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INFLUENCE OF ODD OR EVEN CARBON NUMBERS IN SOLUTES ON THEIR GAS CHROMATOGRAPHIC BEHAVIOUR

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SUMMARY

The regularities of the retentions of homologues of various chemical types, including the contribution of odd or even numbers of carbon atoms in the alkyl chains, were investigated. The relationship between the logarithm of the relative retention of two consecutive homologues and the carbon number has the form of a zig-zag line, the shape of which depends both on the nature of the solutes and on the polarity of the stationary phase.

INTRODUCTION

The recent successful development of various non-analytical applications of gas chromatography is due not only to its traditional advantages (speed of physico-chemical measurements, simplicity of the equipment) but also to the reliability of the data obtained as a result of the high precision of the measurements of chromatographic values.

The reliability of chromatographic data has increased in the last few years, which has permitted some fine differences in the retention behaviour of solutes to be revealed, *e.g.*, the deviation from the generally postulated linear relationship between the logarithm of retention volumes and the number of carbon atoms in solute homologues[1]. The non-linear relationships between the logarithm of retention volumes and the carbon number or the boiling point of the solutes make qualitative analyses difficult to perform, especially if multi-component mixtures are to be separated. Theoretical and experimental aspects are considered in this paper.

EXPERIMENTAL

The experiments were carried out on a Pye 104 gas chromatograph with a flame-ionization detector. The instrument was adapted for the use of an open-tubular column. Triethylene glycol dibutyrate was used as the stationary phase and argon as the carrier gas. The column was made of stainless steel with dimensions 40 m × 0.2 mm I.D. The inlet pressure was 1.65 atm. The stability of the pressure during the analysis was ±0.002 atm and that of the oven temperature was ±0.05°. The measure-

ment of the retention times was carried out with a double-handed stop-watch with a relative error of speed of 0.02%.

The relative error of the determination of the retention times (the difference between parallel determinations) was 0.25%. However, each individual value of σ_z (eqn. 2) was determined from a single chromatogram, which is why there was a correlation between the errors of retention time determination of two homologues; the reproducibility of the σ_z values was about 0.02%. The availability of the above compensation effect is in accordance, for example, with the data in refs. 2–4.

The efficiency of the open-tubular column was about $200–250 \cdot 10^3$ theoretical plates (calculated for the n-pentane and n-hexane peaks), which contributes to reliability of the measurements. As a result, the error of the determination of D_F (eqn. 6) was reduced to about ± 1 J/mole.

THEORETICAL AND RESULTS

The retention of solute homologues can be described in a general form by expressing the deviations described under Introduction as a power function of the carbon number, z:

$$\log t'_{Rz} = a + bz + cz^2 + \cdots \tag{1}$$

where t'_{Rz} is the adjusted retention time of the solute and a, b and c are constants.

The relationship between the adjusted retention times of homologues with carbon numbers z and $z - 1$ follows[5] from the relationships of the saturated vapour pressures, P^0, and activity coefficients, γ, of the solutes in the liquid stationary phase:

$$\sigma_z = \frac{t'_{Rz}}{t'_{R(z-1)}} = \frac{P^0_{(z-1)}}{P^0_z} \frac{\gamma_{(z-1)}}{\gamma_z} \tag{2}$$

It follows from eqn. 2 that the deviation of σ_z for neighbouring homologues from a constant value may result either from the irregularities in the properties of the solutes shown by the non-linearity of the plot of $\log P^0$ versus z or from the properties of the stationary phase when the curvature of the plot of $\log \gamma$ versus z is observed. For instance, the irregularity in the retention of the n-alkylbenzenes[6], which is characterized by a minimum on the plot of log (relative retention) versus z, is caused by the properties of the solutes proper because log (saturated vapour pressure) gives a similar relationship whereas the variation of log (activity coefficient) is linear.

With the increased precision of chromatographic measurements, we can establish even finer variations in the relationship between the structure of molecules, their physico-chemical properties and their chromatographic behaviour.

By using high-efficiency chromatographic columns it is possible to elucidate the contribution of odd or even numbers of carbon atoms in alkanes to their retentions[7] (in parallel with the well known influence of this parameter on the melting points[8]).

It should be noted that as far as the pioneering paper by Kováts[9] is concerned, retention indices were calculated on the basis of the retention volumes of the even-carbon n-alkanes. This was later acknowledged to be unnecessary and interpretations began to be made on the basis of the retentions of neighbouring n-alkanes.

In our work[7], when the effect had been clearly established on polyethylene glycol open-tubular columns, calculations showed that the retention indices of the even-carbon n-alkanes determined on the basis of the retentions of odd-carbon n-alkanes differ by 1–2 units from the carbon number multiplied by 100. About half of the above effect is due to the general curvature of the relationship of log t'_R versus z and the other half to the influence of the odd or even carbon number.

Hence, in parallel with the relationship between the melting points and z there is the possibility of correlating log t'_R of homologues and z by equations such as

$$\log t'_{Rz} = a_t + b_t z + c_t z^2 + d_t z^3 + D_t \varphi_z \tag{3}$$

where a_t, b_t, c_t, d_t and D_t are constants and φ_z is $+1$ for even z and -1 for odd z.

The form of the line corresponding to eqn. 3 is given in Fig. 1. The thin solid line (1) reflects the general curvature of the relationship of log t'_R versus z. The thick stepped line (2) reflects the odd and even number of z. The broken curve (3) corresponds to the odd-carbon series of solutes and the broken curve (4) to the even-carbon series. The distance between the latter two curves along the ordinate is equal to twice the value of the constant D_t in eqn. 3.
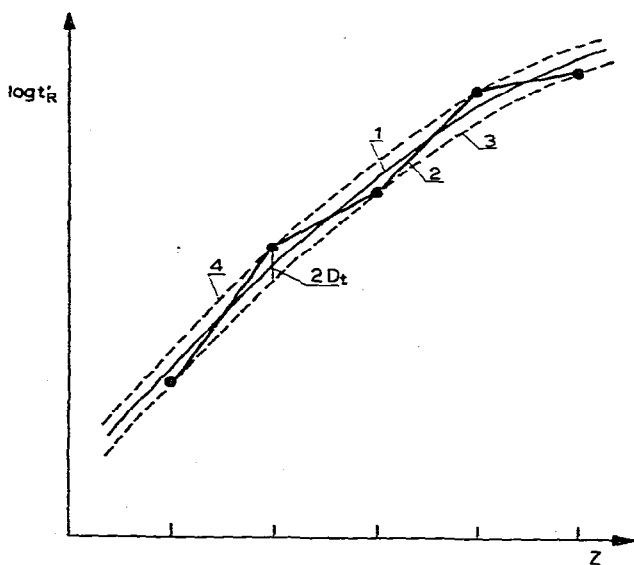

Fig. 1. General plot of the logarithm of the adjusted retention times *versus* the carbon number of molecules of n-alkanes. 1, Solid line corresponding to eqn. 1; 2, broken line corresponding to eqn. 3; 3 and 4, broken lines corresponding to the retention of the odd and even carbon number n-alkanes, respectively. D_t = the odd or even factor in eqn. 3 corresponding to the difference on the ordinate between curves 3 and 4.

The difference in the free molar enthalpy of solution of two homologues z and z − 1 is given by

$$\sigma(\Delta F^\circ)_z = RT \ln(t'_{Rz}/t'_{R(z-1)}) = RT \ln \sigma_z \tag{4}$$

Hence the contribution of the odd or even carbon number can be expressed in energy units.

The distance between the lines corresponding to even- and odd-carbon series can be characterized (with some approximation owing to the general curvature of the relationship of log t'_R versus z) by the criterion of alternation[10]:

$$A_z = \log\sigma_{(z+1)} - \log\sigma_z = \log t'_{R(z+1)} + \log t'_{R(z-1)} - 2\log t'_{Rz} \qquad (5)$$

It is easy to show with the example of n-alkanes (the even-carbon number series having a stronger retention than the odd-carbon number series) that the criterion of alternation is negative when z is an even number and positive when z is an odd number. Hence the regular alternation of the sign of A_z is evidence of the contribution of the odd or even carbon number of the molecule to the properties of the substances under investigation.

The effect of alternation of the retention of the solutes increases when the stationary phases and solutes are polar substances. In such instances the effect is explicit even with packed columns of moderate effeciency. For instance, the influence of the odd or even carbon number in the molecules on the retention of free fatty acids and their methyl esters was observed[10] using a column of 2% of polyethylene glycol adipate and 2% of orthophosphoric acid as stationary phase on Chromosorb W.

Naturally, the high efficiency of open-tubular columns involves a higher precision of the determination of the retention values. This enables the influence of the odd or even carbon number on the retention of solutes that do not interact strongly with the stationary liquids to be established.

Thus, the effect of the odd or even carbon number of several homologous series was established by using an open-tubular column coated with triethylene glycol dibutyrate with an efficiency of about $200–250 \cdot 10^3$ theoretical plates.

The plots of $\delta(\Delta F^0)_z$ against the carbon number of n-alkanes, 1-bromoalkanes and 2-alkanones are given in Fig. 2; the relationships were obtained at 40 and 80°.

It can be seen from Fig. 2 that the influence of odd or even carbon number is displayed to a greater extent with solutes that interact rigorously with the stationary phase (increasing in the order n-alkanes < bromoalkanes < alkanones).

The data also demonstrate that the influence of temperature on the effect under consideration is small (with a temperature range of 40°). A decrease in temperature displaces the plot in the direction of higher values of $\delta(\Delta F^0)_z$ but the shape of the line remains the same.

The effect of the alkyl chain on the influence of the carbonyl group can be clearly seen in Fig. 2. With an increase in the alkyl radical chain the difference $\delta(\Delta F^0)_z$ for homologous alkanones is similar to that for n-alkanes.

The dependence of $\delta(\Delta F^0)_z$ on z, by analogy with eqn. 2, can be expressed as follows:

$$\delta(\Delta F^0)_z = a_F + b_F z + c_F z^2 + D_F \varphi \qquad (6)$$

where the constants correspond to the similar constants in eqn. 3.
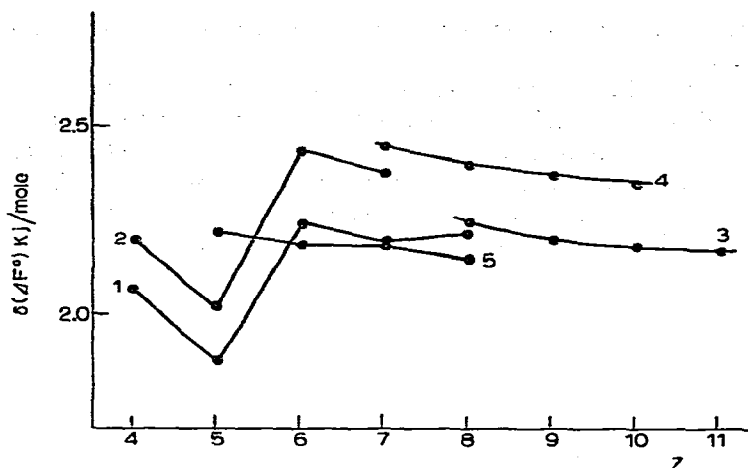
Fig. 2. Relationship between the homologous difference in the free molar enthalpy of solutes in triethylene glycol dibutyrate and the carbon number of the solute. 1 = 2-Alkanones, 80°; 2 = 2-alkanones, 40°; 3 = n-alkanes, 80°; 4 = n-alkanes, 40°; 5 = 1-bromoalkanes, 80°.

It follows from eqns. 3, 4 and 6 that the minimum number of homologues essential for the determination of D_F, taking into account the general curvature of the line, is five. With a smaller number of solutes the results are, of course, less correct.

The values of the odd or even factor D_F (Table I) were calculated on the basis of the retention data for homologous series with four (D_{F4}), five (D_{F5}) and six (D_{F6}) members.

TABLE I

THE VALUES OF ODD OR EVEN CONSTANTS D_F (EQN. 6)

Stationary liquid, triethylene glycol dibutyrate. Temperature, 80°.

No.	Homologous series	Functional group	D_{F4} (J/mole)	D_{F5} (J/mole)	D_{F6} (J/mole)
1	n-Alkanes	CH₃	—	—	1.6
2	1-Bromoalkanes	Br	8.8	8.8	—
3	2-Alkanones	C=O	122.0	92.5	—

D_F increases in the order n-alkanes < 1-bromoalkanes < 2-alkanones; the value for n-alkanes is of the same order as the experimental error (see below). Further, an increase in the number of homologues under consideration leads to a decrease in D_F for alkanones. On the other hand, D_{F4} for bromoalkanes is identical with D_{F5}, which is why the coefficient c_F in eqn. 6 (and also d_t in eqn. 3) is sufficiently small.

It is of interest that a 1-bromoalkane with an even number of carbon atoms corresponds to a lower value of $\delta(\Delta F^0)_z$ than one with an odd number of carbon atoms, i.e., an opposite effect to that with n-alkanes. Such an effect can be explained by the role of the bromine atom in position 1, which makes the chain longer. In other words, the number of "chain-forming" atoms in 1-bromoalkanes is $z_c = z + 1$,

whereas in n-alkanes it is $z_c = z$. For 2-alkanones $z_c = z$ and the odd or even sign
is the same as for n-alkanes.

The form of the line for n-alkanes is similar to that of the lines of $\Delta \log t'_{Rz} = \log \sigma_z$ and of l, the latter being characteristic of the relative position of the carbon
atoms in the molecules (without taking into account twisting of the chain). The value
of l in Fig. 3 is the distance between the extreme carbon atoms in the molecule (taking
into account the valence angle of 109.5°). Δl is the difference in l corresponding to
two consecutive homologues and l_2 is the distance between two neighbouring carbon
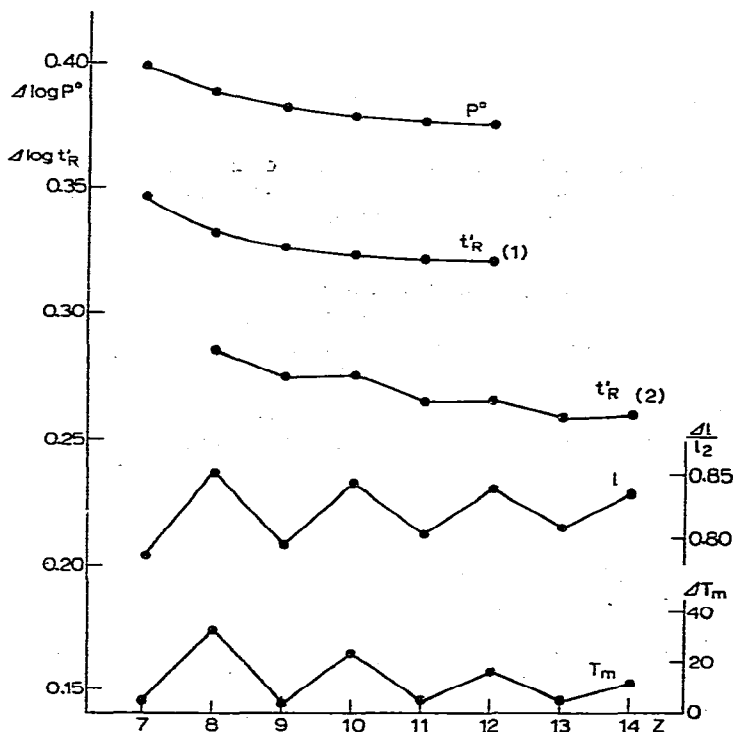atoms (in ethane).

Fig. 3. Relationships showing the influence of odd or even carbon number on some properties of
n-alkanes. The lines marked P°, T_m, $t'_{R(1)}$ and $t'_{R(2)}$ correspond to the homologous differences in
saturated vapour pressure (at 80°), melting points, and logarithm of adjusted retention times (at
80°) on columns of triethylene glycol dibutyrate (1) and polyethylene glycol 400 (2). Curve marked l
corresponds to the increment of a CH_2 group in the distance between the extreme carbon atoms of
the molecule, Δl, divided by the length of the C–C bond, l_2.

The general curvature of the retention lines in Fig. 3 is due to the same form
of the saturated vapour pressure line $[\Delta \log P^0 = \log P^0_{(z-1)} - \log P^0_z]$. However, in
the retention of n-alkanes on polyethylene glycol 400 (ref. 7) the influence of the odd or
even carbon number is greater than in the retention on triethylene glycol dibutyrate,
which has a less rigid molecular structure.

The plot of the difference in melting points $[\Delta T_m = T_{mz} - T_{m(z-1)}]$ for

homologous n-alkanes (according to Van Nes and Van Westen[8]) is also given in Fig. 3. As this line and the lines for l and $t'_{R(2)}$ are similar, this is additional evidence for the close connection between the properties under consideration and molecular structure.

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