GENERAL CONTRIBUTION TO THE THEORY OF RETENTION INDEX SYSTEMS IN GAS–LIQUID CHROMATOGRAPHY

II. ADDITIVITY OF GAS CHROMATOGRAPHIC INTERACTIONS EXPRESSED BY RETENTION INDICES

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SUMMARY

The additivity of gas chromatographic interactions expressed by retention indices is discussed. Some examples are presented to demonstrate the applicability of the method in practice.

INTRODUCTION

In the course of investigations on the relationship between retention index and molecular structure, we decided to examine also the additivity of the components of the retention index interaction (I_t) and/or individual interactions (I_{ti}). After studying the literature on gas chromatographic interactions, it was decided that this effect would be taken into account in our work, recognizing the necessity of the distinction between effects of five kinds of interaction forces, according to Rohrschneider[1] and Kováts[2].

Although the interaction index contribution depends on column temperature, in addition to the quality of the substance examined and of the stationary phase used, and the widespread practical application of the increments determined is difficult, the calculations are interesting from a theoretical viewpoint. Benzene derivatives were used as model substances and squalane, PEG-1540 and the Citroflex A/4 were used as stationary phases at 100.0°.

THEORETICAL

The retention index consists of the following additive components[3]:

$$I = I_a + I_b + I_t = I_m + I_t \tag{1}$$

where

I = the retention index under isothermal conditions, in index units (i.u.);

I_a = atomic index contribution (i.u.);
I_b = bond index contribution (i.u.);
I_i = interaction index contribution (i.u.);
I_m = molecular index contribution (i.u.).

The interaction index contribution (I_i) consists of two additive components:

$$I_i = I_{ig} + I_{ii} \tag{2}$$

where

I_{ig} = the average interaction index contribution (i.u.);
I_{ii} = the individual interaction index contribution (i.u.).

The average interaction index contribution is due to dispersion forces, while the individual interaction index contribution is due to other interaction forces, and it follows that I_{ii} is virtually zero on squalane. The individual interaction index contribution is zero by definition on a non-polar (apolar) standard stationary phase.

The average interaction index contribution was established by definition for any stationary phase:

$$I_{ig} = I_i^{sq} \tag{3}$$

Knowing that $I_{ig} = I_i^{sq}$ for any substance on any stationary phase, I_{ii}^{p} can be calculated as follows:

$$\Delta I = I^p - I^{sq} = I_i^p - I_i^{sq} = I_{ii}^p + I_{ig}^p - I_i^{sq} = I_{ii}^p \tag{4}$$

Thus, eqn. 4 means that if the value of ΔI is known, the individual interaction index contributions can be determined.

On squalane as stationary phase at 100.0°, the ratio of the molecular and interaction index contributions is

$$I_m : I_i^{sq} = 1 : 3.00 \tag{5}$$

Thus

$$I_{\text{aromatic compound}}^{sq} (100.0°) = (4/3)\, I_i^{sq} \tag{6}$$

Thereafter the index values of the individual increments can be calculated as outlined in Part I, on a thermodynamic basis:

$$I_i^{sq} = I_{ig} = i_{i,1} + i_{i,2} + i_{i,3} + \cdots \tag{7}$$

where i_i = interaction increment.
Similarly,

$$I_{ii}^p = i_{ii,1} + i_{ii,2} + i_{ii,3} + \cdots \tag{8}$$

In connection with this, it should be noted that, as opposed to bond increments, these values depend on the stationary phase and the column temperature.

The code system can be applied to model aromatic substances by using the previously mentioned "a" index and by denoting the π-bond by "p". The applicability of the method is demonstrated in both instances for 1,3,5-trimethylbenzene. The values of the increments for benzene, toluene and m-xylene are required for the calculations, and the codes for these compounds are given below.

Benzene

$$(6 \cdot {}^{2a}_{2a}C_2a_2a) + (6 \cdot {}^{2a}_{2a}H_2a_2a_2a) + (1 \cdot p).$$

TABLE I

VALUES OF THE INTERACTION INCREMENTS OF AROMATIC COMPOUNDS ON SQUALANE AT 100.0°

Code	Value (i.u.)	Code	Value (i.u.)
${}^{2a}_{2a}C_2a_2a$	31.19	${}^{2a}_{2a}H_2a_2a_2a$	35.90
"p"	84.29	${}_2a_2aH_{13}a$	34.16
${}^{2a2a}_{0}C_3a_1$	29.72	${}^{12a}_{2a}H_2a_2a_3a$	33.62
${}^{12a}_{2a}C_3a_2a$	29.68	${}^{3a}_{2a}H_2a_2a_2a$	33.54
${}^{3a}_{2a}C_2a_2a$	29.65	${}^{12a}_{12a}H_2a_3a_3a$	23.00
${}^{12a}_{3a}C_3a_2a$	29.00	${}^{3a}_{3a}H_2a_2a_2a$	35.31

TABLE II

VALUES OF THE INTERACTION INCREMENTS OF AROMATIC COMPOUNDS ON PEG-1540 AT DIFFERENT COLUMN TEMPERATURES

Code	Value (i.u.)		
	100.0°	110.0°	120.0°
${}_2a_2aH_{13}a$	50.38	50.74	51.10
${}^{2a}_{2a}H_2a_2a_2a$	61.33	61.76	62.20
${}^{12a}_{2a}H_2a_2a_3a$	47.03	47.37	47.70
${}^{12a}_{12a}H_2a_3a_3a$	47.72	48.06	48.40
${}^{2a}_{2a}C_2a_2a$	47.71	48.05	48.39
${}^{3a}_{2a}C_2a_2a$	38.38	38.66	39.94
${}^{2a2a}_{0}C_3a_1$	47.45	47.78	48.12
${}^{12a}_{2a}C_3a_2a$	38.07	38.34	38.61
${}^{12a}_{3a}C_3a_2a$	21.81	21.97	22.12
p	143.13	144.14	145.16

TABLE III

VALUES OF THE INDIVIDUAL INTERACTION INCREMENTS OF AROMATIC COMPOUNDS ON CITROFLEX A/4 AT 70.0°

Code	Value (i.u.)	Code	Value (i.u.)
$_{2a}^{2a}C_2a_2a$	12.32	p	4.10
$_{2a}^{3a}C_2a_2a$	7.92	$_{2a}a_2aH_{13}a$	6.98
$_{0}^{2a_2a}C_3a_1$	6.88	$_{2a}^{2a}H_2a_2a_2a$	9.40
$_{2a}^{12a}C_3a_2a$	8.20	$_{12}^{12a}H_2a_2a_3a$	6.20
$_{3a}^{12a}C_3a_2a$	4.52	$_{12a}^{12a}H_2a_3a_3a$	2.07

TABLE IV

COMPARISON OF MEASURED[4] AND CALCULATED RETENTION INDICES OF 1,3,5-TRIMETHYLBENZENE ON PEG-1540 AT DIFFERENT COLUMN TEMPERATURES

Column temperature (°C)	Retention index (i.u.)		Difference (i.u.)
	Measured[4]	Calculated	
100.0	1255.0	1254.6	+0.4
110.0	1262.1	1261.8	+0.3
120.0	1268.7	1269.0	−0.3

TABLE V

VALUES OF INDIVIDUAL INTERACTIONS OF AROMATIC COMPOUNDS AND DEVIATIONS FROM THE AVERAGE VALUES ON PEG-1540 AT 120.0°

Compound	Individual interaction (i.u.)	Deviation from average (i.u.)
Benzene	316.6	−11.9
Toluene	310.4	−5.7
Ethylbenzene	304.2	+0.5
m-Xylene	302.4	+2.3
p-Xylene	296.2	-8.5
o-Xylene	323.9	−19.2
Isopropylbenzene	287.6	+17.1
n-Propylbenzene	295.7	+9.0

Toluene

$$(3 \cdot {}_{2a}a_2aH_{13}a) + (1 \cdot {}_{0}^{2a_2a}C_3a_1) + (2 \cdot {}_{2a}^{12a}C_3a_2a) + (2 \cdot {}_{2a}^{3a}C_2a_2a) + (2 \cdot {}_{2a}^{2a}C_2a_2a) +$$

$$+ (2 \cdot {}_{2a}^{12a}H_2a_2a_3a) + (2 \cdot {}_{2a}^{3a}H_2a_2a_2a) + (1 \cdot {}_{2a}^{2a}H_2a_2a_2a) + (1 \cdot p).$$

m-Xylene

$$(6 \cdot {}_2a_2aH_{13}a) + (2 \cdot {}^{2}a_2{}^{a}_{0}C_3a_1) + (2 \cdot {}^{12}_2{}^{a}aC_3a_2a) + (2 \cdot {}^{12}_3{}^{a}aC_3a_2a) + (2 \cdot {}^{3}_2{}^{a}aC_2a_2a) +$$

$$+ (2 \cdot {}^{12}_2{}^{a}aH_2a_2a_3a) + (1 \cdot {}^{12}_{12}{}^{a}aH_2a_3a_3a) + (1 \cdot {}^{3}_3{}^{a}aH_2a_2a_2a) + (1 \cdot p).$$

1,3,5-Trimethylbenzene

$$(9 \cdot {}_2a_2aH_{13}a) + (3 \cdot {}^{12}_{12}{}^{a}aH_2a_3a_3a) + (6 \cdot {}^{12}_3{}^{a}aC_3a_2a) + (3 \cdot {}^{2}a_2{}^{a}_{0}C_3a_1) + (1 \cdot p).$$

It is obvious from the codes that the value for 1,3,5-trimethylbenzene can be obtained from the increments for benzene, toluene and *m*-xylene. The numerical values are given in Tables I–III.

The measured[4] and calculated retention indices for 1,3,5-trimethylbenzene on PEG-1540 are compared in Table IV at different column temperatures. The results are most encouraging. The possibilities inherent in the method become apparent if the data in Table V are considered. These data demonstrate well the individual contributions, *i.e.*, that approximations cannot be made by using "average" values.

REFERENCES

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