CHROM. 13,230

Note

The possibility of using osmotic phenomena in an eluent pump for column liquid chromatography

Ye. B. SHMIDEL, V. G. BEREZKIN* and L. N. KOLOMIETS

Institute of Petrochemical Synthesis, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

Advances in liquid chromatography (LC) over the past few years have been dramatic, but its wider implementation is hindered by the complexity of the apparatus involved. One of the most complex and essential units of a liquid chromatograph is the device for initiating an eluent flow (pump). Many investigators have been involved in pump design and much has been published, the excellent review by Martin and Guiochon[1] being a good example. An LC pump must obviously meet the following requirements: (1) simple design, (2) practically complete absence of pressure fluctuations, (3) reliability and (4) moderate cost. Naturally, the pump must not be a source of impurities that may contaminate the eluent.

In order to assess the feasibility of new pump designs, we have tried a pump based on a principle never before used in liquid chromatography, namely osmosis[2]. A paper by Pretorius *et al.*[3] dealt with the use of electroosmosis and not osmosis; the technique described influenced the separation process in the column.

The performance of the proposed pump is based on providing an eluent flow in LC by means of osmotic pressure. The pressure is created by an osmotic system in which the concentration of the solution is maintained constant by keeping it in contact with the solid phase of the solute. The temperature of the system is also constant. As is well known[4], osmosis depends on the phenomenon that contact between a solute and a solvent through a semi-permeable membrane gives rise to an increase in pressure, called the osmotic pressure, as a result of penetration of the solvent into the solution. As far as concentrated solutions are concerned, the parameters on which the osmotic pressure is dependent are not yet well known, nor is the functional relationship between them. The equilibrium osmotic pressure is a function of solute concentration and temperature:

$$P = \varphi(C,T) \tag{1}$$

where C is the solute concentration and T is temperature.

In known osmotic systems the solute concentration tends to decrease because of dilution of the solution by the solvent flow, which results in a pressure drop. However, by maintaining the solute concentration in the solution constant one can attain a constant osmotic pressure at an appropriate flow-rate. In particular, the solute concentration can be maintained constant by keeping the solution of a sub-

stance in contact with its solid phase. This is precisely what is used in the first version of our osmotic cell as a source of pressure for LC.

Fig. 1 shows as an example a version of the device embodying the proposed method for creasing an eluent flow in LC[4]. The eluent occupies a compressible volume (1) confined by a flexible partition (2) (or by the eluent and immiscible solution interphase) inside a rigid container (3) communicating with that space (4) of the osmotic system which accommodates a saturated solution of the substance and the solid phase (5) of the latter, separated by a semi-permeable membrane (6) from the solvent occupying another space (7) of the osmotic system.
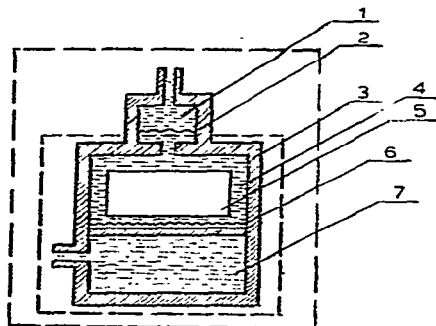

Fig. 1. Osmotic cell. 1 = Eluent; 2 = flexible partition; 3 = rigid container; 4 = saturated solution; 5 = solid phase of the substances; 6 = semi-permeable membrane; 7 = solvent (water).

The operation of the device can be described as follows. Contact between the solution and solvent through the membrane, which is permeable to the solvent and impermeable to the solute, initiates a solvent flow which gives rise to an osmotic pressure. Under the effect of osmotic forces the solvent passes through the semipermeable membrane into a vessel containing the solvent. To maintain the solution concentration constant at the saturation level at a given temperature, the solution is made to contact an excess amount of the solute which, in a particular instance, is a salt in the solid phase. The osmotic pressure arising in the solvent container is transmitted to the vessel with the eluent. Thus, the eluent flows at a constant rate. To corroborate this finding we recorded, for comparison, the pressure fluctuations in the proposed osmotic pump and in a commercially available pump. In the former the pressure fluctuations were virtually nil, whereas in the MP-2C pump the fluctuations in flow constitute 1–2 % of the nominal value.

EXPERIMENTAL

The test the proposed method for providing a uniform eluent flow in LC we developed a special device consisting of two compartments separated by a semipermeable membrane of acetate cellulose on a cermet substrate. Distilled water was used as the solvent. A saturated solution of magnesium sulphate in water was placed above the membrane and magnesium sulphate (solid phase) was used to maintain the solution concentration constant. Water was fed from the cermet substrate side. The membrane area was 25 cm^2, the cell temperature was 22°C and n-hexane was used as the eluent.

Fig. 2 shows schematically the arrangement of the osmotic system for studying the effect of cell parameters on the eluent flow-rate.

Fig. 2. Osmotic system for studying the effect of cell parameters on the eluent flow-rate. 1 = Osmotic cell; 2 = eluent; 3 = fine-adjustment valve; 3a = liquid column; 4, 5 = automatic pressure recorder; 6 = metering capillary; 7 = distilled water; 8, 10 = pressure gauges; 9 = syringe.

RESULTS AND DISCUSSION

Fig. 3 shows the eluent flow-rate *versus* pressure in the osmotic cell.

The functional relationship between the eluent flow-rate and pressure can be explained with the aid of the equivalent shown in Fig. 4.

By analogy with an equivalent electric circuit diagram where the osmotic cell

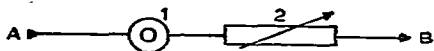
Fig. 3. Eluent flow-rate *versus* osmotic cell pressure.

Fig. 4. Diagram to illustrate the relationship between eluent flow-rate and osmotic pressure. A and B = inlet and outlet, respectively of the system at a pressure of about 1 atm; 1 = osmotic cell; 2 = flow resistance, including the variable resistance used for controlling the flow through the chromatographic column plus the constant flow resistance.

may be regarded as equivalent to a battery, we can write

$$P_0 = WR_0 + WR \qquad (2)$$

where P_0 is the total pressure in the system, W is the eluent flow-rate in the system, R_0 is the flow resistance of the osmotic cell and R is the variable flow control resistance plus the column resistance. As can be inferred from eqn. 2, the column inlet pressure

$$P_{in} = P_0 - WR_0 \text{ (where } P_{in} = WR) \qquad (3)$$

Eqn. 3 shows that P_{in} decreases linearly with increasing eluent flow-rate, W, in the system. The derived equation agrees well with experiment (see Fig. 3).

A chromatogram obtained with the above-described osmotic system is shown in Fig. 5.

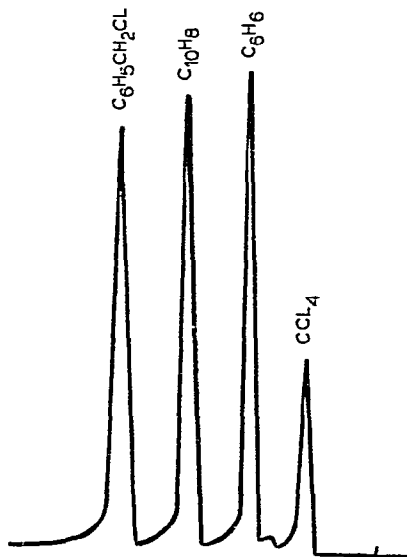We believe that such pumps will be particularly useful in microcolumn chromatography.

Fig. 5. Chromatogram taken on a VKS-11 liquid chromatograph incorporating the proposed osmotic pump. Column, silica gel Separon SI VSK (5 μm), packing, length 15 cm, I.D. 4 mm; eluent, n-hexane, flow-rate 3 ml/h; sample, CCl_4 + C_6H_6 + $C_{10}H_8$ + $C_6H_5CH_2Cl$ (2.5 l).

REFERENCES

1 M. Martin and G. Guiochon, in J. F. K. Huber (Editor), *Instrumentation for High-Performance Liquid Chromatography*, Elsevier, Amsterdam, 1978, pp. 11–40.
2 E. B. Shmidel, V. G. Berezkin, L. N. Kolomiets, Y. L. Sheftelevich and V. E. Shepelev, *Verfahren und Vorrichtung zur Erzeugung einer Elutionsmittelströmung in der Flüssigkeits-Chromatographie sowie ihre Verwendung*, Offenlegungsschrift 2,918,080 (G.F.R.).
3 V. Pretorius, B. J. Hopkins and J. D. Schieke, *J. Chromatogr.*, 99 (1974) 23.
4 D. Ishii, *Actual Chim.*, No. 7 (1977) 17.