THE PARTITION CHROMATOGRAPHY OF HOMOLOGOUS SERIES III[1]

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The introduction of the concept "true retention volume" R_t, being the retention volume of a compound minus the volume of mobile phase in the column, has led to the derivation and experimental confirmation of a linear connection between the logarithms of the true retention volumes of terms of homologous series and the order of those terms[1], which can be expressed as follows:

$$\log \left(R_{t_{m+n}}/R_{t_m}\right) = n\,c. \qquad \text{(A)}$$

c depends on the nature of the group added to each term and on the partition system.

The interesting experimental relationship found by JAMES for his gas/liquid separation of aliphatic amines can be explained and extended by means of this equation. JAMES established a characteristic linear relationship for each of the series primary, secondary and tertiary aliphatic amines between $\dfrac{\text{Retention volume of the amine}}{\text{Retention volume of ethylamine}}$, both in the system N_2/liquid paraffin, and the corresponding quotient with the system N_2/Lubrol M.O., and by this means it was found possible to determine whether a primary, secondary or tertiary amine was involved[2].

If we apply equation A to two partition systems I and II and divide

$$\text{then } \frac{\log \left(R_{t_{m+n}}/R_{t_m}\right)\,\mathrm{I}}{\log \left(R_{t_{m+n}}/R_{t_m}\right)\,\mathrm{II}} = \frac{c_{\mathrm{I}}}{c_{\mathrm{II}}}.\ \text{Only if } c_{\mathrm{I}} = c_{\mathrm{II}} \text{ is } \frac{\left(R_{t_{m+n}}/R_{t_m}\right)\mathrm{I}}{\left(R_{t_{m+n}}/R_{t_m}\right)\mathrm{II}} = \text{constant} = 1. \qquad \text{(B)}$$

which gives a linear relationship between $\left(R_{t_{m+n}}/R_{t_m}\right)$ I and $\left(R_{t_{m+n}}/R_{t_m}\right)$ II, forming a line at 45° to the axis.

However, if we relate the retention volumes R_t of different aliphatic series p = $P(CH_2)P'$ and q = $Q(CH_2)Q'$ to the retention volume R_t of one term of the p series, then the 45° relationship is valid only in the p series, while for the other series a change must be made to the first one as follows:

$$\frac{{}^{q}R_{t_{m+n}}}{{}^{p}R_{t_m}} = \frac{{}^{q}R_{t_{m+n}}}{{}^{q}R_{t_m}}\;\frac{{}^{q}R_{t_m}}{{}^{p}R_{t_m}}$$

In this case equation B becomes:

$$\frac{\left({}^{q}R_{t_{m+n}}/{}^{p}R_{t_m}\right)\mathrm{I}}{\left({}^{q}R_{t_{m+n}}/{}^{p}R_{t_m}\right)\mathrm{II}} = \frac{\left({}^{q}R_{t_m}/{}^{p}R_{t_m}\right)\mathrm{I}}{\left({}^{q}R_{t_m}/{}^{p}R_{t_m}\right)\mathrm{II}}$$

which is in general not equal to 1 (owing to the different attractions of the groups P,P′, Q and Q′ for the phases of the systems I and II), thus forming a line at an angle to the axis, characteristic for the series q. These linear relationships should be true for all forms of partition methods, with or without a support for one of the phases, *e.g.* for paper chromatography by substituting $(1/R_F - 1)$ for R_t[1,3] and for counter-current procedures by substituting the partition coefficient α for R_t[1,4]. The general conditions $c_{\mathrm{I}} = c_{\mathrm{II}}$ and ideal behaviour of the solutions and chromatographic system must, of course, be fulfilled within narrow limits. The validity is not limited to aliphatic series, but theoretically applies to all series obtained by successive additions or replacements of given groups to or in a molecule[1]. In JAMES' experiments, the condition $c_{\mathrm{I}} = c_{\mathrm{II}}$ was approximated, so that, in spite of neglecting the small correction for the volume of mobile phase in the column itself, the characteristic linear relationships were obtained which made possible the identification of primary, secondary and tertiary aliphatic amines.

REFERENCES

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