

ON THE RELATION BETWEEN SIDE CHAIN LENGTH AND R_M VALUE

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All the investigations concerning the partition chromatography of homologous series start from MARTIN'S theoretical suppositions¹ about an additive influence of functional group increments on the values of the partition coefficients. BATE-SMITH AND WESTALL² confirmed the validity of these suppositions for hydroxy, carboxy and methylene group increments, and at the same time deduced a linear relation between the number of these groups and the R_M value. LONG³ proved that this relation was roughly linear for methylene group increments in the homologous series of carboxylic acids. On the other hand, some other authors such as ISHERWOOD AND HANES⁴ and KALBE⁵ showed that for mono- and dicarboxylic acids the linear relation between R_M values and the number of carbon atoms is valid in a limited range only.

In the course of our studies on the relation between the structure of organic substances and their chromatographic behaviour, we have established earlier⁶ that a substantial difference exists according to whether the increase by the homologous increment takes place in the substituent attached to an aromatic nucleus or to a side chain. When a methyl group is introduced into the aromatic nucleus, the formula deduced by BATE-SMITH is valid. On the other hand, if a methylene group is introduced into the side chain, the relation between the R_M value and the number of carbon atoms is linear practically for the first three members only; the R_M value increments for further members, however, decrease with the length of the chain (Fig. 1).

The relation between the number of hydroxy and carboxy groups and the R_M

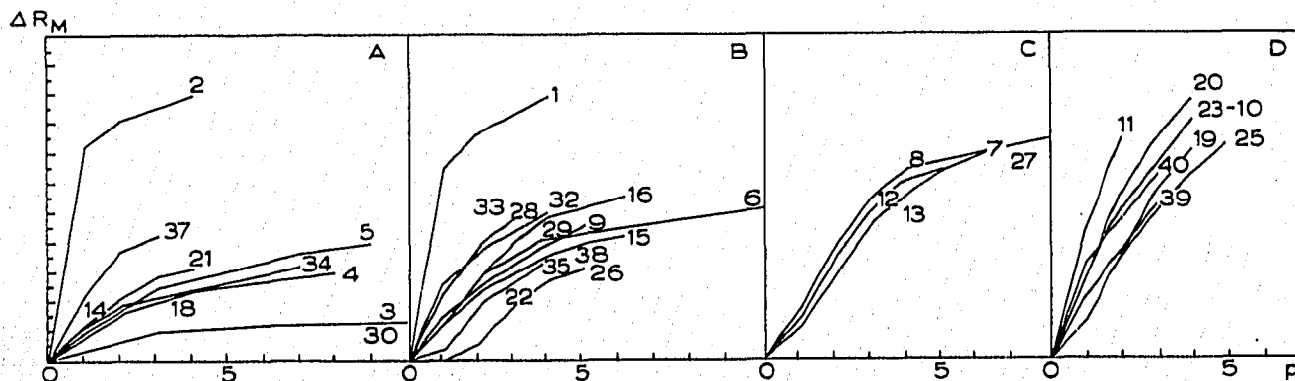


Fig. 1. A, B, C, D. Relation between the number of carbon atoms of a side chain and the difference in R_M values. (p represents the difference in the number of carbon atoms.) The numbers correspond to those in Table I.

value cannot be estimated in more than about three members of homologous series, because the presence of such groups causes an appreciable difference in R_M values. Where more of the groups are present, further members of the series are found in an inconvenient R_M range, *i.e.* in close proximity to the start or the front.

For the above reason, in this investigation we have studied only the homologous increment $-\text{CH}_2-$ which can be followed in a sufficient number of members of homologous series. In this case, increase of the number of methylene groups by one link results in only slight changes in the R_M values. We selected from the literature the R_M values of a wide variety of organic compounds forming comparatively long homologous series.

DEDUCTION OF THE RELATION BETWEEN THE HOMOLOGOUS INCREMENT AND THE R_M VALUES

The relation between the ΔR_M value and the homologous increment for a number of homologous series derived from the literature is plotted in a linear scale in Fig. 1. It is obvious from this figure that the relation is not linear in any of the quoted examples. The logarithmic relation makes simpler and more exact expressions possible. This is evident from Fig. 2, where the given dependence was plotted logarithmically. Thus, the following equations can be proposed:

$$R_{Mp} = k \cdot \log p + R_{M1} \quad (1)$$

$$k = \frac{R_{Mp} - R_{Mq}}{\log(p/q)} \quad (2)$$

where k is constant for a given homologous series and given chromatographic conditions, and R_{Mx} corresponds to the x -th member of a homologous series after the

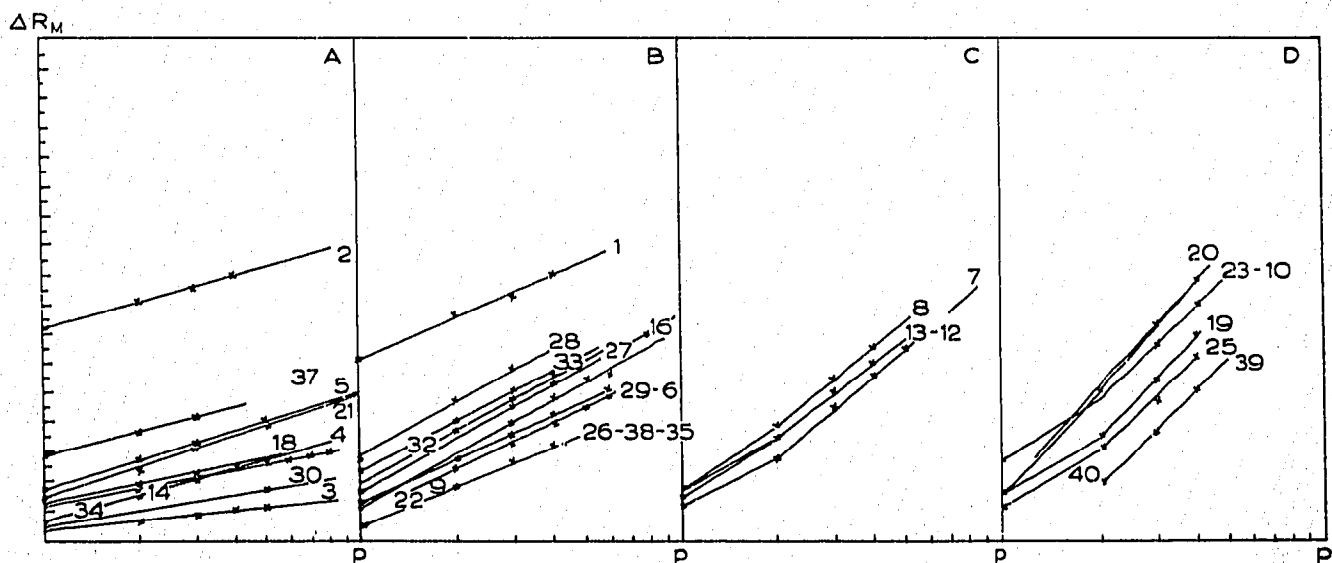


Fig. 2. A, B, C, D. Relation between the number of carbon atoms of a side chain and the difference in R_M values. (p values are given in the logarithmic scale.) The numbers correspond to those in Table I.

TABLE I
 LIST OF CONSTANTS k AND ($R_{Mp}-R_{Mo}$) VALUES

No.:	k	$R_{Mp}-R_{Mo}$	Type	Stationary phase	Mobility phase	Reference
15	0.76	0.23	A-B		isoamyl alcohol-aq. ammonia-water	7
16	1.28	0.18	B		heptane-methanol	7
5	0.72	0.33	A	dimethylformamide		8
27	1.06	0.47	B	dimethylformamide		11
28	1.14	0.58	B	dimethylformamide		12
29	0.96	0.25	B		<i>n</i> -amyl alcohol-acetic acid-water	13
32	1.26	0.38	B		ethyl acetate-dioxane-water	9
33	1.12	0.50	B	dimethylformamide	cyclohexane	12
22	1.06	0.14	B	dimethylformamide	chlorocyclohexane	14
23	2.08	0.31	D	formamide	chlorocyclohexane	14
10	2.08	0.30	D	formamide	tetrachloromethane	14
18	0.44	0.25	A	dimethylformamide	chlorobenzene	15
19	2.30	0.32	D	formamide	cyclohexane-butanol	15
20	2.42	0.31	D	formamide	chlorobenzene	15
39	2.00	—	D	acetamide	cyclohexane-butanol	16
40	2.02	—	D	acetamide	cyclohexane	16
21	0.72	0.22	A		light petrol-methanol-ethyl acetate	17
13	1.68	0.18	C	methanol	heptane	18
3	0.48	0.06	A		ethyl ether-light petrol	19
37	0.60	0.56	A	dimethylformamide	cyclohexane	20
26	0.92	0.08	B		<i>n</i> -butanol-acetic acid-water	21
9	0.86	0.14	B		<i>m</i> -cresol-acetic acid-water	22
38	0.90	0.12	B		butanol-aqueous ammonia-water	23
4	0.42	0.24	A		phenol	24
6	1.00	0.24	B		<i>n</i> -butanol	24
35	0.96	0.08	B		butanol-dimethylformamide-water	25
7	1.72	0.06	C		amyl alcohol-acetic acid-water	26
8	1.76	0.32	C		methyl ethyl ketone	27
25	1.96	0.12	D		isoamyl alcohol-collidine-water	28
14	0.50	0.24	A		butanol-formic acid-water	16
30	0.42	0.06	A		aqueous ammonia	29
1	0.88	1.26	B		<i>tert</i> .-butanol-benzyl alcohol-water-formic acid	29
2	0.56	1.44	A		iso-octane-ethanol-acetone-formic acid	29
11	2.00	0.86	D		acetone-water-aqueous ammonia	30
34	0.60	0.14	A		ethanol-water	31
41	2.60	—	C		butyl acetate-water	33
12	1.68	0.18	C		isoamyl alcohol-aqueous ammonia-water	32

fundamental member. From the chromatographic point of view, the k value is a criterion of the partitioning power of the system used.

We computed the k value for a number of homologous series and compiled the calculated results in Table I together with the $(R_{Mp} - R_{Mo})$ values which make plotting easier than the R_{Mp} values alone. Comparing the various k values, we find that it is possible to divide them roughly into four groups (see Fig. 2 A, B, C, D), in which this value depends substantially on the properties of the stationary and mobile phases only, the character of the chromatographed substance being of slight significance. It is interesting that the highest k values are found in solvent systems where the difference between the dielectric constants of the stationary and mobile phases is greatest (e.g. formamide-cyclohexane). The energy of possible intermolecular hydrogen

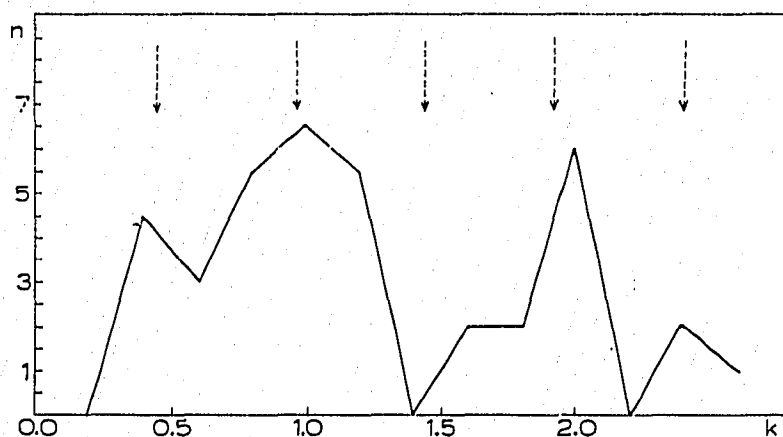


Fig. 3. The relation between the frequency n in an interval of $(K - 0.1; K + 0.1)$ and the k value.

bonds between the chromatographed substance and the solvent system seems to be decisive in this case. Therefore, the k values do not follow the statistical distribution, but show certain quantization. For example, the k value for a mobile phase with dimethylformamide as the stationary phase is approximately half that for the same mobile phase with formamide or acetamide as the stationary phase. Fig. 3 showing the statistical distribution of the k values clearly demonstrates that these values are arranged into several groups which differ from each other by about $\Delta R_M = 0.48$. Only the third group departs from this rule, probably owing to the small number of examples in this group. The value $\Delta R_M = 0.48$, however, corresponds to the change of R_M value caused by one intermolecular hydrogen bond of the type $O-H \cdots O^{10}$.

The $(R_{Mp} - R_{Mo})$ values are probably influenced by the number of polar groups in the molecule, and increase with the number of these groups (e.g., in the case of dicarboxylic acids).

The number of factors influencing the values discussed, however, is very large. Thus, it is hardly possible to draw accurate conclusions, since the range of experimental data is not very wide. In spite of this, we make the supposition that the relation between the number of carbon atoms in the side chain of the molecules and the R_M value is not linear but logarithmic.

SUMMARY

A study was made of the R_M values, given in the literature, of a wide variety of organic compounds forming homologous series. An equation is proposed in which the R_M value is related to the number of carbon atoms in the members of the homologous series.

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