Variation in viscous fingering pattern morphology due to surfactant-mediated interfacial recognition events

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The study of the formation of finger-like patterns during displacement of a viscous fluid by a less viscous one is of technological importance. The morphology of the viscous-finger patterns generated is a function of many parameters such as the flow rate, difference in viscosities of the two fluids and the interfacial tension. We demonstrate herein that the morphology of patterns formed during viscous fingering in a Hele-Shaw cell during displacement of paraffin oil by aqueous solutions of the surfactant sodium dodecyl sulphate (SDS), is extremely sensitive to interfacial tension variation brought about by complexation of divalent cations with the surfactant SDS. The variation in morphology of the patterns formed has been quantified by measuring the fractal dimensions of structures formed in a radial Hele-Shaw cell as well as the average finger width in a linear Hele-Shaw cell. This technique shows promise for studying other interfacial phenomena in chemistry such as biorecognition as well as dynamic processes occurring at interfaces.

THE displacement of a viscous fluid by a less viscous one leads to the formation of finger-like patterns known as 'viscous fingers'[1]. First observed by petroleum engineers during secondary oil recovery[2], the study of the phenomenon of viscous fingering has application in a range of fundamental and industrially important problems such as fluid flow in porous media[3], dendritic solidification[4], combustion in two dimensions[5] and electrochemical deposition[6], to name just a few. While considerable research effort has been directed at understanding the various physical factors governing viscous fingering[7–10], application of viscous fingering pattern formation to problems in chemistry has not been attempted with much seriousness[11]. This is especially surprising given that the interfacial tension between the two fluids plays an important role in the evolution of the viscous-finger morphology[1a,8,9] and should thus

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provide fertile ground for studying a range of static and dynamic interfacial phenomena. We show herein one such potential application of viscous fingering pattern formation in interfacial chemistry. More specifically, we demonstrate that interfacial recognition events involving suitable surfactants and analytes from solution lead to a dramatic variation in the morphology of the viscous-fingering patterns formed during displacement of paraffin oil (viscous fluid) by aqueous solutions of the surfactant, sodium dodecyl sulphate (SDS).

The process of viscous fingering is conveniently studied in a radial Hele-Shaw cell (Figure 1, ref. 1b). The radial Hele-Shaw cell used in this study comprised two 1 cm thick, 30×30 cm^2 float-glass plates. Spacers of size $b = 0.2$ mm were used between the top and bottom glass plates. The viscous fluid paraffin oil (viscosity = 1.7 poise, surface tension = 35 dyn/cm) was taken in the cell gap and thereafter the aqueous solution was injected through a hole (0.5 mm diameter) drilled at the centre of the top glass plate using an automated fluid delivery system (Figure 1). The experiments were performed for different aqueous solutions as the displacing fluid, namely water, a 1×10^{-2} M solution of SDS and a 1×10^{-2} M aqueous SDS solution to which 10^{-4} M CdSO$_4$ solution was added. The surface tensions of the aqueous solutions together with their viscosities are listed in Table 1 (ref. 12). The critical micelle concentration (CMC) of SDS in water is 8.1×10^{-3} M (ref. 13) and thus the surface tension of the aqueous solutions with SDS at a concentration of 1×10^{-2} M would be close to its lowest value, indicating saturation of the surface with SDS molecules. A small amount of KMnO$_4$ was added to all the aqueous solutions to yield sufficient contrast between the aqueous and oil phases, thus enabling easy capture of the images with the CCD (charge-coupled device) camera (Figure 1). The monovalent K ion is not expected to interfere with the stronger binding of the divalent Cd cation with the sulphate group of SDS. The viscous fingering experiments were performed at different volumetric flow rates (VFR, flow rate of the aqueous solutions into the paraffin oil phase) ranging from 0.06 to 2.7 ml/min. The evolution of the finger pattern with time was followed for the above cases using a CCD camera connected to a video recorder at an image capture rate of 25 images/s. The images were then digitized and computer-analysed using standard image processing software (Figure 1).

Morphologies of the patterns obtained for different flow rates for the various aqueous solutions mentioned above are shown in Figure 2. One can clearly notice a variation in the morphologies for the different solutions at a given flow rate. Especially dramatic are the differences in the pattern morphology observed at the lowest VFR of 0.06 ml/min, where it is observed that as the interfacial tension decreases (i.e. on going from water to water + SDS to water + SDS + CdSO$_4$, Table 1), the
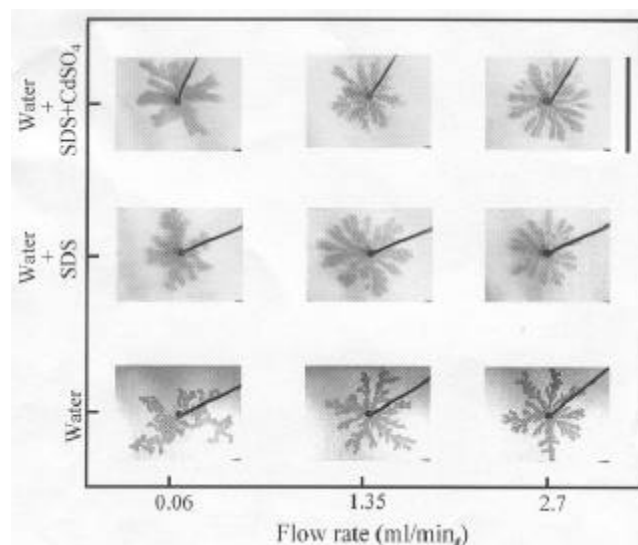
Table 1. Values of the various parameters varied/obtained in experiments carried out on the different aqueous solutions in a linear Hele-Shaw cell at a flow rate of 0.06 ml/min

Displacing fluid	Surface tension (dyn/cm)	Viscosity (poise)	Fractal dimension[a]	Normalized finger width, l[b]
Water	75	1.5×10^{-2}	1.66 ± 0.02	0.17
Water + SDS	32	1.8×10^{-2}	1.79 ± 0.02	0.31
Water + SDS + CdSO$_4$	28	1.7×10^{-2}	1.80 ± 0.02	0.42

[a]Fractal dimensions have been estimated from an analysis of the viscous-fingering patterns obtained in the radial Hele-Shaw cell and shown in Figure 2 (lowest flow rate); [b]Normalized finger widths were obtained from the finger patterns formed in a linear Hele-Shaw cell.
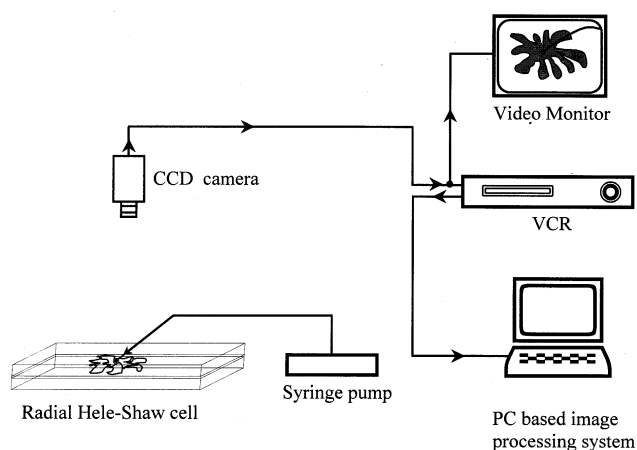
Figure 1. Various elements in the experimental set-up for the study of patterns in a radial Hele-Shaw cell.

Figure 2. Viscous fingering-patterns obtained for water, water + SDS and water + SDS + CdSO$_4$ at different flow rates of the displacing fluid (see text for details). The vertical scale is 15 cm long.

morphology of the patterns becomes progressively less branched, with larger fingers appearing in the patterns (Figure 2). The fractal dimensions of the patterns have been determined for this flow rate and are listed in Table 1. While there is a substantial increase in the fractal dimensions on going from water to water + SDS, the difference in fractal dimensions of the patterns formed with aqueous SDS solution and the surfactant complexed with Cd^{2+} ions is negligible (Table 1). This insensitivity of the calculated fractal dimensions to visible differences in morphology has been observed by Nittmann and Stanley[14] in their studies on pattern formation in diffusion limited aggregation (DLA). They observed that increasing amounts of noise in DLA simulations resulted in patterns with extensive branching and thinner fingers, but that the fractal dimensions of the patterns were relatively insensitive to the noise level[14]. From the patterns obtained in this study, it appears that reduction in interfacial tension due to complexation of Cd^{2+} ions with interface-bound SDS molecules results in reduction of noise (and therefore fluid-dynamical instabilities at the interface) in the system. Whatever be the physical mechanism determining the noise and instabilities at the interface, it is clear that events such as electrostatic complexation of ions with surfactants at the

interface between the two fluids lead to a change in the viscous fingering morphology and it is this point we wish to highlight.

As mentioned earlier, the thickness of the individual fingers in the radial Hele-Shaw patterns obtained for the different solutions are quite different (Figure 2). This is conveniently quantified by carrying out a viscous fingering experiment in a linear Hele-Shaw cell[9] at a VFR of 0.06 ml/min, where a solitary finger evolves in a channel of known dimensions. It is well established that at such low flow rates, interfacial effects dominate over kinetic effects in determining the fingering-pattern morphology[15]. The ratio (l) of the finger width (w) to the width of the channel (W, 4 cm in this study), was measured at this flow rate and the values obtained are given in Table 1. It is observed from the table that the finger width increases as the interfacial tension between the paraffin oil and aqueous phases decreases. While the change in the interfacial tension is large as one goes

from water to water + SDS and could result in a large difference in pattern morphologies for the two cases (Figure 2 and Table 1, fractal dimensions), what is interesting is that complexation of Cd^{2+} ions with SDS molecules at the interface leads to a further significant increase in the finger width (as well as a visible change in the morphology of the patterns in the radial Hele-Shaw cell), even though the surface tension difference is small (ca. 4 dyn/cm). According to theory, the width of viscous fingers is determined by the capillary number, $Ca = \Delta m U / g$, where Δm is the difference in viscosity between the two liquids; U is the finger velocity and g is the surface tension[9]. Any factor leading to an increase in the capillary number would lead to a decrease in the finger width in a linear Hele-Shaw experiment (i.e. there is an inverse relationship between the capillary number and finger width[9]). In this study, the interfacial tension decreases as one progresses from water to water + SDS to water + SDS + $CdSO_4$ and should, according to theory, result in a decrease in finger width, contrary to what is observed. This is an important result of this study. It may be pointed out here that differences in viscosity of the displacing fluid could also affect the morphology of the patterns[9]. However, the viscosities of the aqueous solutions used in this study are nearly identical (Table 1) and therefore the changes observed in the morphology may be attributed to purely interfacial tension effects. The fact that extremely small changes in the interfacial tension leads to dramatic changes in the viscous finger widths immediately suggests interesting application in problems such as binding of proteins/DNA with lipids at interfaces. Very recently, some of us have studied the hybridization of DNA mediated by cationic lipids at the air–water interface using a Langmuir trough[16]. While the hybridization of the complementary DNA strands could be ascertained only after transfer of the films onto suitable substrates[16], small changes in the interfacial energy brought about by the hydrogen bonding process may be conveniently studied in real time using the Hele-Shaw cell in the manner described above. This and other related problems are currently being pursued.

Morphology differences are also seen in the three cases studied at higher flow rates (Figure 2). However, these differences are not as prominent as they are in the case of the low flow regime. At higher flow rates, kinetic effects dominate over interfacial effects[15]. For example, the relative timescales of creation of new surface area versus diffusion of surfactant from bulk to the interface to reduce the interfacial tension would become important[15,17]. One would also have to consider the rearrangement of surfactant molecules at the interface during creation of a new surface of varying curvature[9].

In conclusion, it has been shown that viscous fingering patterns in a Hele-Shaw cell are extremely sensitive to changes in the interfacial tension brought about by complexation of ions with charged surfactants. This technique shows promise for further development and application in interfacial chemistry/biology-related problems as well as in the study of dynamic processes occurring at interfaces such as dynamic surface tension measurements which are known to be difficult to perform[17].

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