

only approximative, eqn. 6 may be proposed for informatory calculations in the planning of liquid chromatographic separations.

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Imbrication patterns

WALRAVEN, LADON and KEULEMANS have recently described¹⁻³ imbrication plots or roofing tile patterns as an aid in the tentative identification of organic compounds. Isomers of homologous compounds were shown to form staggered parallel plots depending on the carbon number when examined on two stationary phases. It is shown that the series of parallel linear relationships representing isomeric compounds that are produced when logarithmic expressions of retention on two stationary phases are plotted according to carbon number are simply a particular extension of established homologous plots. The overlapping plots are parallel only when the structural parameters of the isomers are non-interacting or where interactions are present these are independent of the structures of the variable portions of the isomers. An example of the plots is shown in Fig. 1a, using data of methyl esters of monocarboxylic acids⁴.

Linear relationships of homologous compounds on two stationary phases are well known. JAMES⁵ with aliphatic amines plotted relative retention on a polar and a non-polar stationary phase to produce linear plots radiating from the origin for each homologous series. With hydrocarbons a series of parallel lines were produced by JAMES AND MARTIN⁶ using the logarithm of retention obtained on two phases. Concurrently primary, secondary and tertiary alkanols, alkanones and *n*-alkanes were shown to produce parallel linear plots using two polar phases⁷. Similar results have been achieved with fatty esters by the use of a "new" and an "aged" polyester stationary phase⁸. Differences in behaviour of these esters have also been observed by the use of a single polar column using two temperatures⁹ while plots of isomeric alkanes C₅-C₉ have been reported using squalane at 30° and 70° (ref. 10).

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This work shows the mathematical basis of parallel plots of isomeric homologous series on two stationary phases and of the parallel (imbrication) plots linking the isomeric compounds of the same carbon number.

Discussion

Fig. 1 shows a typical example of an imbrication pattern with parallel plots of isomeric esters of the same carbon number. The dotted lines on the figure show parallel plots of the methyl esters of (a) *n*-carboxylic acids and (b) 2,2-dimethylcarboxylic acids. The other points shown similarly produce linear plots of the methyl esters of the 2-, 3- and 4-methylcarboxylic acids and of the 3-methyl-3-ethyl- and 4-methyl-4-propylcarboxylic acids.

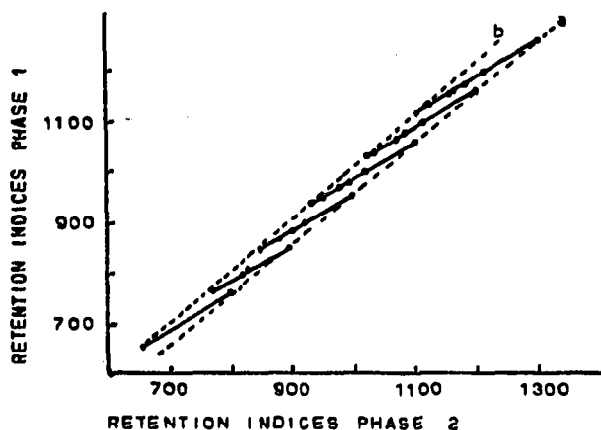


Fig. 1. Retention plots of the methyl esters of homologous monocarboxylic acids on a polar and a non-polar stationary phase. Solid lines show parallel plots of esters of the same chain length and dotted lines of esters of (a) *n*-carboxylic acids and (b) 2,2-dimethylcarboxylic acids.

It is shown mathematically that homologous series which produce parallel plots of slope m_1 with any logarithmic representation of retention and carbon number on one stationary phase and similar parallel plots of slope m_2 on a second phase will produce further parallel plots of slope m_3 when retention values on both phases form the co-ordinates.

If the separation factors for several homologous series are constant on two phases with values α_1 and α_2 then multiple retention representation will again produce parallel plots.

Simple retention plots (*i.e.* log retention *versus* carbon number) of a homologous series on two stationary phases (1) and (2) may be shown as

$$\text{Log } r_1 = m_1 C + a_1 \quad (1)$$

$$\text{Log } r_2 = m_2 C + a_2 \quad (2)$$

$$\text{Log } r_1 - \text{log } r_2 = (a_1 - a_2) + C(m_1 - m_2) \quad (3)$$

From eqn. 2 follows:

$$C = \frac{1}{m_2} \text{log } r_2 - \frac{a_2}{m_2}$$

Eqn. 3 now becomes:

$$\text{Log } r_1 = \text{log } r_2 + (a_1 - a_2) + (m_1 - m_2) \frac{1}{m_2} \left(\text{log } r_2 - \frac{a_2}{m_2} \right) \quad (4)$$

$$\text{Log } r_1 = a_1 - a_2 \frac{m_1}{m_2} + \text{log } r_2 \left(1 + \frac{m_1 - m_2}{m_2} \right) \quad (5)$$

$$\text{Log } r_1 = \frac{a_1 m_2 - a_2 m_1}{m_2} + \frac{m_1}{m_2} (\text{log } r_2) \quad (6)$$

As eqn. 6 is of the form for a linear plot the multiple retention plots of the homologous series are parallel with slope m_1/m_2 .

It has been shown with the α -alkyl acrylic esters¹¹ that a network of plots is produced with a linear relationship existing between isomers of the same total carbon number when a variable structural parameter and the logarithm of retention form the co-ordinates. While one series of slopes has been calculated the second series may be similarly obtained. This situation is analogous to that described by eqns. 1 and 2 although a normal slope linking the isomers does not occur and the linear parallel nature of the imbrication pattern may be shown by obtaining slopes on pairs of points:

$$\text{Log } r_{11} = a_{11} + m_1 C \dots \text{log } r_{21} = a_{21} + m_2 C$$

$$\text{Log } r_{12} = a_{12} + m_1 C \dots \text{log } r_{22} = a_{22} + m_2 C$$

$$\text{Log } r_{13} = a_{13} + m_1 C \dots \text{log } r_{23} = a_{23} + m_2 C$$

The slope of a line between two isomer points is obtained from the equation above.

$$\frac{\text{Log } r_{11} - \text{log } r_{12}}{\text{Log } r_{21} - \text{log } r_{22}} = \frac{a_{11} - a_{12}}{a_{21} - a_{22}}$$

The slope is independent of the carbon number, constant for the various sets of points and two series of parallel lines exist.

While WALRAVEN *et al.*^{2,3} have reported parallel plots for isomers of carboxylic esters, hydrocarbons and phenyl and cycloalkanes, many series of isomers do not show this linearity. The linearity exists where the structural parameters of the isomers are non-interacting or, if interactions occur, these are independent of the structurally variable portion of the isomers. In such series retention is simply an additive effective or a summation of contributions due to component parts of the molecule and ac-

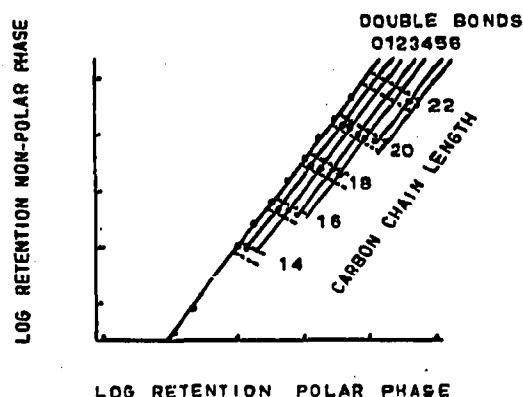


Fig. 2. Retention plots of saturated and unsaturated fatty esters on a polar and a non-polar stationary phase¹².

cordingly retention of near homologues may be calculated with considerable precision.

Imbrication plots were in effect proposed by JAMES¹² as shown in Fig. 2 for determining the number of double bonds in unsaturated fatty esters. Linear plots were not achieved as the positions of unsaturation are not equivalent; however, the grouping of the points into zones was of some value.

Recognition of the end carbon chain relationship¹³ allows a network plot of unsaturated fatty esters¹⁴ but the relationships are restricted to isomers where unsaturation is isolated from the chain extremities. This limitation applies to the variety of mathematical procedures that have been developed as aids in the tentative identification of unsaturated fatty esters¹⁵⁻¹⁷. Retention data available for complete series of fatty compounds have been listed¹⁴ and the inequality of retention contributions due to the position of unsaturation or chain substituents is widely apparent. In such cases linear imbrication plots are not obtained.

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