

## Transition of viscous fingering patterns in polymer solutions

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**Abstract:** Viscous fingering patterns of aqueous hydroxypropyl methyl cellulose (HPMC) solutions pushed by air in the Hele-Shaw cell were observed as a function of isopropyl alcohol under a constant pressure of 15 cm H<sub>2</sub>O. We found a morphological transition from side branching patterns to tip splitting ones with increasing isopropyl alcohol content, accompanied with a decrease in surface tension. The observed morphology transition was classified as a second-order one by a comparison of the average tip velocity as a function of isopropyl alcohol content.

### Introduction

Small anisotropies such as roughening the plates,<sup>1-3</sup> introduction of a wire,<sup>4</sup> and entrainment of a bubble,<sup>5</sup> or using a nematic liquid crystal<sup>6</sup> in the flow have led to drastic changes in the morphology of the observed fingering patterns in the Hele-Shaw cell. Similar results were obtained by computer simulation experiments by taking into account anisotropy.<sup>7,8</sup> In particular, Ben-Jacob and Garik concluded that anisotropy was a necessary factor for dendrite growth.<sup>9</sup> In this paper, we describe the results of experiments on radial viscous

fingering in the Hele-Shaw cell of aqueous solutions of hydroxypropyl methyl cellulose (HPMC) involving isopropyl alcohol.

### Experimental Section

**Materials.** An HPMC kindly supplied by Shin-Etsu Chemical company was purified by the method described previously.<sup>10</sup> The molecular weight of HPMC was determined to be  $271 \times 10^3$  by an intrinsic viscosity measurement in a 0.1 M aqueous NaCl solution at 25 °C.<sup>10</sup> The degree of substitution (DS) of OCH<sub>3</sub> group and the molar substitution (MS) of OC<sub>3</sub>H<sub>6</sub>OH group had values of 1.8 and 0.18, respectively, as obtained from the manufacturer.

Water purified by a Millipore Q-TM system was used. Spectroscopic-grade quality isopropyl alcohol was used without further purification.

HPMC dissolved in water and the resulting aqueous HPMC solution and isopropyl alcohol was mixed in 100 : 0, 99 : 1, 97 : 3, 95 : 5, 93 : 7, 90 : 10, and 85 : 15 volume ratios of water and isopropyl alcohol. The final HPMC concentration in all solutions was 1.5 g/100mL. In order to obtain high-contrast patterns in the fingering experiments, the HPMC solutions were colored by adding methylene blue.

Viscosities of the water and isopropyl alcohol mixtures were determined from their effluent times using a Ubbelohde viscometer at 25 °C.

**Rheometer.** The shear flow measurements of HPMC solutions were carried out in the shear rate range 0.1 - 400 s<sup>-1</sup>, and their dynamic

measurements were performed in the frequency range 0.031-12.4 rad. s<sup>-1</sup> using an MR-300 Soliquid Meter produced by Rheology Co. Ltd. (Kyoto, Japan), with a coaxial cylinder geometry (od. 4.003 cm; id. 3.898 cm; immersion length, 0.897 cm). The temperature of the sample chamber was maintained at 25 °C.

**Surface Tension Measurements.** Surface tensions of the HPMC solutions and mixtures of water and isopropyl alcohol were determined by using the same instruments as reported previously.<sup>11</sup> A glass trough with a diameter of 10 cm was filled with HPMC solutions and its temperature was controlled within 25 °C. The trough was placed on a stage that can be moved up and down to adjust the position of the trough. The height of the trough was adjusted to touch the edge of a sandblasted platinum plate (24 x 10 x 0.1 mm<sup>3</sup>) connected to a Cahn 2000 electrobalance. The surface tensions of the HPMC solutions were determined from the electrobalance connected to a digital voltmeter. We regarded it as important for attaining a constant surface tension, namely, an equilibrium value unless it does not remain constant over 10 min.

**Hele-Shaw Cell.** The fingering experiments were prepared in radial geometry, in a rectangle Hele-Shaw cell made by using two plane-parallel glass plate (0.8 x 50 x 35 cm<sup>3</sup>) with eight silicone wafer spacers of 0.05 cm thickness clamped in between. The Hele-Shaw cell was placed on a white board on which there are concentric circles with the radii of 1, 2, 3, 4, 5, 7, and 9 cm. Air was injected through a small hole (0.2 cm in diameter) at the center of the top plate under a constant pressure of 15 cm H<sub>2</sub>O, which is applied by the hydrostatic pressure generated using a water filled cylinder with the air in a cup with a volume of 3000 mL. The cup volume was enough large to maintain a

drop in the pressure less than 1% during the experiments. In order to avoid lifting of the plates in the experiments eight clamps were applied symmetrically around the boundary. Records of the developed patterns were taken by a CCD video camera/recorder method. The images of the recorded patterns were printed out by a video printer.

## Results and Discussion

An aqueous solution of an HPMC displays weak shear-thinning behavior: the shear viscosity is almost constant in the lower shear rates than  $100 \text{ s}^{-1}$ , regarding as a fast Newtonian region, which is called zero-shear viscosity, and above the shear rate the viscosity gradually decreases with an increase in the shear rate and finally approaches a less 10% reduction of the zero-shear viscosity at the highest shear rate of  $400 \text{ s}^{-1}$  measured in the present study. The aqueous HPMC solution was surface active and its surface tension showed a little time-dependence and finally attained an equilibrium value of  $47.0 \text{ mN/m}$  after 30 min.

Isopropyl alcohol shows a lower surface tension than that of the aqueous HPMC solution and addition of isopropyl alcohol to the HPMC solution should lead to a decrease in its surface tension. As expected, the surface tensions of the HPMC solutions were decreased with an increase in isopropyl alcohol, and above at 10 vol. % isopropyl alcohol the surface tension showed a shorter time-dependence than that of the pure aqueous HPMC solution. The equilibrium surface tensions are summarized in Table 1 as a function of isopropyl alcohol content.

Shear viscosities of the HPMC solutions in the presence of isopropyl alcohol also showed shear-thinning and the zero-shear viscosity data are listed in Table 1. An increase in the shear viscosity

with isopropyl alcohol content would be mainly attributed to the fact that the viscosity of isopropyl alcohol is more twice as large as that of water. Furthermore, from the zero-shear viscosity and solvent viscosity data, we can calculate the relative viscosities of HPMC solutions and the magnitudes decrease above the isopropyl alcohol contents larger than 5 vol. % as shown in Table 1. This means that HPMC chains have more compact forms in aqueous isopropyl alcohol solutions with an increase in isopropyl alcohol. The solution properties can be interpreted reasonably by taking account of isopropyl alcohol as a poor solvent for HPMC.

Figure 1 displays an effect of isopropyl alcohol content on the morphological transition of the viscous fingering patterns. Without isopropyl alcohol (Figure 1a) the side branching fingers are stable and some tips in the finger grow with a dendrite pattern. On increasing isopropyl alcohol content (Figures 1b and 1c) the side branching growth is suppressed and the interfacial pattern becomes less dense. At 7 vol. % isopropyl alcohol the tip splitting growth in the pattern is dominated and a less side branching is observed. Further increasing isopropyl alcohol content (Figures 1e and 1f) leads to a tip splitting pattern, which is similar to that obtained using a Newtonian isotropic liquid.<sup>1-5</sup>

Recent studies based on diffusion limited aggregation model<sup>12,13</sup> suggest that the finger in the pattern first becomes slightly asymmetric, then the tip of the finger splits, and a highly branched and apparently dendrite structure is produced with a decrease in surface tension. The surface tension dependence on the pattern transition is opposite to the present finding. The pattern growth continuously produces a new interface between the HPMC solution and air and its speed is much shorter than the time to attain the equilibrium surface tension of the

HPMC solutions, resulting that a real surface tension in the fingering front should be higher than the equilibrium one due to a slower diffusion rate of HPMC chain than the solvent. Such dynamics will influence the transition of the viscous fingering patterns, but at the moment there are not any reasonable explanations.

As mentioned above, isopropyl alcohol should play a role in shrinking HPMC chains and it is expected to lead to the less elastic repulsive energy with an increase in isopropyl alcohol. Although an elastic modulus determined from the dynamic measurements of HPMC solutions was much less than a viscous one, its magnitude clearly decreased with an increase in isopropyl alcohol content. Thus, larger elastic modulus would be related with the generation of the side branching patterns for HPMC solutions with lower isopropyl alcohol contents than 5 vol. %. A variety of the side branching patterns were observed for viscoelastic materials such as clay slurries.<sup>14</sup>

In addition, the tip velocity is also a useful quantity to understand the dynamics of the viscous fingering. Figure 2 demonstrates the average tip velocity for the HPMC solutions, measured at the outermost part when it is 7 cm from the center, as a function of isopropyl alcohol content. The velocity has a maximum at around 3 vol. % isopropyl alcohol and it gradually decreases with an increase in isopropyl alcohol content. A comparison of Figure 1 and Figure 2 shows that the observed transition is characterized as second-order since the tip velocity itself is continuous but the morphology changes. A similar plot in which there is the maximum in the velocity of pattern growth was observed for the experiments by electrochemical deposition.<sup>15</sup>

Our main aim here has been to report the experimental discovery of the morphological transition of the viscous finger patterns in the

homogeneous polymer solutions shown in Figures 1a -1f without any anisotropy.

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Table 1. Surface tension and viscosity data of the HPMC solutions

Isopropyl alcohol content (vol. %)	0	1	3	5	7	10	15
Surface tension (mN/m)	47.0	46.3	45.4	43.9	42.4	40.1	36.2
Zero Shear viscosity (Pa•s)	0.114	0.122	0.135	0.143	0.148	0.160	0.198
Solvent viscosity (mPa•s)	0.890	0.926	1.00	1.08	1.17	1.31	1.60
Relative viscosity	128	132	135	132	126	126	124

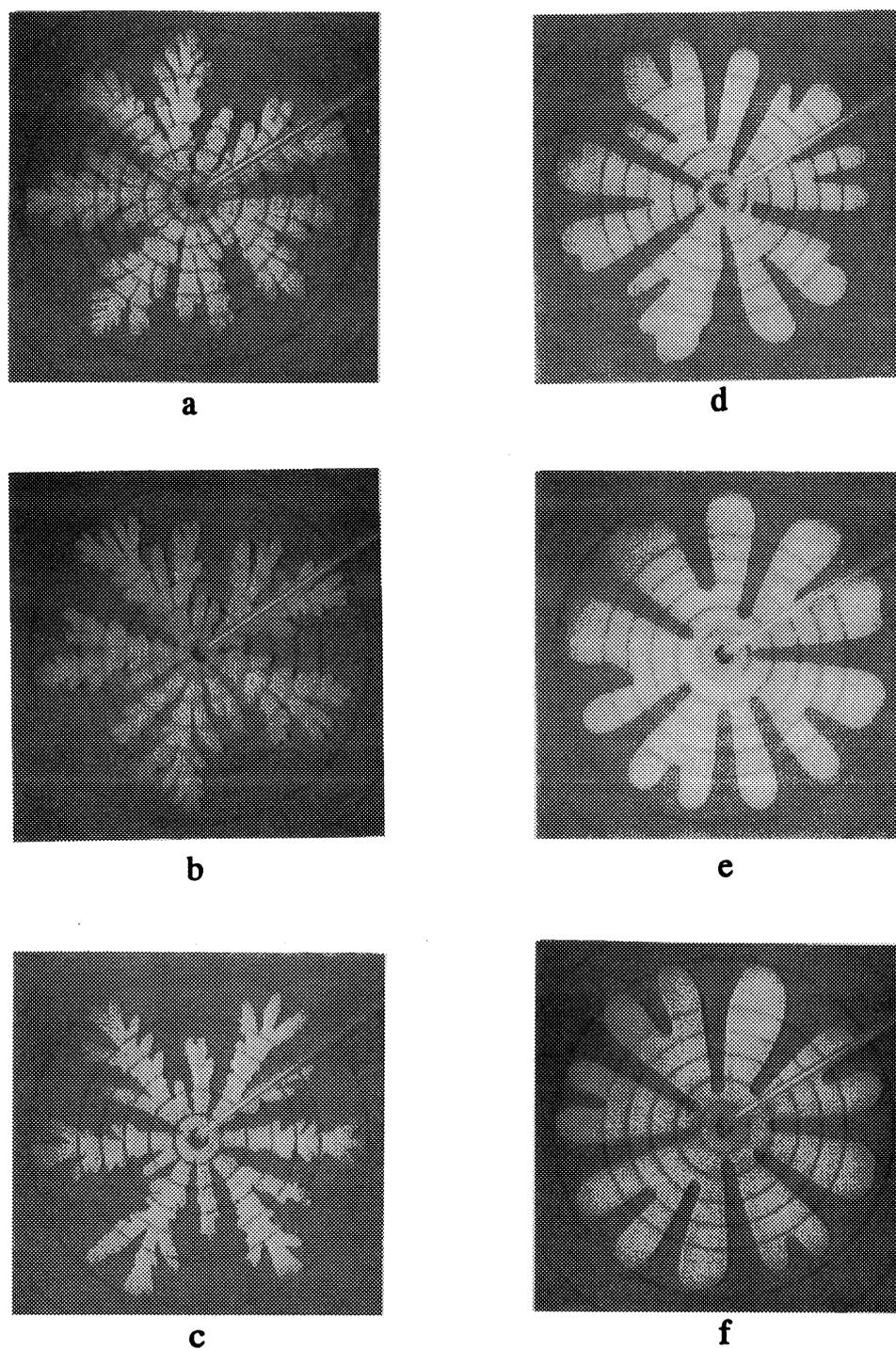


Figure 1. Morphology transition in viscous fingering patterns of the HPMC solutions as a function of isopropyl alcohol content  $\phi$ : a,  $\phi = 0$  vol. %; b,  $\phi = 3$  vol. %; c,  $\phi = 5$  vol. %; d,  $\phi = 7$  vol. %; e,  $\phi = 10$  vol. %; f,  $\phi = 15$  vol. %. The concentric circles in the photographs have the radii of 1, 2, 3, 4, 5, 7, and 9 cm, respectively.

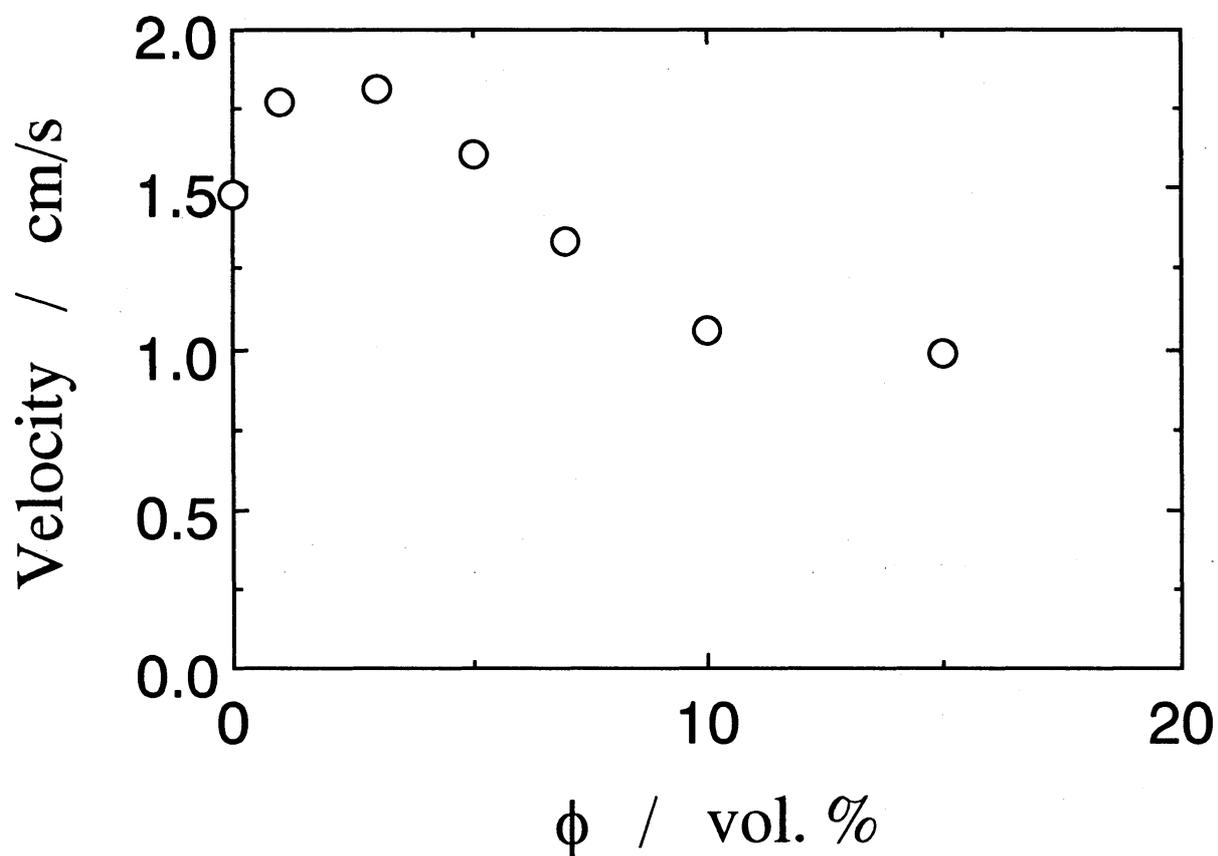


Figure 2. The average tip velocity of the viscous fingering pattern as a function of isopropyl alcohol