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Visualization of viscous fingering in high-performance liquid chromatographic columns Influence of the header design

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Abstract

Using an on-column visualization technique, band profiles of solutes migrating along an HPLC column were studied. The study showed that, under conditions where viscous fingering is prevalent, the design of the inlet header has little influence on the outcome of the viscous fingers. Two types of headers were studied. The first contained a small diameter inlet frit, which localized the majority of the sample in or near the central region of the column. The second header contained a wide frit and produced a more uniform radial distribution of the sample. In both cases, the extent of viscous fingering was essentially the same.

Keywords: Viscous fingering; Header design; Column headers

1. Introduction

The importance of achieving uniform sample concentration and flow velocity distributions across the head of a chromatographic column has been understood for decades. Numerous studies evaluated transverse dispersion in liquid chromatography [1–4], to understand why the specifications are more drastic in LC than in GC. Other studies investigated the so-called ''wall effect'' [1,2,5–8], which is the source of radial heterogeneity during the migration itself. Still other studies examined the axial and radial profiles of bands during their migration using on-column visualization by either NMR [9–11] or optical methods, in packed glass columns with mobile and stationary phases of matched refractive indices [12–16]. In recent studies [15,16], the importance of the radial distributions of the flow velocity at the head of the column and of the sample concentration during injection were illustrated in cases in which the diameter of the inlet frit was narrower than that of the column or the frit permeability was much smaller than that of the packed bed. With inadequate frits, it was found that the sample was often concentrated in the central region of the packing, rather than distributed more or less homogeneously across the whole column head. Be-

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cause of the poor sample distribution, the column efficiency was poor.

Flow heterogeneities, however, do not arise only because of the design of the chromatographic column and of its peripherals, sampling valve, connecting tube, head fitting, frits, or distributor. Differences between the solute and the mobile phase viscosities can also affect the migration of the solute bands. Such an effect is called viscous fingering or, more correctly, the Saffmann and Taylor instability [17]. Some authors voiced concern that poor concentration distribution of the sample and viscous fingering could be inter-related and that the former phenomenon could, under certain conditions, trigger the latter [18]. If the viscosity differences between sample and solvent are sufficiently different, nothing may prevent viscous fingering from occurring, except sample dilution. However, poor sample distribution results in a radially heterogeneous band. Viscous fingering will arise first in the regions of higher sample concentration. The design of a column header that provides uniform distributions of the flow velocity and the sample concentration distributions across the cross-section of the column with minimal dispersion of the injection plug might help in reducing viscous fingering.

As explained by Saffmann and Taylor [17], viscous fingering occurs as a result of differences in the viscosities between two solutions migrating in a porous medium, one pushing the other one. When the viscosities are sufficiently different, the less viscous solution, if it is second, will finger into the more viscous one. Viscous fingering in chromatographic columns is well documented [17,19–23] and further discussions of this effect are not warranted here.

In this study we show and compare photographs obtained with a method previously described [13–16]. These photographs illustrate viscous fingering with two different column headers, the first providing poor radial distributions of the flow velocity and the sample concentration, the second providing more uniform distributions. We discuss these results.

2. Experimental

2.1. Chemicals

Reagent grade carbon tetrachloride was obtained from Sigma (St. Louis, MO, USA); reagent grade methanol, HPLC grade dichloromethane, and 98% pure *n*-pentane from Mallinckrodt (Paris, KY, USA).

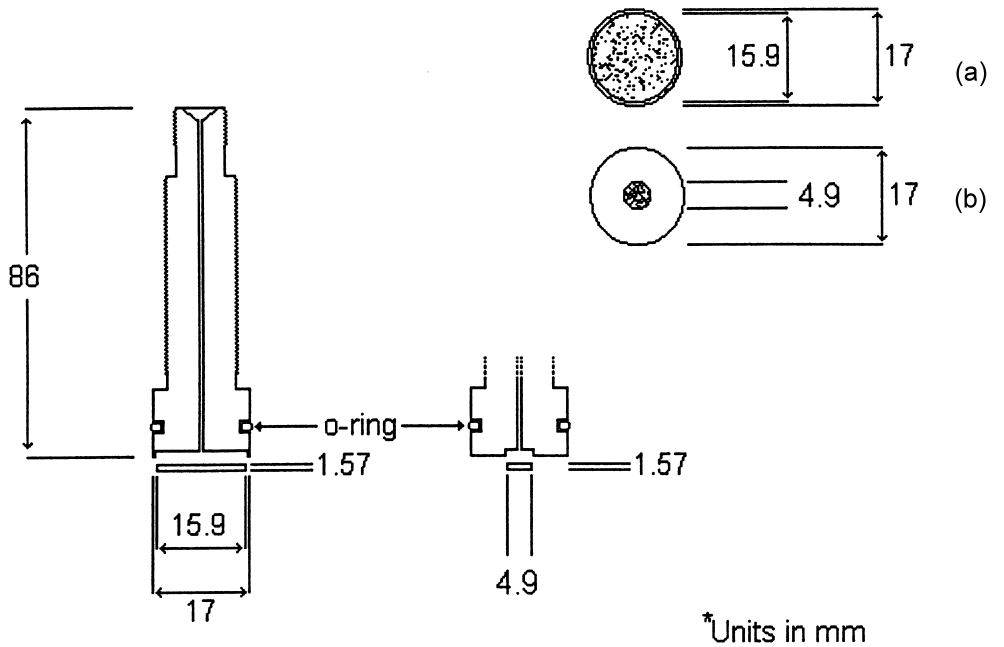

Fig. 1. Diagram of the column header containing the frit.

Iodine (99.9%) was obtained from General Chemical Division (New York, NY, USA). All mobile phases were sparged with helium during the entire experiments.

2.2. Columns and packing material

All chromatographic experiments were performed on a 100×17 mm (I.D.) borosilicate (Pyrex) glass column supplied by Omni (Cambridge, UK). The column end fittings were prepared by the University of Tennessee workshop and machined from Delrin plastic. These fittings included a fixed length outlet fitting and an adjustable inlet fitting that allowed axial compression of the column. Stainless steel frits having a diameter of 15.9 mm and a thickness of 1.57 mm were obtained from Bodman (Aston, PA, USA). High molecular weight polyethylene frits having a diameter of 4.6 mm and a thickness of 1.57 mm were obtained from Upchurch Scientific (Oak Harbor, WA, USA).

The stationary phase used was YMC C_{18} silica (Kyoto-Fu 613, Japan). This material is spherical with a particle size distribution given as 15–30 μm and an average particle size of 21 μm. The column was slurry packed in a downward configuration using conditions previously described [12–16]. To improve visualization and minimize the cylindrical lens effect, the entire column assembly was placed into an in-house, rectangular, box-shaped, viewing cell filled with dichloromethane. The cell assembly was described in a previous communication [13].

2.3. Equipment

The chromatographic system consisted of two high-performance liquid chromatographic (HPLC) pumps (model 510, Waters Associates, Milford, MA, USA) controlled by a Waters automated gradient controller. The mobile phase was 100% carbon tetrachloride and the flow-rate 1.5 ml/min throughout. Sample injection was achieved through a Rheodyne injection valve (model 7010, Rheodyne, Cotati, CA, USA). All injection volumes were either 20 μl or 500 μl as stated where relevant. The sample injected was either a solution of iodine in carbon tetrachloride (12 g/l) or a saturated solution of iodine in *n*-pentane. Sample visualization of the band profiles was achieved using two Pentax ZX-M SLR 35 mm cameras fitted, one with a Promaster 100 mm macro lens, the other with a Makinon 80–200 mm macro zoom lens. Kodak Ektachrome 200 ASA Professional slide film was used throughout. The photographic images were digitized using a Nikon CoolScan II (Nikon, Melville, NY, USA) film scanner. All images were acquired at the maximum resolution of the scanner (2700 dots per inch). Adobe Photoshop 5.0 (Adobe Systems, San Jose, CA, USA) was used to perform image manipulation. Further analysis was done using SigmaScan Pro 4.01 (Jandel Scientific, San Rafael, CA, USA) image analysis software.

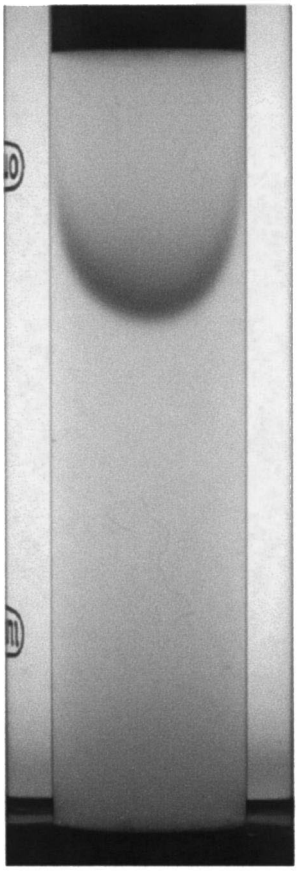

Fig. 2. Photograph of a 20 μl injection of a 12 g/l sample of iodine in carbon tetrachloride solution through a narrow (4.6 mm diameter) frit. Flow rate=1.5 ml/min.

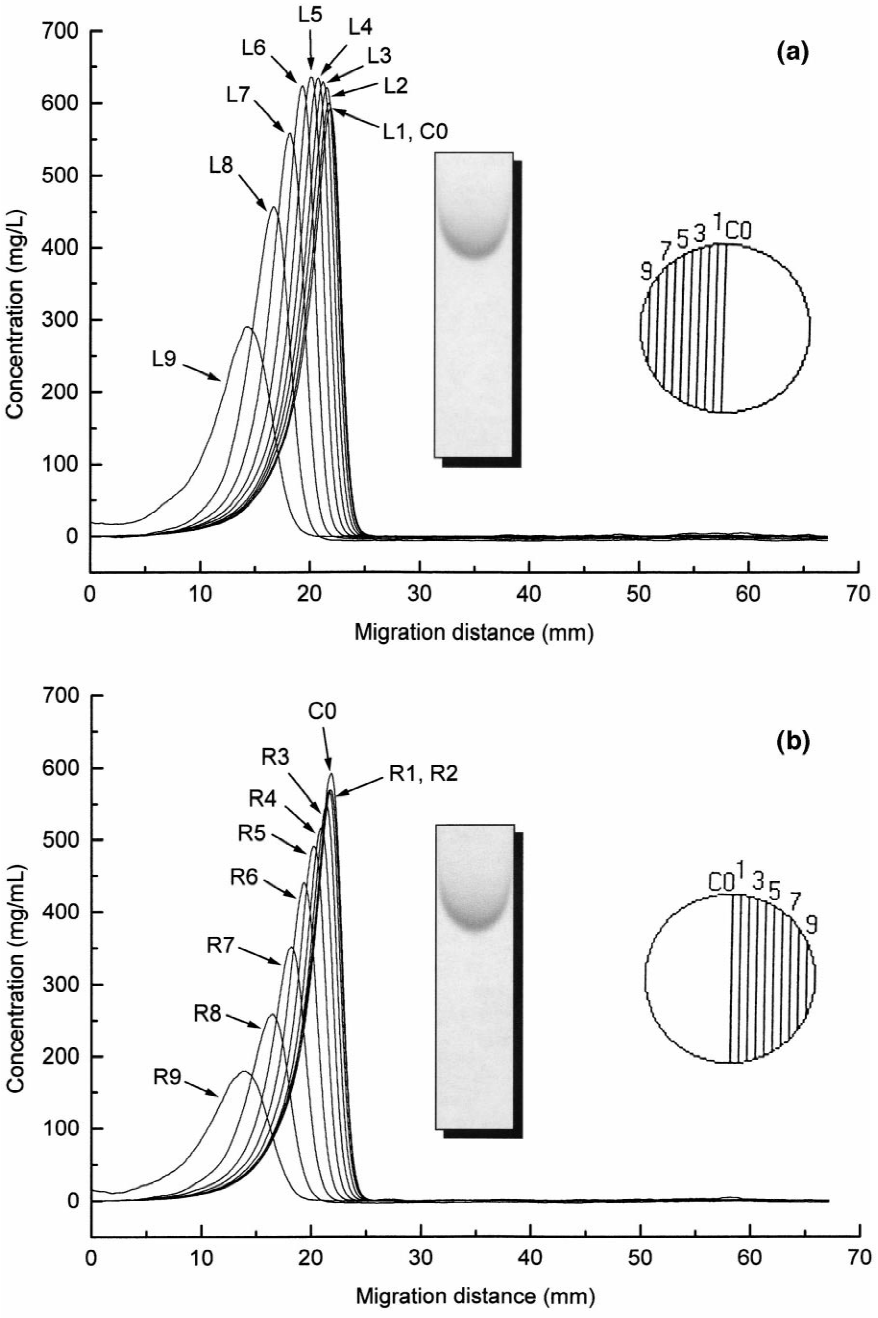

Fig. 3. Axial concentration profiles obtained by scanning the vertical bands (whose horizontal traces are shown in the right inset) of the image in the left inset, obtained with camera 1, 2 min after sample injection on a column with a 4.6 mm diameter 10 μm frit. The photograph was taken under the same conditions as Fig. 2. Each band is 0.81 mm wide (approximately 40 particle diameters). The image was divided into 19 sections radially across the column, as indicated in the right inset. (a): Profiles for the left hand side of the column including the center. (b): Profiles for the right hand side of the column including the center.

3. Results and discussion

Two header designs were selected for this study. The first header contained an inlet frit that was approximately four times smaller than the column internal diameter, while the second header contained an inlet frit that had almost the same diameter as the column internal diameter. Both header designs were previously examined in detail in previous communications [15,16]. Their design is shown in Fig. 1. Both inlet frits were 10 μm in pore size and differed only in their diameter and the construction material.

Fig. 2 shows the band profile obtained upon injection of a 20 μl sample of the iodine solution through the first header (narrow diameter frit). The profile appears nearly parabolic. The on-column concentration profiles are shown in Fig. 3a and b. The left hand side region contains more sample than the right hand side one. The profiles are strongly tailing. Little amount of solute dispersed to the wall (Fig. 3). The design shown in Fig. 1b is particularly poor. By contrast, the distribution of the sample obtained upon introduction of the same sample through the second header (wide frit) gives a more uniform sample distribution, as shown in Fig. 4 with the concentration profiles in Fig. 5. These mildly tailing profiles demonstrate a slightly parabolic radial distribution of the band velocity. The frit was not as good as other similar ones previously used [15,16]. It is slightly heterogeneous and gives higher concentrations in the left of the center of the band than in the rest of it. Yet, the performance obtained are reasonable. This confirms previous observations regarding the lack of reproducibility of the frit characteristics and their poor general quality [15,16]. In the experiments just discussed, the results of which are illustrated in Fig. 5a and b, no viscous fingering was observed nor was any expected because the two solutions, mobile phase and sample differ little and have nearly the same viscosity.

To observe viscous fingering, it was necessary to change the viscosity of the injection plug. A solution of iodine in pentane was used as the sample. The viscosity of pentane (0.240 cP @ 20°C) is 0.25 times that of carbon tetrachloride, which gives a large viscosity difference, well sufficient to induce Saffmann-Taylor instability. The limited sensitivity of photographic detection in the observation of refractive index differences required the use of a larger size sample, 500 μl, to visualize viscous fingering. The photographs in Fig. 6 give a dramatic representation of the viscous fingering arising at the head of the solute band. The viscous fingers began to form immediately when the sample entered the column. The photograph in Fig. 6d shows that, by the time the rear of the sample plug entered in the center of the column, the fingers had almost reached the column exit. However, the onset of viscous fingering was not related to the size of the injection volume, as illustrated by a comparison between the photographs in Figs. 6d and 7. This latter photograph shows a 500 μl injection of an iodine solution in carbon tetrachloride. The profile is nearly identical to the one of a 20 μl injection shown in Fig. 2.

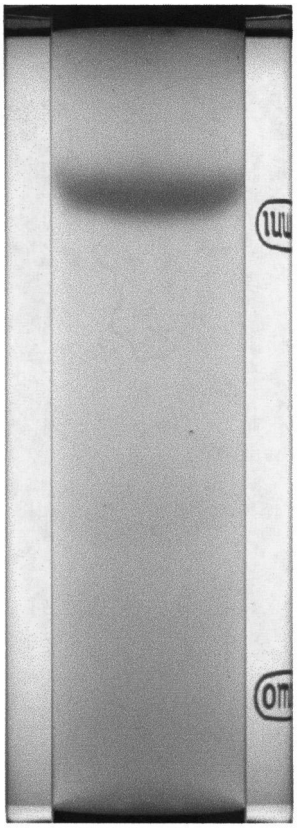

Fig. 4. Photograph of a 20 μl injection of a 12 g/l sample of iodine in carbon tetrachloride solution through a wide (15.9 mm diameter) frit. Flow rate=1.5 ml/min.

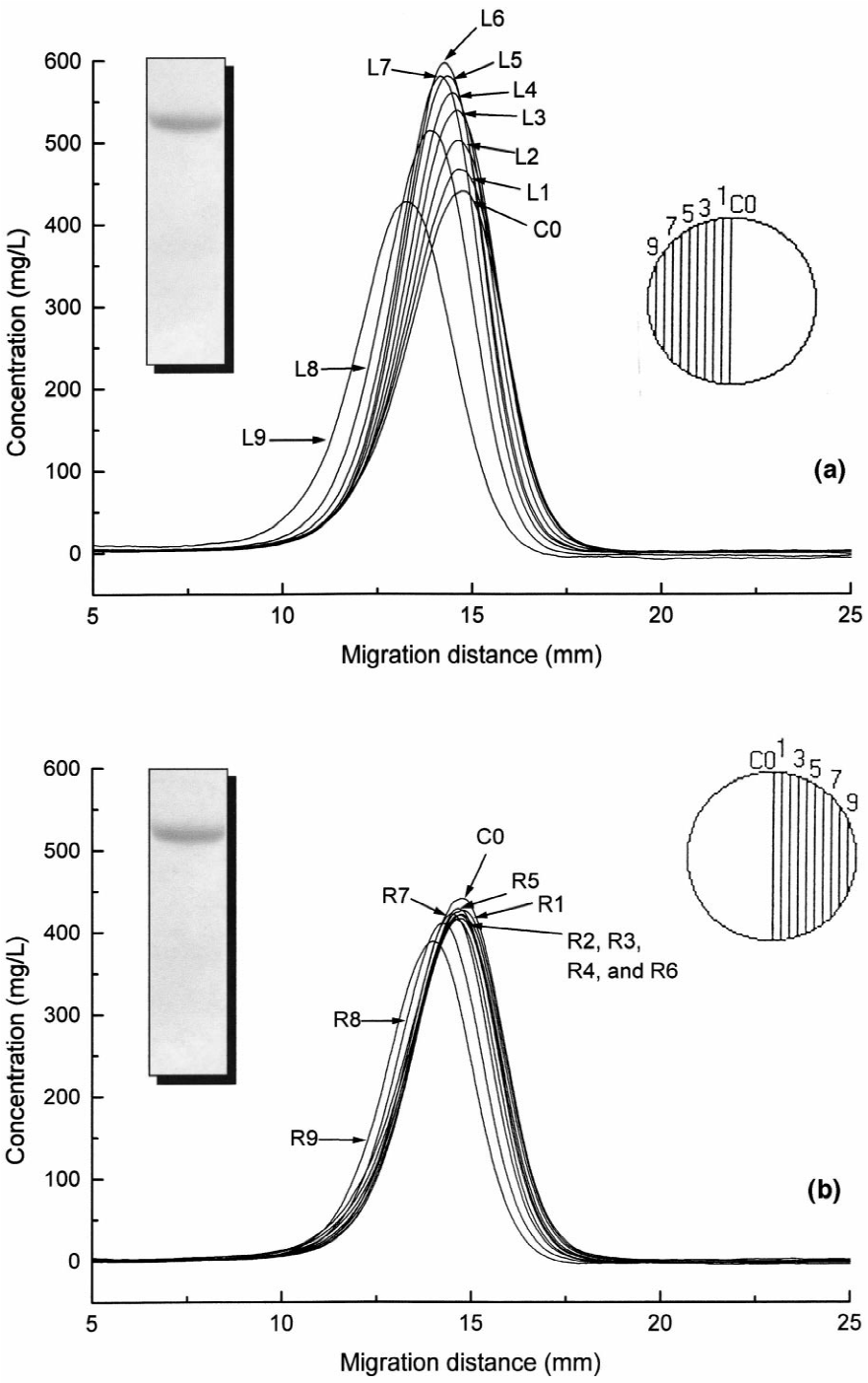

Fig. 5. Axial concentration profiles obtained by scanning the vertical bands of the image in the left inset, obtained 2 min after sample injection on the column. The photograph was taken under the same conditions as Fig. 4. (a): Profiles for the left-hand side of the column, including the center. (b): Profiles for the right-hand side of the column, including the center.

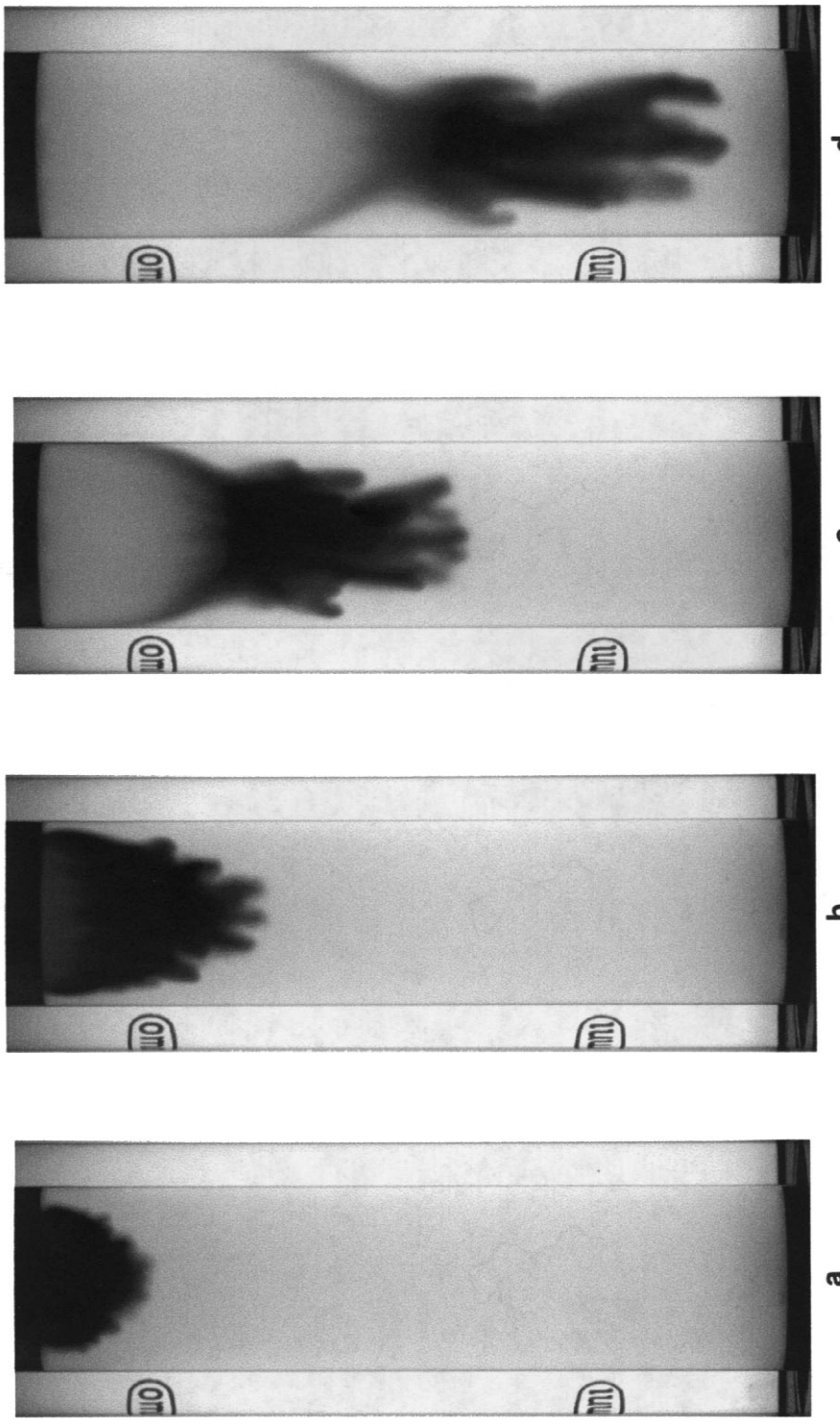

Fig. 6. Photographs of a 500 μl injection of a saturated iodine in pentane solution through the narrow (4.6 mm diameter) frit. Flow rate=1.5 ml/min. (a) t=30 s, (b) t=60 s, (c) t=120 s, and (d) t=210 s.

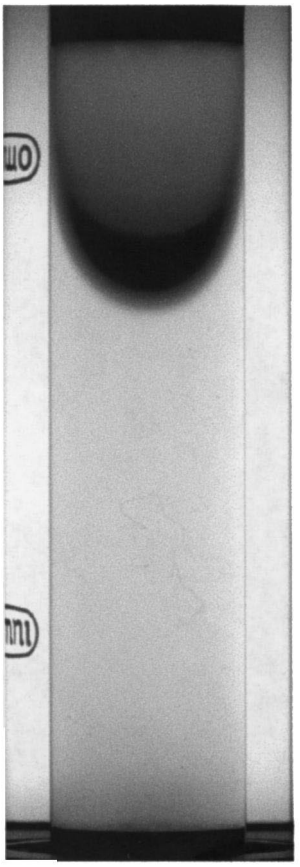

Fig. 7. Photograph of a 500 μl injection of a 12 g/l sample of iodine in carbon tetrachloride solution through the narrow (4.6 mm diameter) frit. Flow rate=1.5 ml/min.

Fig. 8 shows the profiles obtained upon the injection of the same volume of the same iodine/pentane solution through the second header (wide frit). In this case again, viscous fingers form almost instantaneously. Their length is unaffected by the sample distribution. The only significant difference between Figs. 6 and 8 is that the density of fingers in the wall region is higher in Fig. 8 than in Fig. 6 which is reasonably explained by the much higher concentration achieved in the wall region (compare Figs. 3 and 5). By the time the sample band migrated by half the column length, the first of the fingers was near the column exit (Fig. 8d). The injection of a 500 μl sample of the carbon tetrachloride solution showed that the band profile was the same as for a 20 μl injection volume (data not shown).

In a previous communication on the visualization of viscous fingering, we noted that the sample band appeared to move away from the wall [12]. This result is now easily explained. The corresponding experiments were performed with the narrow diameter frit (see Fig. 6). Following the work done in the mean time on the calibration of the photographic detection system and on the analysis of the concentration profiles along the column [14–16], we now know that what appeared to be a movement away from the wall was an optical illusion brought about by the behavior of the head-fitting and its narrow frit. This conclusion is confirmed by the comparison between Figs. 6 and 8, as discussed above.

In addition to the results reported in this study, a detailed video of the migration of various bands and the formation of viscous fingers was recorded. A series of short sequences depicts viscous fingering in ''real time'' and provides valuable insight into the dynamic of a phenomenon which is not easily observed and understood from still photographs. Copies of this video on a CD will be provided upon request from the authors.

4. Conclusion

These results clearly illustrate that viscous fingering arises independently of the quality of the design of the column header employed. The occurrence of viscous fingering depends on the difference between the viscosities of the mobile phase and the sample. When it can take place, it arises very quickly and then the long fingers keep growing. It is true that a header design that does not distribute the sample uniformly across the column may increase the likelihood of viscous fingering in the high concentrations of the band. However, small changes in the viscosity of the sample solution do not seem to matter much. Furthermore, a poor sample distribution leads to really poor chromatographic performance, irrespective of the occurrence of viscous fingering.

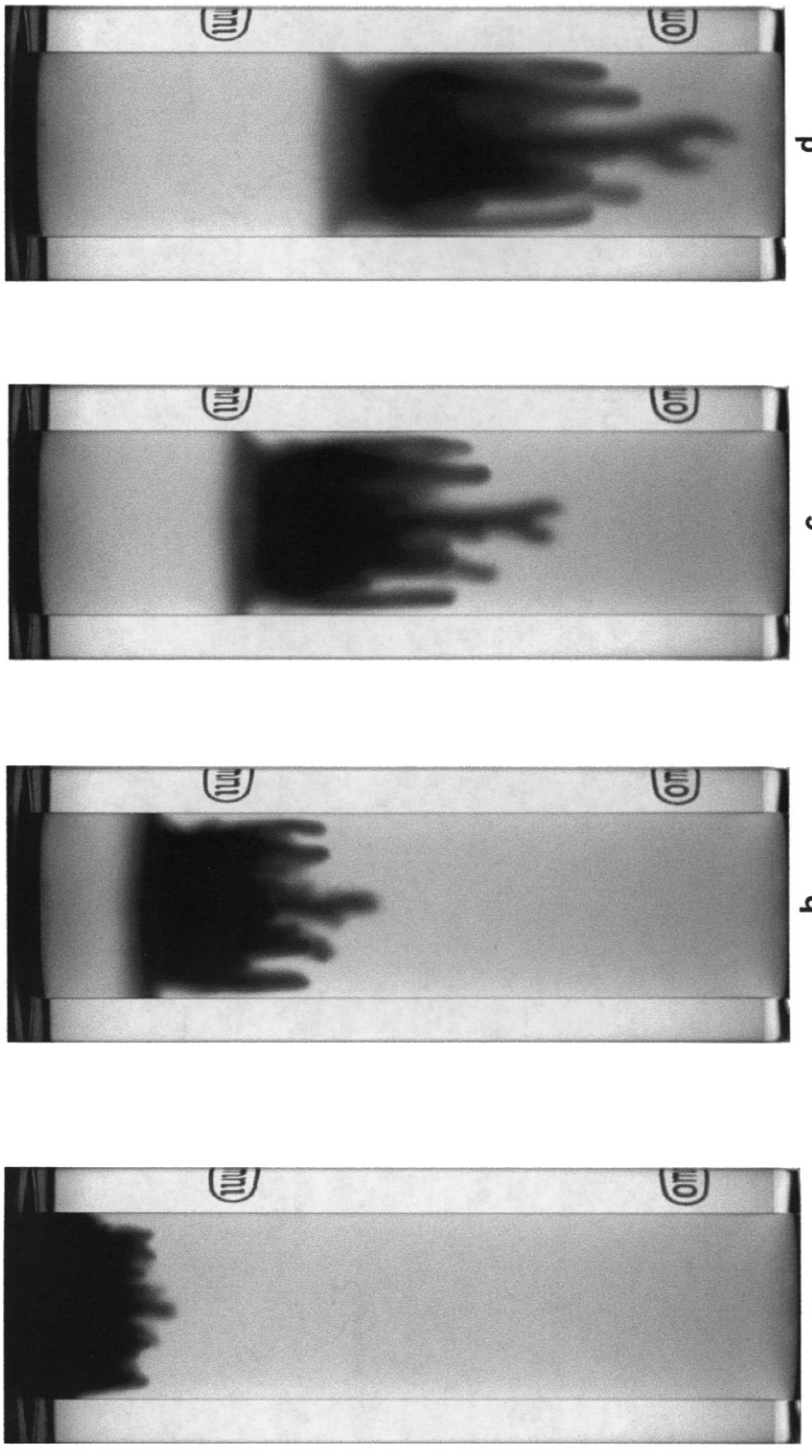

Fig. 8. Photographs of a 500 μl injection of a saturated iodine in pentane solution through the wide (15.9 mm diameter) frit. Flow rate=1.5 ml/min. (a) t=60 s, (b) t=120 s, (c) t=180 s, and (d) t=240 s.

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