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INCREMENTATION OF POLAR EFFECT CONSTANTS IN GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

In chromatographic studies polar effect constants σ_c^*, similar to those of Taft and Ingold, can be obtained from an empirical additivity relationship which takes into account three structural increments.

INTRODUCTION

Each carbon atom of an alkyl group contributes to some extent to the final values of chromatographic retention data. Consequently, in this area σ^* values of alkyl groups beyond those of the classical Taft scale are often needed. This situation differs considerably from that encountered in reactivity studies, where the contribution of the alkyl groups remains constant, once a certain size has been reached.

In previous papers[1,2] we have shown that a scale of polar effect constants σ_c^* can be determined by means of the following relation:

$$\sigma_c^* = \frac{1}{\varrho^*}\left[\log t'_{RRZ} - h\,(n_H - 3)\right] \qquad (1)$$

in which $\log t'_{RRZ}$ is the reduced relative retention time of an aliphatic saturated compound RZ (R alkyl group, Z functional group), n_H is the number of hydrogen atoms attached to the carbon atom of R neighbouring the functional group, and ϱ^* and h are the sensitivities to the polar and ramification effects in the chromatographic phenomenon. Using this approach, we determined 42 values of σ_c^* (Table I).

The results reported here indicate the existence of an empirical additivity relationship which can be used for the calculation of any σ_c^* value.

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TABLE I

CHROMATOGRAPHIC POLAR EFFECT CONSTANTS σ_c^*

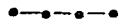
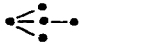
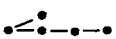
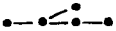
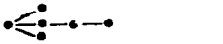
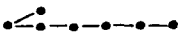
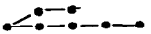
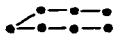
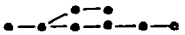
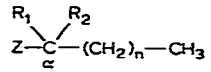
R	*Topological graph*	σ_c^* *set 1 calc. by eqn. 1*	σ_c^* *set 2 calc. by eqn. 2*	*Deviation*
Me		0		
Et		−0.101	—	—
nPr		−0.116	−0.115	1
iPr		−0.195	−0.195	—
nBu		−0.131	−0.129	2
iBu		−0.124	−0.123	1
sBu		−0.210	−0.209	1
tBu		−0.288	−0.289	−1
nPent		−0.145	−0.143	2
iPent		−0.140	−0.137	3
sPent		−0.223	−0.223	—
3-Pent		−0.222	−0.223	−1
2-Me-1-Bu		−0.140	−0.137	3
2-Me-2-Bu		−0.305	−0.303	2
3-Me-2-Bu		−0.220	−0.217	3
2,2-DiMe-1-Pr		−0.130	−0.131	−1
nHex		−0.159	−0.157	2
2-Hex		−0.237	−0.237	—
3-Hex		−0.235	−0.237	−2
2-Me-1-Pent		−0.153	−0.151	2
3-Me-1-Pent		−0.156	−0.151	5
4-Me-1-Pent		−0.155	−0.151	4
2-Me-2-Pent		−0.317	−0.317	—
3-Me-2-Pent		−0.235	−0.231	4
4-Me-2-Pent		−0.231	−0.231	—
2-Me-3-Pent		−0.231	−0.231	—
3-Me-3-Pent		−0.319	−0.317	2
2-Et-1-Bu		−0.154	−0.151	3
2,2-DiMe-1-Bu		−0.147	−0.145	2
2,3-DiMe-2-Bu		−0.317	−0.311	6
3,3-DiMe-2-Bu		−0.226	−0.225	1
nHept		−0.173	−0.171	2

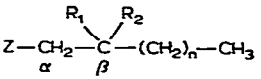
TABLE I *(continued)*

R	*Topological graph*	σ_c^* *set 1 calc. by eqn. 1*	σ_c^* *set 2 calc. by eqn. 2*	*Deviation*
2-Hept		−0.251	−0.251	—
3-Hept		−0.249	−0.251	−2
4-Hept		−0.248	−0.251	−3
2,2-DiMe-1-Pent		−0.159	−0.159	—
2,4-DiMe-3-Pent		−0.238	−0.239	−1
3-Et-3-Pent		−0.333	−0.331	2
nOct		−0.187	−0.185	2
2-Oct		−0.265	−0.265	—
2-Et-1-Hex		−0.179	−0.179	—
2-Et-4-Me-1-Pent		−0.173	−0.173	—

CONTRIBUTION OF METHYLENE UNITS

For the determination of this contribution we have defined five structural series:





Series	R_1	R_2
α_0	H	H
α_1	Me	H
α_2	Me	Me
β_1	Me	H
β_2	Me	Me

Basic structures are obtained when $n = 0$; groups belonging to all five series are listed in Fig. 1, in which we have plotted the alkyl group σ_c^* values *vs.* number of methylene units. The slopes of the fairly straight lines obtained are identical; this means that the contribution of a methylene unit is constant over all series (Table II).

For every alkyl group R generated from the basic structures by inserting methylene units, the R σ_c^* values are obtained by adding to the basic σ_c^* value the contributions I_{CH_2} of the corresponding number of methylene groups.

EFFECT OF METHYL SUBSTITUTION

Two successive basic structures of the α or the β series differ by one methyl group. The data analysis (Table II) shows that the contribution of a methyl group is not the same at the α as at the β position.

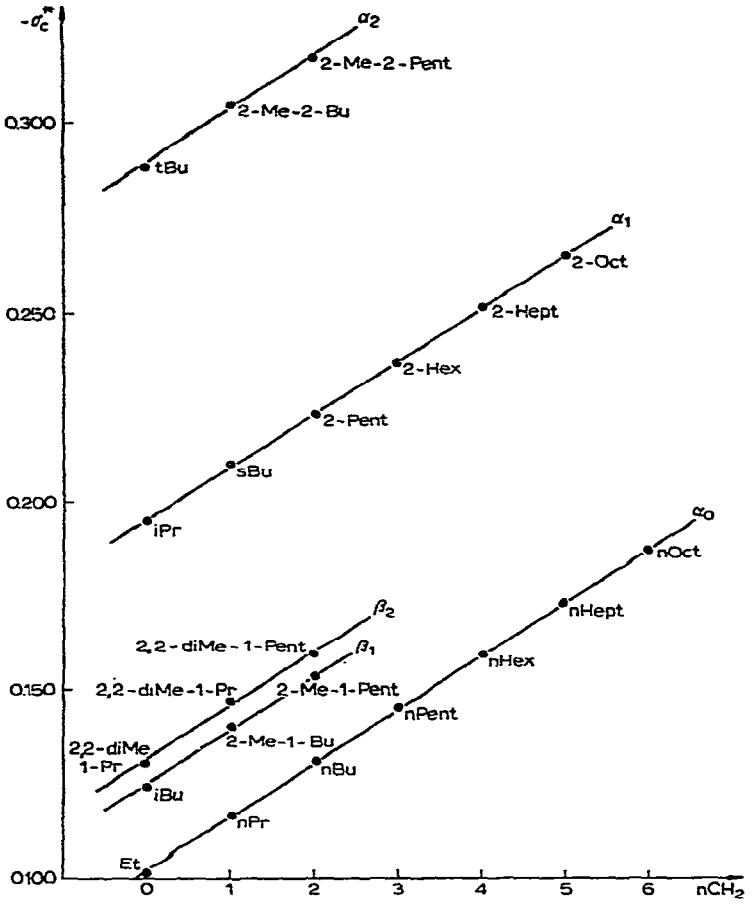


Fig. 1. Plot of the alkyl group σ_c^* values *vs.* number of methylene units.

TABLE II

METHYLENE UNIT INCREMENT AND σ_c^* VALUES OF BASIC STRUCTURES

Series	*Individual terms of each series*	I_{CH_2}*	σ_c^{*}**	r***	ψ***
α_0	Et, nPr, nBu, nPent, nHex, nHept, nOct	−0.014	−0.101	0.999	0.01
α_1	iPr, sBu, 2-Pent, 2-Hex, 2-Hept, 2-Oct	−0.014	−0.195	0.999	0.01
α_2	tBu, 2-Me-2-Bu, 2-Me-2-Pent	−0.014	−0.288	0.995	0.17
β_1	iBu, 2-Me-1-Bu, 2-Me-1-Pent	−0.014	−0.124	0.998	0.10
β_2	2,2-DiMe-1-Pr, 2,2-diMe-1-Bu, 2,2-diMe-1-Pent	−0.014	−0.130	0.995	0.17

* Contribution of a methylene unit.

** σ_c^* of the basic structure, obtained when $n = 0$.

*** r is the correlation coefficient. The Exner test ψ is a measure of the quality of a correlation[3]. It simultaneously takes into account the correlation coefficient r, the number of parameters and the number of experimental points. According to Exner, a perfect correlation is obtained when $\psi < 0.10$, a correct one for $0.10 < \psi < 0.20$.

α-Branching

From examination of σ_c^* values of alkyl groups in the α_0, α_1 and α_2 series we can deduce the mean contribution of each methyl substituent:

$$I_{Me_\alpha} = -0.094$$

When the methyl group is replaced by a longer alkyl chain, the contribution of each methylene is the same as above. For instance, the predictional contribution of an α-ethyl group will be the sum of the contributions of the α-methyl and one methylene

$$I_{Et_\alpha} = (-0.094) + (-0.014) = -0.108$$

β-Branching

Similarly, analysis of the β-branching yields the mean contribution of the β-methyl group

$$I_{Me_\beta} = -0.008$$

It is interesting to note that the increment I_{Me_β} can be considered as a general contribution of a methyl substitution effect in all positions except α.

$$I_{Me} \equiv I_{Me_\beta}, I_{Me_\gamma}, I_{Me_\delta} \ldots$$

ADDITIVITY RELATIONSHIP OF σ_c^* VALUES

Comparison of the basic structures shows that they are generated from the ethyl group by successive methylations. Consequently the ethyl group will be the foundation of our incrementation system.

The above results show that, depending on the branching position along an alkyl chain, the contribution of a methyl group is −0.094 or −0.008. On the other hand, in all cases examined the contribution of a methylene group is fairly constant, wherever it is inserted.

Definitively, the polar effect constant σ_c^* values can be calculated by means of the empirical relation

$$\sigma_{cR}^* = \sigma_{cEt}^* + \Sigma I_{CH_2} + \Sigma I_{Me_\alpha} + \Sigma I_{Me} \qquad (2)$$

The definite values of the increments are obtained by correlation of the values of σ_c^* set 1 (Table I):

$$I_{CH_2} = -0.014$$
$$I_{Me_\alpha} = -0.094$$
$$I_{Me} = -0.008$$

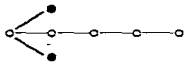
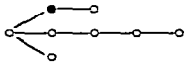
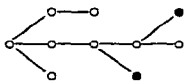
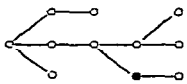
correlation coefficient $r = 0.999$
Exner Test $\psi = 0.04$

As expected, the polar effect constants are strictly additive[4].

The σ_c^* values calculated by eqn. 2 are listed in Table I (set 2). Depending on the precision of chromatographic measurements, the differences between values of the two sets (mean value 1.5/100, upper limit 3/100) enhance the quality of the additivity relationship (eqn. 2).

Contrary to eqn. 1, the latter can be used to determine σ_c^* values without knowledge of any chromatographic data.

The calculation of a σ_c^* value is now fairly simple; it needs six consecutive operating steps. For instance, the polar effect constant of the 3,6-dimethyl-5-ethyl-3-heptyl group is obtained as follows:

Operating steps	*Topological evolution*	*Contributions*	
Foundation			−0.101
Methylene insertions on foundation		3× − 0.014	−0.042
Me α-branching		2× − 0.094	−0.188
Methylene insertions on α branches		1× − 0.014	−0.014
Other Me branchings		2× − 0.008	−0.016
Other methylene insertions		1× − 0.014	−0.014
			$\sigma_c^* = -0.375$

Next to its independence of chromatographic data, the main importance of eqn. 2 lies in the fact that only four factors are needed for the determination of the σ_c^* value of any alkyl groups, whatever its structure*. Furthermore, in chromatography this equation shows that there is no levelling effect in σ_c^* values.

REFERENCES

1 R. Fellous, R. Luft and J.-P. Rabine, *J. Chromatogr.*, 133 (1977) 7.
2 R. Fellous, R. Luft and J.-P. Rabine, *J. Chromatogr.*, 136 (1977) 5.
3 O. Exner, *Collect. Czech. Chem. Commun.*, 31 (1966) 3222.
4 J. MacPhee and J. E. Dubois, *Tetrahedron Lett.*, (1976) 2471, and literature cited therein.

* In practice we can determine unknown σ_c^* values of alkyl groups R′, generated from R, by addition of the appropriate methyl and methylene increments to the known σ_c^* of R

$$\sigma^*_{c_{R'}} = \sigma^*_{c_R} + \Sigma(I_{CH_2}, I_{Me\alpha}, I_{Me})$$