

Chapter 2

Chemically-Driven Miscible Viscous Fingering: How Can a Reaction Destabilize Typically Stable Fluid Displacements?

L.A. Riolfo, Y. Nagatsu, P.M.J. Trevelyan, and A. De Wit

Abstract We experimentally demonstrate that chemical reactions, by producing changes in viscosity at the miscible interface between two fluids, can be the very source of viscous fingering in systems that are otherwise stable in the absence of a reaction. We explain how, depending on whether the reaction product is more or less viscous than the reactants, different patterns develop in the reaction zone.

2.1 Background

Viscous fingering (VF) is the hydrodynamic instability that classically appears when a fluid with a given viscosity displaces another more viscous one in porous media or a Hele-Shaw cell [1]. It has diverse implications in various fields such as hydrology [2], petroleum recovery [1], liquid crystal [3], polymer processing [4], chromatography [5] or CO₂ sequestration to name a few [6].

Experimental [7, 8] and theoretical [9, 10] studies have shown that chemical reactions, by modifying the viscosity of the solutions at hand, can influence miscible VF. Changes in the viscosity profile, induced by a chemical reaction, give rise to variations in the displacement evolution and hence different patterns are observed.

The present work, going further, presents experimental demonstration of reaction-driven viscous fingering of the interface between a more viscous liquid displacing a less viscous one, a displacement that in absence of reaction would typically be stable. It has been theoretically predicted [9, 10] that the necessary condition for such a reactive displacement to undergo fingering is to yield a reaction product with a viscosity either larger or smaller than the viscosity of the reactants. Specifically,

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if μ_i and μ_d denote the viscosity of the invading solution and that of the displaced solution respectively, purely chemically-driven VF of the classically stable $\mu_i > \mu_d$ situation should occur provided μ_r , the viscosity in the reaction zone, is either larger than μ_i or smaller than μ_d [9, 10].

We study here both scenarios, viscosity maximum ($\mu_r > \mu_i$) and minimum ($\mu_r < \mu_d$), exploiting the viscosity dependence of polymer solutions on pH. From the experimental findings, the different fingering patterns are analyzed as a function of the viscosity contrast generated by the chemical reaction [11].

The article organizes as follows: In the next section we explain the experimental set up and the chemicals utilized in the experiments. Also in this second section we present our experimental findings. In Sect. 2.3 we discuss and explain the evolution on the displacements presented in the second section. Finally, conclusions are drawn while highlighting the possible impact of this experimental work.

2.2 Methods

Experiments are carried out in a horizontal Hele-Shaw cell consisting of two transparent glass plates 100 mm wide, 500 mm long and 14 mm thick separated by a gap width $b = 0.25$ mm. The fluids are injected linearly at a constant flow rate q . As the displacing more viscous fluid, we use aqueous polymer solutions. When these solutions displace a less viscous dyed non-reactive solution, no instability is observed at the miscible interface between the fluids. However, if the displaced fluid reacts with the polymer, generating a maximum or a minimum in the viscosity profile, the interface can become unstable undergoing fingering. In the displacement experiments where the maximum develops, a more viscous aqueous solution of 0.30 %wt polyacrylic acid (PAA—1250000 MW—Sigma Aldrich) displaces a dyed 0.06M sodium hydroxide (NaOH) aqueous solution. The liquids react at the miscible interface. The reaction product, sodium polyacrylate (SPA), typically presents a viscosity larger than that of both reactants. The chemical reaction at the miscible interface is $\text{PAA} + \text{NaOH} \rightarrow \text{SPA}$.

On the other hand, in the case where the minimum in viscosity develops, a sodium polyacrylate (SPA—2100000–6600000 MW—Wako) aqueous solution 0.125 %wt pushes a less viscous 60 %wt glycerol aqueous solution containing 0.5M HCl. In this case the polymer reacts with the acid producing PAA, which here has a viscosity lower than that of both reactants. The reaction is then $\text{SPA} + \text{HCl} \rightarrow \text{PAA} + \text{NaCl}$.

Figure 2.1 shows the temporal evolution of reaction-driven VF observed in a linear displacement for both cases. When the maximum in viscosity develops, fingers grow behind the reactive interface (Fig. 2.1(a)). On the other hand, in the case of a minimum in viscosity, the interface undergoes fingers that grow towards the displaced fluid (Fig. 2.1(b)).

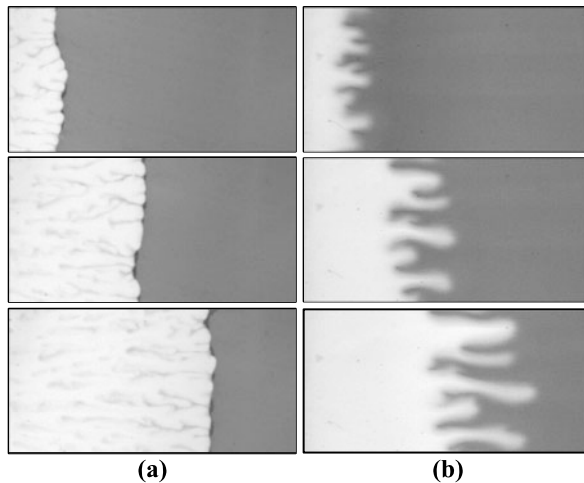


Fig. 2.1 Temporal evolution of reaction-driven VF in a linear displacement. **(a)** A more viscous solution of PAA displaces from left to right a less viscous aqueous dyed solution of NaOH in concentration 0.06M. Flow rate $q = 0.5$ ml/min. Time from top to bottom $t = 75, 150$ and 225 s. **(b)** A more viscous SPA solution displaces from left to right an aqueous dyed solution of 60 %wt glycerol + HCl 0.5M. Flow rate $q = 0.25$ ml/min. Time $t = 140, 280$ and 360 s. Field of view of each image = $4 \text{ cm} \times 8 \text{ cm}$

2.3 Results

In order to understand the systems' evolution we analyze experimentally the viscosity contrasts generated during the displacement experiments. We measure the viscosity of the pure reactants and estimate the viscosity developed in the reaction zone as the viscosity of a mixture of the pure reactants. The respective viscosities are measured with a rotational viscosimeter (Brookfield—Pro Extra II) at the shear rate corresponding to the experimental conditions.

In the displacement experiments with a maximum in viscosity the reactants viscosity are: invading fluid (0.3 %wt PAA) $\mu_i = 870$ cp, displaced fluid (0.06M NaOH) $\mu_d = 1$ cp. Hence, the initial viscosity contrast is stable, because the more viscous fluid displaces the more mobile one. However, in the reaction zone the viscosity developed is approximately $\mu_r = 3880$ cp. Therefore, an unstable contrast of viscosity is developed between the invading fluid and the reaction zone: $\mu_i < \mu_r$ and we have locally a less viscous fluid pushing a more viscous one. As the unstable region is located between the invading fluid and the reaction zone, the fingers should develop in this region. This is consistent with the experiments (Fig. 2.1(a)), where the fingers develop behind the reaction zone toward the invading fluid.

In the displacement with a minimum in viscosity, the viscosities are: invading fluid (0.125 %wt SPA) $\mu_i = 794$ cp, displaced solution (60 % glycerol + 0.5M HCl) $\mu_d = 10$ cp. The viscosity falls to $\mu_r = 5$ cp in the reaction zone. Therefore, even if the initial viscosity contrast is stable, locally an unstable region develops in time between the reaction zone and the displaced fluid ($\mu_r < \mu_d$). The development

of the instability is then predicted to occur in the region between the reaction zone and the displaced fluid. This conjecture from the viscosity profiles agrees with the experimental findings exposed in Fig. 2.1(b).

We show here that depending on the unstable viscosity contrast developed during the displacement different patterns develop, and the interface deforms towards opposite directions, either in the displacement direction if a viscosity minimum develops, or against the displacement direction if a maximum in viscosity is chemically induced.

In this way, we have provided experimental evidence of viscous fingering triggered by a chemical reaction at the miscible interface between a more viscous solution displacing a less viscous one in a Hele-Shaw cell. Such a situation is classically stable in the absence of a reaction as we have a fluid with low mobility invading another more mobile one. The chemical reaction, by generating a product either more or less viscous than both reactants, triggers in time a non-monotonic viscosity profile. A locally unstable configuration with adverse mobility gradient develops around the extremum. This leads to fingers developing respectively behind or ahead of the reaction zone depending whether the viscosity profile exhibits a maximum or a minimum.

This results may help to prevent undesirable mixing during fluids displacements, such in the case of waste management in soils [12, 13], but also could lead to control of mixing enhancement in a unique direction in complex scenarios such as in microfluidics [14].

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