast, the reaction decreasing the viscosity makes the fingering pattern less dense.[19] Under moderate Da, the reaction increasing the viscosity decreases the area occupied by the pattern around the injection hole, which, as a result, makes the fingering pattern less dense. In contrast, the reaction decreasing the viscosity increases the area occupied by the pattern around the injection hole, which, as a result, makes the fingering pattern more dense.[20] These results show that the effects of a chemical reaction on the fingering pattern for moderate Da are the opposite of those for a very high Da in the cases where the viscosity is either increased or decreased.

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APPENDIX: CALCULATION OF THE CONCENTRATION OF STARCH SYRUP

As mentioned in Sec. II B, we regarded the average concentrations of starch syrup and NaOH in the boundary region between the less- and more-viscous liquids in the viscous fingering experiment as those obtained when the equal volumes of the less- and more-viscous liquids are mixed. In addition, the concentrations of the starch syrup solution and NaOH solution used in the viscous fingering experiment were determined to be the average concentrations of starch syrup and NaOH in the boundary region in the fingering experiment being the same as the concentrations of starch syrup and NaOH in the vessel after the addition of the less-viscous liquid during the torque measurement. In fact, in the present study, we determined the concentration of the starch syrup solution employed in the torque measurement on the basis of the use of 87 wt % starch syrup solution as the more-viscous liquid in the viscous fingering experiment. We note that the density of water is 1.0 g/ml and that of the starch syrup used in the present study is 1.45 g/ml. For simplicity, to calculate the average concentration of the starch syrup in the boundary region between the less- and more-viscous liquids in the viscous fingering experiment, we considered a mixture of 500 ml of the less-viscous liquid and 500 ml of the more-viscous liquid (since the amount of the mixture solution in the torque measurement was 1000 ml). If x g of the starch syrup and y g of water are used to prepare the more-viscous liquid of the viscous fingering experiment, the following equations are satisfied:

$$\frac{x\ \text{g}}{1.45\ \text{g/ml}} + \frac{y\ \text{g}}{1.0\ \text{g/ml}} = 500\ \text{ml}, \qquad \text{(A1)}$$

$$\frac{x\ \text{g}}{x\ \text{g} + y\ \text{g}} \times 100 = 87\ \text{wt}\ \%. \qquad \text{(A2)}$$

From Eqs. (A1) and (A2), we obtain $x=595.9$ g and $y=89.0$ g. After mixing in the less-viscous liquid, the mixture consists of 595.9 g of starch syrup and $(89.0+500)$ g of water. Thus, the concentration of the starch syrup is given as follows:

$$\frac{595.9\ \text{g}}{595.9\ \text{g} + 89.0\ \text{g} + 500\ \text{g}} \times 100 = 50.3\ \text{wt}\ \%. \qquad \text{(A3)}$$

In the torque measurement, since 950 ml of the more-viscous liquid and 50 ml of the less-viscous liquid was used, we were able to obtain the more-viscous liquid used in the torque measurement by adding 450 ml of water to 500 ml of 87 wt % starch syrup solution. Thus, the concentration of the starch syrup solution used in the torque measurement is given by the following equation:

$$\frac{595.9\ \text{g}}{595.9\ \text{g} + 89.0\ \text{g} + 450\ \text{g}} \times 100 = 52.5\ \text{wt}\ \%. \qquad \text{(A4)}$$

Calculation of the concentration of NaOH was simple. We used a concentration of NaOH that was twice as much as the average concentration in the boundary between the more- and less-viscous liquid as the less-viscous liquid in the viscous fingering experiment, and a concentration of NaOH that was 20 times as much as that obtained after the addition of the less-viscous liquid as the less-viscous liquid in the torque measurement.

[1] S. Hill, "Channeling in packed columns," Chem. Eng. Sci. **1**, 247 (1952).

[2] P. G. Saffman and G. I. Taylor, "The penetration of a fluid into a porous medium or Hele-Shaw cell containing a more viscous liquid," Proc. R. Soc. London, Ser. A **245**, 312 (1958).

[3] G. M. Homsy, "Viscous fingering in porous media," Annu. Rev. Fluid Mech. **19**, 271 (1987).

[4] K. V. McCloud and J. V. Maher, "Experimental perturbations to Saffman-Taylor flow," Phys. Rep. **260**, 139 (1995).

[5] S. Tanveer, "Surprises in viscous fingering," J. Fluid Mech. **409**, 273 (2000).

[6] M. Jahoda and V. Hornof, "Concentration profiles of reactant in a viscous finger formed during the interfacially reactive immiscible displacement in porous media," Powder Technol. **110**, 253 (2000).

[7] Y. Nagatsu and T. Ueda, "Effects of reactant concentrations on reactive miscible viscous fingering," AIChE J. **47**, 1711 (2001).

[8] Y. Nagatsu and T. Ueda, "Effects of finger-growth velocity on reactive miscible viscous fingering," AIChE J. **49**, 789 (2003).

[9] Y. Nagatsu and T. Ueda, "Analytical study of effects of finger-growth velocity on reaction characteristics of reactive miscible viscous fingering by using a convection-diffusion-reaction model," Chem. Eng. Sci. **59**, 3817 (2004).

[10] Y. Nagatsu, T. Ogawa, Y. Kato, and Y. Tada, "Investigation of reacting flow fields in miscible viscous fingering by a novel experimental method," AIChE J. **55**, 563 (2009).

[11] T. Podgorski, M. C. Sostarecz, S. Zorman, and A. Belmonte, "Fingering instabilities of a reactive micellar interface," Phys. Rev. E **76**, 016202 (2007).

[12] T. Gérard and A. De Wit, "Miscible viscous fingering induced by a simple $A+B \rightarrow C$ chemical reaction," Phys. Rev. E **79**, 016308 (2009).

[13] J. Fernandez and G. M. Homsy, "Viscous fingering with chemical reaction: Effect of in-situ production of surfactants," J. Fluid Mech. **480**, 267 (2003).

[14] Y. Nagatsu, S.-K. Bae, Y. Kato, and Y. Tada, "Miscible viscous fingering with a chemical reaction involving precipitation," Phys. Rev. E **77**, 067302 (2008).

[15] Y. Nagatsu, A. Hayashi, M. Ban, Y. Kato, and Y. Tada, "Spiral pattern in a radial displacement involving a reaction producing gel," Phys. Rev. E **78**, 026307 (2008).

[16] A. De Wit and G. M. Homsy, "Viscous fingering in reaction-diffusion systems," J. Chem. Phys. **110**, 8663 (1999).

[17] A. De Wit and G. M. Homsy, "Nonlinear interaction of chemical reactions and viscous fingering in porous media," Phys. Fluids **11**, 949 (1999).

[18] S. H. Hejazi, P. M. J. Trevelyan, J. Azaiez, and A. De Wit, "Viscous fingering of a miscible reactive $A+B \rightarrow C$ interface: A linear stability analysis," J. Fluid Mech. **652**, 501 (2010).

[19] 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).

[20] Y. Nagatsu, Y. Kondo, Y. Kato, and Y. Tada, "Effects of moderate Damköhler number on miscible viscous fingering involving viscosity decrease due to a chemical reaction," J. Fluid Mech. **625**, 97 (2009).

[21] P. Petitjeans and T. Maxworthy, "Miscible displacements in a capillary tube. Part 1. Experiments," J. Fluid Mech. **326**, 37 (1996).

[22] J.-D. Chen, "Growth of radial viscous fingers in a Hele-Shaw cell," J. Fluid Mech. **201**, 223 (1989).