PARTITION CHROMATOGRAPHY OF HOMOLOGOUS SERIES

by

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In a theoretical discussion of the movement of dissolved substances through partition chromatogram columns, MARTIN AND SYNGE[1], arrived at the following relationship:

$$a = \frac{A}{RA_s} - \frac{A_L}{A_s} \qquad (1)$$

in which a = partition coefficient, *i.e.* $\frac{\text{g solute/l of non-mobile phase}}{\text{g solute/l of mobile phase}}$

$R = \frac{\text{Movement of position of maximum concentration of solute}}{\text{Simultaneous movement of surface of developing phase in empty part of tube above chromatogram column}}$

A = Area of cross-section of the column

A_s = Area of cross-section of the non-mobile phase

A_L = Area of cross-section of the mobile phase.

Later, MARTIN[2] derived the following equation for the partition coefficients a'_A and a'_B of two substances A and B differing by a group X

$$\ln a'_A - \ln a'_B = \frac{\Delta\mu_X}{RT} \qquad (2)$$

in which $\Delta\mu_X$ = the difference in the chemical potential of the group X in the phases of the partition system, and a = the partition coefficient as quotient of the molar concentrations.

By combining equations (1) and (2) and introducing the concept of retention volume, a relationship can be derived which may be of great use in the partition chromatography of homologues. The apparent retention volume R_a is the volume of mobile phase issuing from the column while the middle of a zone moves from the top to the bottom of the column. The true retention volume R_t is equal to the apparent retention volume diminished by the volume V_L of the mobile phase in the column.

From the definition of R it follows that

$$R\frac{A_L}{A} = \frac{V_L}{R_a}$$

Substituting this in (1) and rearranging we have

$$a = \frac{R_a - V_L}{V_s} = \frac{R_t}{V_s}$$

in which V_s = the volume of the non-mobile phase in the column.

Successive terms in homologous series differ by one group, generally a CH_2-group. Since $\ln a'_{C_{n+1}} - \ln a'_{C_n}$ is constant, $\log R_{t_{C_{n+1}}} - \log R_{t_{C_n}}$ will also be constant; in other words:

The logarithms of the true retention volumes plotted against the number of C-atoms lie on a straight line.

Strictly, this relationship is only valid for ideal dilute solutions and ideal columns. However, since for each partition system $\Delta\mu_X$ is constant for successive terms of homologous series, the straight lines $\frac{\text{log retention volume } R_t}{\text{number of C-atoms}}$ will all have the same slope. This means, for example, that for all aliphatic series separated on a given partition system the straight lines must be parallel. Once the slope has been established, it should be possible to identify homologues by their retention volumes when the behaviour of one member of the series on the column is known. At the same time, from the above it appears that the retention volumes have considerable advantages over the R values of MARTIN AND SYNGE.

The above considerations have been confirmed for a number of extended series of aliphatic homologues. Details of this work will be published in *Rec. trav. Chim.*

REFERENCES

[1] A. J. P. MARTIN AND R. L. M. SYNGE, *Biochem. J.*, 35 (1941) 1358.

[2] A. J. P. MARTIN, *Biochem. Soc. Symposia*, 3 (1950) 4.

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