A STUDY OF THE RELATIONSHIP BETWEEN GAS CHROMATOGRAPHIC RETENTION PARAMETERS AND MOLECULAR CONNECTIVITY

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It has previously been demonstrated that a linear relation exists between molecular connectivity and gas chromatographic retention data within a series of related compounds (Millership and Woolfson, 1978). We have now extended this approach to cover combinations of various series of compounds.
Using the retention data for a group of saturated and unsaturated hydrocarbons (Csicery and Pines, 1962) equation 1 was generated involving only the first order connectivity term ($^1\chi$).

$$\log RT = 0.721\ ^1\chi + 0.188 \qquad \text{Equation 1.}$$
$$n = 46,\quad r = 0.880,\quad s = 0.290$$

The use of multiple χ terms produced equation 2 which shows improved correlation and a far lower standard error.

$$\log RT = 1.049\ ^0\chi - 0.609\ ^2\chi - 0.370\ ^1\chi - 0.913 \qquad \text{Equation 2.}$$
$$n = 46,\quad r = 0.958,\quad s = 0.179$$

The use of a DV term, which is derived from the connectivity of those carbon atoms involved in multiple bonding, improves the correlation further, equation 3.

$$\log RT = 0.700\ ^0\chi - 0.374\ ^2\chi + 0.261\ DV - 0.808 \qquad \text{Equation 3.}$$
$$n = 46,\quad r = 0.983,\quad s = 0.115$$

The calculated values of log RT using Equation 3 are in good agreement with the observed values.
Using the retention data for a series of sixty compounds including aldehydes, ketones, esters and alcohols (McReynolds, 1966) we have demonstrated excellent correlation between molecular connectivity and log Vg (log of the specific retention volume), see equation 4.

$$\log Vg = 0.454\ ^1_v\chi - 0.126 \qquad \text{Equation 4.}$$
$$n = 60,\quad r = 0.993,\quad s = 0.052$$

Finally a group of drugs including amphetamines, local anaesthetics and morphine like compounds was investigated. Using the data of Moffat, 1975 equation 5 was generated relating the retention index (RI) to $^0\chi$, $^1_v\chi$ and $^3_p\chi$.

$$RI = 151.880\ ^0\chi - 186.022\ ^1_v\chi + 235.569\ ^3_p\chi + 575.211 \qquad \text{Equation 5.}$$
$$n = 41,\quad r = 0.911,\quad s = 193.029$$

Using this equation the calculated RI for Levallorphan is 2373 which compares favourably with the observed value of 2340. We believe that the standard error may be reduced further by the inclusion of higher order connectivity terms.

Csicery, S.M. and Pines, H. (1962) J. Chromatog. 9, 34-43
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Moffat, A.C. (1975) J. Chromatog. 113, 69-94