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Note

Retention plots of aliphatic esters

J. K. HAKEN
Department of Polymer Science, The University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)
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The introductory work of James and Martin[1] demonstrated the linear relationship between retention and carbon number of homologous compounds. These workers extended the development of retention plots to allow the detection of polarizable groups by the study of the retention behaviour on two or more phases of differing polar character[2,3]. With unsaturated fatty esters[4] a plot of retention on a polyester stationary phase against values on a non-polar stationary phase produced a grid of parallel lines lines from which the number of double bonds or carbon atoms in an unknown ester could be established.

While the retention behaviour of the total carbon number, *i.e.* the complete molecule, was considered in these procedures it was evident that because of their structure various series could be plotted as members of two or three homologous series to produce near-linear relationships. In these cases a correlation was possible between retention behaviour and structural parameters and the procedures were demonstrated with several series of carbonyl compounds[5–7]. On a non-polar stationary phase a grid-type plot was produced when either the carbon number of the alcohol (R') or acid chain (R) was used as the abscissa. A second set of nearly linear lines linked points of esters of constant $R + R'$. Fig. 1 shows the plot for *n*-alkylacrylic esters with the acid chain (R) as the abscissa and the secondary plots formed by linking points having constant values of $R + R'$ in increasing order from 1 to 12. Further studies[8] have shown that ester plots with R', and particularly R, as abscissa exhibit marked deviations from linearity with polar stationary phases, and regular networks as shown in Fig. 1 are not produced.

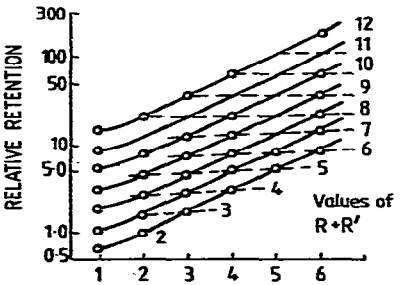

Fig. 1. Retention plot for *n*-alkylacrylic esters using acid chain length (R) as abscissa[5].

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Calixto and Raso[9] have recently shown the same type of plot (Fig. 2) for retention of aliphatic esters with $R + 1/R'$ as the abscissa where the ester is represented by RCOOR'. Linking points which the same total carbon number (n), *i.e.* $n = R + R' + 1$ according to the convention used above, produced a series of curved relationships, with the curvature increasing as n decreased. It is evident that the retention is minimized where the $R + 1/R'$ ratio is near unity, where it is stated that the charge and mass centres are as close as possible.

With such a suggestion it would be prudent to extend the plot to include esters of lower total carbon number, *i.e.* less than seven, and to indicate the effect of polarity, *i.e.* that linearity decreased with increasing phase polarity.

From Fig. 2 it is evident that a set of plots is possible linking points of equal R' and producing a series of lines whose slope increases as R' increases. Such a situation is similar to that shown in Fig. 1 except that the abscissa is an increasing carbon number multiplied by a constant, *i.e.* depending on the carbon number of R' forming the divisor, the value of the constant decreases with increasing value of R' and is largely responsible for the slopes increasing as R' increases from 1 to 6 as shown, rather than the differences obtained on using the total carbon number[8].

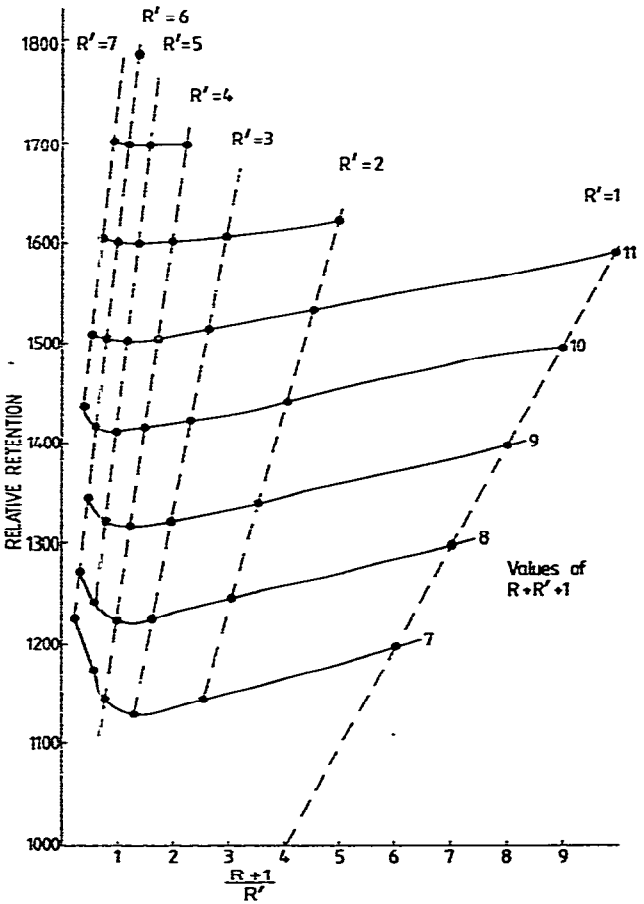

Fig. 2. Retention plot for aliphatic esters with $R + R' + 1 = 7$–13 (ref. 9).

For the data used in Fig. 1 a polynomial expression was produced whereby the retention of aliphatic esters might be calculated. While this relationship may hold for esters where $n < 7$ it is obvious from several data points from the tabulations of Calixto and Raso[9] that as the plots proceed towards the origin they become markedly curved. As this behaviour has been previously reported[8] it is expected that the equation shown is not applicable to many of the common simpler esters.

A plot for all of the simpler esters on SILAR 5CP is shown in Fig. 3 which shows a series of curves. A new polynomial expression is not shown as such an approach is of restricted value. If required the data may be better presented by the construction of a nomogram which, as shown earlier[5], may be drawn to accomodate deviations occuring with the various esters.

The plot shown in Fig. 2 considers the retention of both the methylene and the C = O group to be essentially equivalent, which of course does not occur. A methylene group, irrespective of the stationary phase, exhibits a retention of *ca.* 100 units with a variation of possibly 10 units while the contribution of a carbonyl group has

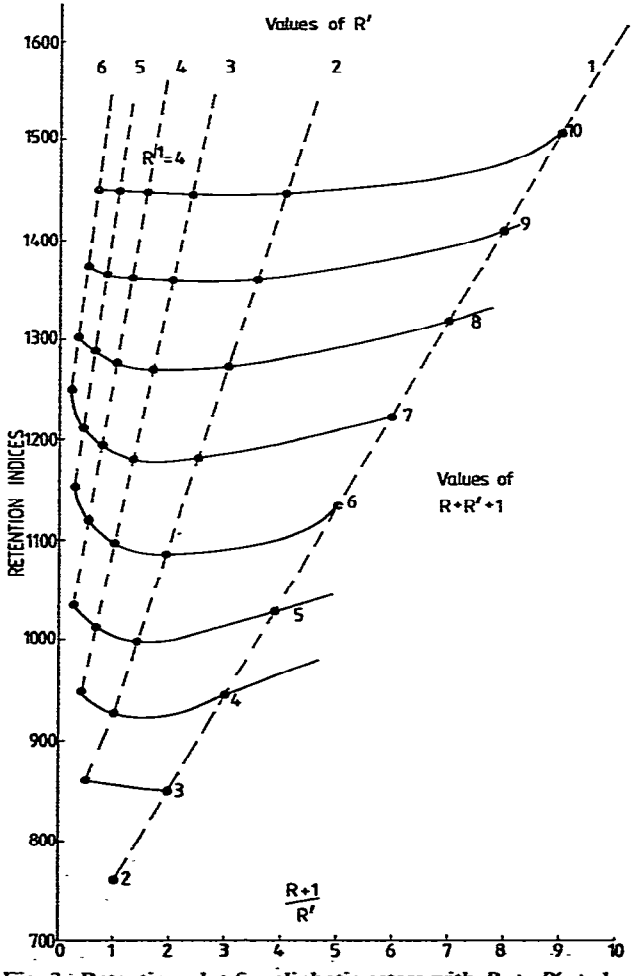

Fig. 3. Retention plot for aliphatic esters with $R + R' + 1 = 2$–10.

been shown elsewhere to vary by possibly 100% depending on the stationary phase used. The contribution of the carboxy group has been determined by graphical procedures for aliphatic esters on a variety of stationary phases[10,11].

A number of other variations of the retention plot are possible depending on the abscissa used while the shape of the plots may be varied by the relative magnitudes of the coordinate scales used. The effects are readily demonstrated by the use of a programmable data plotter.

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