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SOLUTE FOCUSING BY MEANS OF THE SOLVENT EFFECT: FORMATION OF THE FILM

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SUMMARY

Solute focussing using the solvent effect is usually carried out in an open tube. Under such circumstances the sample film can be unstable and this leads to peak distortion. It is shown that when the sample film is formed in a packed bed, the film is much more stable, even when polar solvents are used. A further advantage of packed beds is that large sample volumes can be handled.

INTRODUCTION

An essential feature of solute focusing by means of the solvent effect is the formation of a film of the sample in the inlet[1,2]. This may be done either by injecting the sample into the inlet at a temperature below the boiling point of the solvent (so-called "direct"[3] or "cold on-column"[4] injection), or by first vaporising the sample and subsequently condensing it in a cool portion of the inlet (so-called "splitless"[5] injection).

In general, the film has been formed on the walls of smooth-walled open tubes[2,4,5]; the only exception to this, to our knowledge, was described by Deans[6], who employed a packed bed of organic polymer (PTFE) particles.

It has been claimed that the shape of the film has an important bearing on the solvent effect[2,7]. However, theoretical studies[1] suggest that this is not so. In this paper we present the results of experiments designed to assess the relative merits of packed and open-tubular inlets used for the solvent effect. We shall confine our attention to "cold on-column" injection, although the conclusions reached are generally applicable to "splitless" injection — a matter which will be dealt with elsewhere[8].

REQUIREMENTS FOR THE SAMPLE FILM

The film should result in the effective focusing of solutes by the solvent effect. By this we imply that the solutes should be delivered to the column in a band sufficiently narrow to avoid volume overloading[1].

The film should be simply and reliably formed. The less skill required of the operator the better.

Once formed, the film should be stable, *i.e.*, it should not significantly change its position or shape (this, of course, excludes changes brought about by the evaporation of the film during the time the solvent effect takes place). Film stability is important, as an unstable film can either form lenses that counteract the solvent effect, or the film can emerge from the inlet before the solvent effect has been completed.

The film should occupy the smallest possible volume so that large sample volumes can be handled without excessive inlet volumes.

EXPERIMENTAL

The apparatus (Fig. 1) consisted of a tubular glass inlet, connected to a capillary column (30 m × 0.03 cm I.D.), which was coated[9] with a non-polar stationary phase (SE-30).

The inlet was 15–200 cm long and 0.05–0.06 cm I.D. and was interchangeable so that smooth-walled, rough-walled and packed inlets could be studied. The apparatus was installed in a Varian Model 3700 gas chromatograph, equipped with a flame-ionization detector.

Samples consisted of a dilute solution (*ca.* $1{:}10^5$) of *n*-alkanes (C_8–C_{10}) in a polar (methanol) or a non-polar (*n*-C_7) solvent. They were injected by means of a microsyringe through a septum injector port into the inlet. The sample size was 1–5 μl.

The inlet (and column) temperature was initially 26–40°C and this was main-

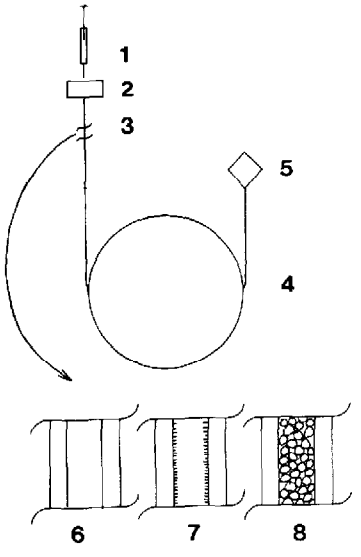

Fig. 1. Schematic diagram of experimental system. 1 = Micro-syringe; 2 = septum injector port; 3 = interchangeable inlet; 4 = capillary column; 5 = flameionization detector; 6 = smooth-walled inlet; 7 = whisker-walled inlet; 8 = packed bed (ground glass or diatomaceous earth).

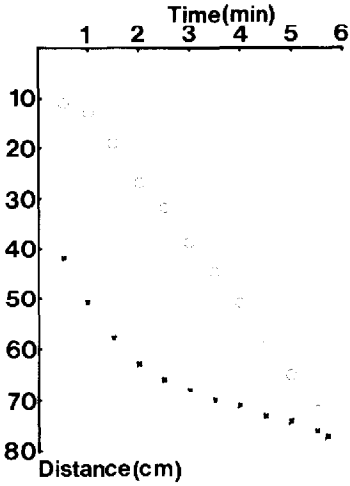

Fig. 2. Position of front (×) and rear (○) of liquid film in a smooth-walled inlet for heptane.

tained until the solvent effect had been completed. Thereafter, the temperature was programmed at 15°C/min.

After the sample had been injected, the positions of the rear and front ends of the film were noted at 30-sec intervals.

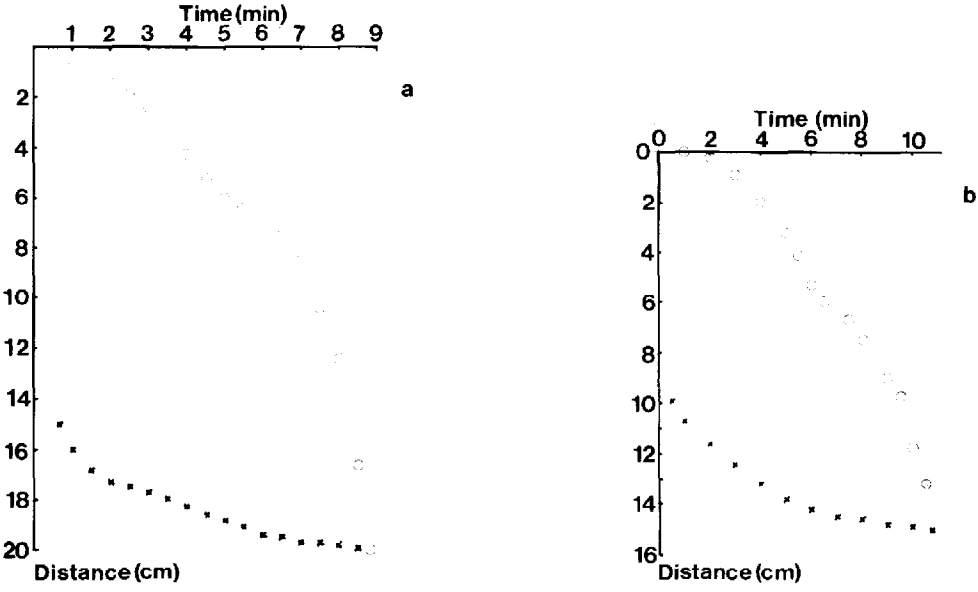

Fig. 3. Position of front (×) and rear (○) of liquid film in a whisker-walled inlet for (a) heptane and (b) methanol.

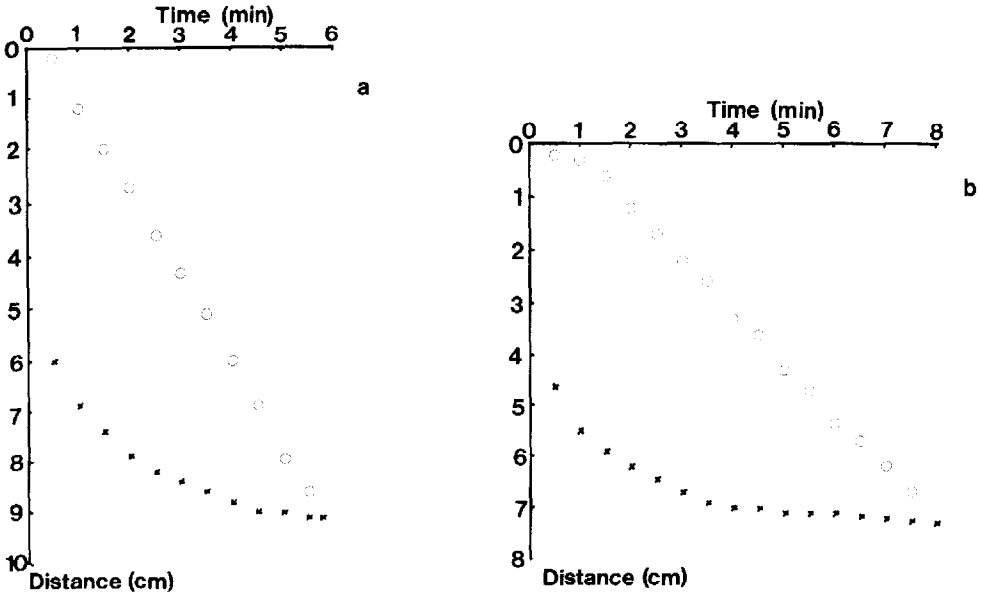

Fig. 4. Position of front (×) and rear (○) of liquid film in a 125-μm ground Pyrex packed bed inlet for (a) heptane and (b) methanol.

DISCUSSION

Film Stability

Smooth-walled open-tubular columns. Lengths of 0.05 cm I.D. Pyrex tubing were made translucent[2]. Injections of 5 μl of heptane and methanol were made.

In general, the films produced were very unstable. Methanol, in particular, was prone to the production of liquid lenses that moved along the inlet at the carrier gas

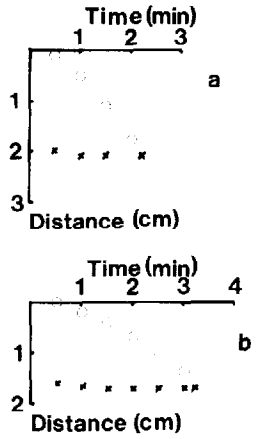

Fig. 5. Position of front (×) and rear (○) of liquid film in a 125-μm diatomaceous earth packed bed for (a) heptane and (b) methanol.

volocity and formed multiple films whose rapid movements could not be accurately measured.

Although the flow velocity in the inlet was outside the range of its application, the Fairbrother–Stubbs equation[10] correctly predicts the variation of film thickness with flow-rate, insofar as lower flow-rates produced thinner films penetrating further into the inlet (Figs. 2–5). Lower flow-rates tended to be less prone to lens formation but were incompatible with the flow-rates needed for optimal chromatographic performance of the column.

From the results, it can be seen that the volume of carrier gas required to evaporate the sample is greater in the case of the open tube than in a diatomaceous earth packed bed. This implies that, with open tubes, radial equilibrium between liquid and vapour is not being achieved to the same extent and that the solvent peak is likely to be wider.

Rough-walled open-tubular columns. Rough-walled columns were prepared by the production of a whiskered surface[1] on the inside of a capillary of 0.05 cm I.D. The films produced on these columns were shorter than in smooth-walled tubes by a factor of about 4, which allows increased sample loading. The films were generally more stable in that lenses were never observed and in that the front edge of the film moved considerably more slowly down the inlet than with smooth-walled tubes. This was true for polar and non-polar solvents.

Packed beds of non-porous particles. A 17 cm × 0.06 cm I.D. Pyrex tube was

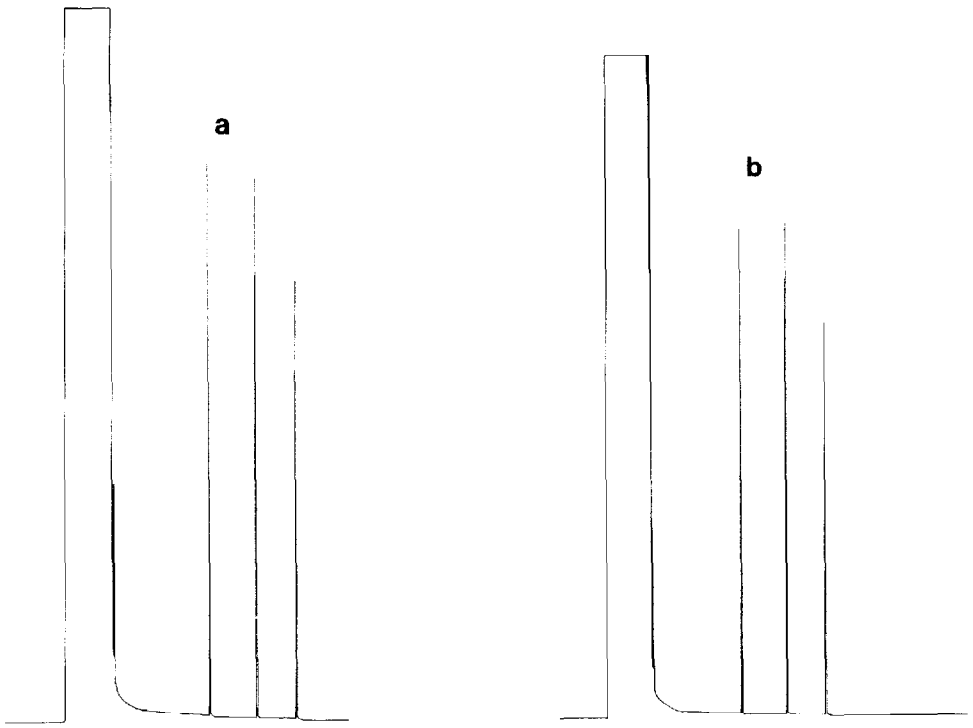

Fig. 6. Chromatogram of C_8, C_9 and C_{10} *n*-alkanes in C_7 solvents: (a) smooth-walled and (b) whisker-walled opentube inlets. Sample volume: 1 μl.

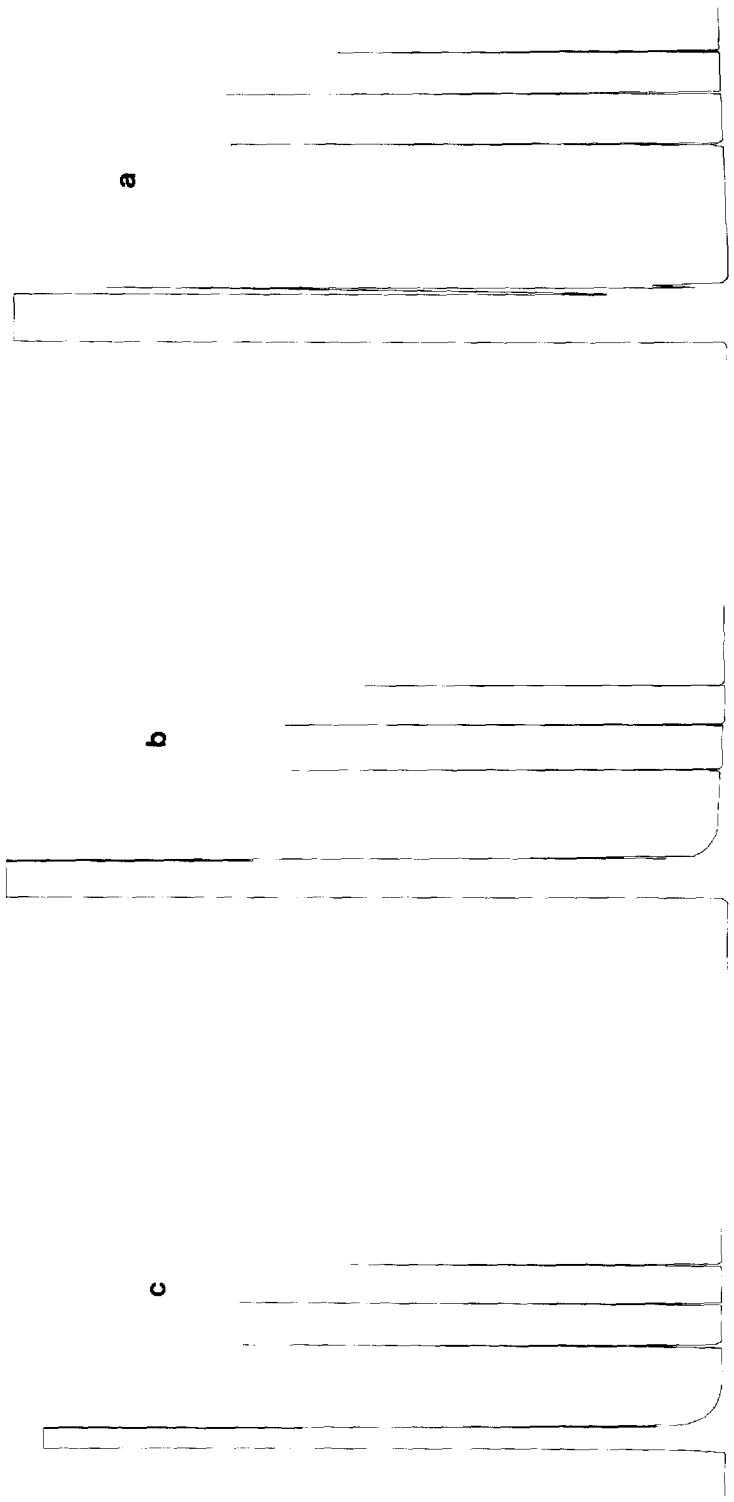

Fig. 7. Chromatogram of C_8, C_9 and C_{10} *n*-alkanes in C_7 solvent. Packed bed inlets: (a) 50-μm ground Pyrex; (b) 120-μm diatomaceous earth; (c) 55-63-μm diatomaceous earth. Sample volume: 1 μl.

filled with 105–125-μm glass particles, produced by manual grinding and sieving. The film produced was markedly more stable than films in open tubes. The solvent effect takes place in a volume approximately 20% of that required in an open tube.

Packed beds of porous particles. With regard to film stability, these systems proved to be the best of all tested. However, the films were the most difficult to observe. Only with the use of carefully placed lights and a magnifying glass could the wet region of the bed be seen.

Two particle sizes of diatomaceous earth were studied, *viz.*, 125 and 60 μm diameter. These particles were packed into a 0.06 cm I.D. column. The films produced on injection of 5 μl of heptane or methanol showed exceptional stability towards migration. (Results for the film movement on 60-μm particles are not given as film observation was too difficult for reliable results.) The narrowness of the solvent band with the 60-μm particles suggests a very high evaporation efficiency.

Results not published here show that smaller particles hold larger amounts of liquid per unit volume than do larger particles. We conclude that the maximum sample load capacity occurs with the minimum particle size. Excessively small particles create the problem of requiring a large pressure drop across the bed to produce the required flow-rate.

Diatomacious earth particles of 125 μm diameter were subjected to injection under a variety of flow-rates, and the variation in film length was measured. Again, it appeared that high flow-rates produced thicker films. The variation of thickness with flow-rate is considerably less for packed inlets than for open-tubular ones.

Solvent effect

An acceptable solvent effect can, in general, be obtained on all the inlet types studied, as is shown in Figs. 6 and 7. Exceptions to this are encountered in smooth-walled inlets when the gas velocity exceeds a critial value or when polar solvents are used. In both instances film instability results, and a poor solvent effect is obtained.

CONCLUSIONS

Packed beds offer the following advantages:

(1) They are relatively insensitive to the method of sample injection. They also have the useful property of drawing the sample into the bed by capillary action.

(2) They can handle relatively large sample volumes.

(3) They can be designed with a gas flow resistance sufficient to allow them to be used in conjunction with a Deans switch. This allows large amounts of solvent to by-pass the analytical column[8].

(4) Non-polar and polar solvents can be used.

Packed bed inlets possess a greatly increased surface area compared with open-tubular inlets and require thorough deactivation. However, with techniques available at present this presents no serious problems.

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