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DISPERSION AND SELECTIVITY INDICES IN GAS CHROMATOGRAPHY

IV^a. CHLORINATED AROMATIC COMPOUNDS

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SUMMARY

The dispersion (I_M) and selectivity (I^*) indices of several series of chlorinated aromatic compounds, including chlorinated benzenes, anisoles (methoxybenzenes), veratroles (1,2-dimethoxybenzenes), phenyl acetates, benzaldehydes, 2-hydroxybenzaldehydes (salicylaldehydes), 4-hydroxybenzaldehydes and phenols, were determined on low-polarity (SE-30) and polar capillary columns. The effect of the individual substituent groups and of multiple substituents and their positions on the aromatic ring are discussed in terms of the relevant polar interactions. The results are compared with those previously reported for aliphatic and aromatic esters.

INTRODUCTION

The division of the Kováts retention index (I) of a solute in gas chromatography into two characteristic components has recently been reported¹. The dispersion index (I_M), indicative of the contribution to retention of the non-polar forces, is related to the molecular weight of a particular solute. The second contribution, the selectivity index (I^*), indicates the polar interactions present, moderated by operative steric effects. The selectivity index was developed by considering the behaviour of a wide range of aliphatic and some aromatic carbonyl compounds. These included normal, branched and unsaturated aliphatic esters with variations of the structural parameters in both the acyl and alkyl chains, simple ketones (2-alkanones), diketones and homologous pyruvate esters, containing both a carboxy and a carbonyl functional group². The aromatic esters were the alkyl, 2-chloroethyl and alkenyl normal and branched-chain benzoate esters and their chlorinated derivatives³.

This work extends the treatment to a wide range of aromatic compounds, including all of the isomeric chlorobenzenes⁴, anisole (methoxybenzene)⁵, veratrole (1,2-dimethoxybenzene)⁶, phenyl acetate⁷, 2-hydroxybenzaldehyde (salicylaldehyde

* For Part III, see ref. 3.

hyde)⁸, 4-hydroxybenzaldehyde⁹, phenol¹⁰ and their chlorinated derivatives on non-polar (SE-30) and polar capillary columns. The results of this study are compared and discussed in terms of the operative polar interactions with electron-donating and accepting groups about the aromatic nucleus. The retention data used in this work were taken from earlier retention studies of the compounds of interest and some minor correlative data⁴⁻¹⁰.

EXPERIMENTAL

The retention indices were determined with Varian Aerograph 2400 and Perkin-Elmer Sigma 3 instruments under the previously reported conditions⁴⁻¹⁰. The columns used were a vitreous silica capillary column (25 m × 0.32 mm I.D.) coated with SE-30 (SGE, North Melbourne, Australia). The polar column used for the chlorobenzenes was a glass capillary column (22 m × 0.3 mm I.D.), coated with Carbowax 20M (SGE) and for the phenols a vitreous silica column (25 m × 0.35 mm I.D.) coated with FFAP (SGE) was used. The polar capillary column used for the other compounds was of fused silica (25 m × 0.32 mm I.D.) coated with OV-351 (Orion Analytica, Espoo, Finland).

The column temperature was 160°C in all instances and the retention indices were calculated by computerized procedures, as reported previously^{4,5}.

RESULTS AND DISCUSSION

The dispersion (I_M) and selectivity (I^*) indices for the chlorobenzenes on the SE-30 column are given in Table I. It is evident that the I_M values increase with

TABLE I

DISPERSION (I_M) AND SELECTIVITY (I^*) INDICES OF CHLORINATED BENZENES ON SE-30 AND CARBOWAX 20M AT 160°C

Isomer	SE-30			Carbowax 20 M	
	I	I_M	I^*	I	I^*
Monochloro-	832	788.1	43.9	1257	468.9
1,3-Dichloro-	964	1033.6	-69.6	1415	381.4
1,4-Dichloro-	970	1033.6	-63.6	1438	404.4
1,2-Dichloro-	1005	1033.6	-28.6	1445	413.4
1,3,5-Trichloro-	1131	1279.2	-148.2	1515	235.8
1,2,4-Trichloro-	1177	1279.2	-102.2	1630	350.8
1,2,3-Trichloro-	1211	1279.2	-68.2	1705	425.8
1,2,3,5-Tetrachloro-	1326	1527.7	-201.7	1754	226.3
1,2,4,5-Tetrachloro-	1326	1527.7	-201.7	1764	236.3
1,2,3,4-Tetrachloro-	1366	1527.7	-161.7	1871	343.3
Pentachloro-	1496	1770.3	-274.3	1956	185.7
Hexachloro-	1656	2015.9	-359.9	2141	108.1

addition of chlorine and the corresponding increase in molecular weight. The selectivity indices decrease substantially with added chlorine substituents. The value for benzene is not shown, because it is difficult to measure accurately the retention of this low-boiling solute at 160°C. However, the retention index is well known, having a value of *ca.* 660 (SE-30) and a selectivity index of *ca.* 120.

The I^* value of monochlorobenzene is reduced (43.9) but remains positive. The addition of further chlorine substituents produces progressive decreases in I^* due, as indicated previously^{1,4}, to the effect of the screened electrons of the halogen atoms. As has been discussed previously, the greatest retention occurs with the isomers in which the substituents are closest together and decreases as the position around the ring allows greater separation⁴. Thus, the I and I^* values for the homologues follow the sequence 1,2- < 1,4- < 1,3-.

TABLE II

DISPERSION (I_M) AND SELECTIVITY (I^*) INDICES OF ANISOLE AND VERATROLE AND THEIR CHLORINATED DERIVATIVES ON SE-30 AND OV-351 AT 160°C

Compound	I_M	I^*	
		SE-30	OV-351
Anisole	756.6	123.4	616.4
2-Chloro-	1002.1	96.9	687.9
3-Chloro-	1002.1	82.9	625.9
4-Chloro-	1002.1	91.9	653.9
2,3-Dichloro-	1247.7	61.3	729.3
2,4-Dichloro-	1247.7	24.3	657.3
2,5-Dichloro-	1247.7	16.3	644.3
2,6-Dichloro-	1247.7	-49.7	484.3
3,4-Dichloro-	1247.7	37.3	651.3
3,5-Dichloro-	1247.7	-4.7	552.3
2,3,4-Trichloro-	1493.3	-5.3	710.7
2,3,5-Trichloro-	1493.3	-56.3	577.7
2,3,6-Trichloro-	1493.3	-122.3	449.7
2,4,5-Trichloro-	1493.3	-70.3	586.7
2,4,6-Trichloro-	1493.3	-160.3	343.7
3,4,5-Trichloro-	1493.3	-39.3	586.7
2,3,4,5-Tetrachloro-	1738.8	-105.8	601.2
2,3,4,6-Tetrachloro-	1738.8	-218.8	332.2
2,3,5,6-Tetrachloro-	1738.8	-220.8	332.2
2,3,4,5,6-Pentachloro-	1984.4	-285.4	294.6
Veratrole	970.6	143.4	732.4
3-Chloro-	1216.2	17.3	646.8
4-Chloro-	1216.2	56.3	742.8
3,4-Dichloro-	1461.8	-10.8	665.2
3,5-Dichloro-	1461.8	-49.8	563.2
3,6-Dichloro-	1461.8	-18.8	424.2
4,5-Dichloro-	1461.8	-21.2	741.2
3,4,5-Trichloro-	1703.3	-94.3	604.7
3,4,6-Trichloro-	1703.3	-204.3	352.7
3,4,5,6-Tetrachloro-	1952.9	-262.9	348.1

TABLE III
EFFECT OF ADJACENT GROUPS OF THE SAME AND DIFFERENT TYPES ON SELECTIVITY IN CHLORINATED AROMATIC DERIVATIVES

Number of pendant groups	I*	Same functional group		Different functional group	
		Chlorobenzenes	Veratroles	Phenyl acetates	Anisoles
2	Max.	1,2-Dichloro ^a	—	4-Chloro ^a	2-Chloro ^a
	Min.	1,3-Dichloro ^a	—	2-Chloro ^a	3-Chloro ^a
3	Max.	1,2,3-Trichloro ^a	4-Chloro ^a	3,4-Dichloro ^a	2,3-Dichloro ^a
	Min.	1,3,5-Trichloro ^a	3-Chloro ^a	2,6-Dichloro ^b	2,6-Dichloro ^a
4	Max.	1,2,3,4-Tetrachloro ^a	3,4-Dichloro ^b	3,5-Dichloro ^c	2,3,4-Trichloro ^a
			4,5-Dichloro ^c	3,4,5-Trichloro ^b	2,3,4-Trichloro ^c
	Min.	1,2,3,5-Tetrachloro ^c	3,5-Dichloro ^b	2,4,6-Trichloro ^a	2,4,6-Trichloro ^a
			1,2,4,5-Tetrachloro ^b	3,6-Dichloro ^c	

^a Both phases.

^b Non-polar phase.

^c Polar phase.

On the polar stationary phase, the retention indices are higher for all of the compounds, and accordingly the I^* values are also higher. It is apparent that on both phases I^* decreases with increasing extent of chlorination, the increased screening effect being responsible. This effect has been previously observed in terms of retention increments.

The dispersion and selectivity indices for anisole and veratrole and each of their chlorinated products are shown in Table II. The chlorinated anisoles and veratroles generally follow the elution pattern of the chlorobenzenes. This pattern is very similar on both the low-polarity and polar phases, with only minor variations, which when they occur, are small.

The anisole compounds on SE-30 show considerably higher values of I^* than the chlorinated benzenes. This effect is expected from the structures, the chlorobenzenes having substantial polar groups attached to the aromatic nucleus of donor character and also possessing a π -bonding system. The anisoles with the pendant methoxy group have a localized donor site, and the acceptor and shielding effects are reduced. On the acceptor phase, the values of I^* for both series are increased substantially, but those for the anisoles remain highest. On both phases, the species with maximum and minimum retentions and I^* are as shown in Table III.

It is apparent that the lowest values of I^* occur for the isomers with two similar groups, shielding another functional group. The situation is the opposite of that in which the pendant groups are the same and enhancement of retention occurs, as shown in Table III for the chlorobenzenes.

With the polar phase, all of the I^* values are increased as expected; with the lower degrees of substitution the same trend occurs as on SE-30, but as the degree of substitution increases, the values of I^* for the anisoles become greater than those for the veratroles. On the electron-withdrawing phase, the effect for the compounds with more acceptor groups becomes predominant.

The relative effect of *o*-chloro and *p*-methoxy substitution on isomeric anisoles was reported by Korhonen¹¹. He observed that the incremental effects of an additional chlorine atom in isomeric veratroles were generally lower than those for anisoles. The methoxy group had a greater effect than a chlorine atom, each substituted in the *ortho*-position without an adjacent chlorine atom. Lower retention enhancements were observed with the methoxy group adjacent to the chlorine atom than with the corresponding chlorine substitution. The I^* values shown in Table II further illustrate these observations.

The selectivity indices for the chlorinated phenyl acetates are shown in Table IV. They decrease substantially with added chlorine substituents. The values of I^* on the non-polar stationary phase are similar to those of the chlorobenzene isomers, whereas on OV-351 the values are higher. The elution trends of the various isomers closely parallel those of the chlorobenzenes. This behaviour can be reasonably explained, as discussed in earlier work⁴.

The retention (I), dispersion (I_M) and selectivity (I^*) indices of phenol and of the various chlorinated phenols, determined on SE-30 and FFAP at 160°C, are shown in Table V.

On SE-30, monochlorination causes a small increase in I . However, the dispersion indices also increase, owing to their relationship with molecular weight. The I^* value of 2-chlorophenol is greatly reduced compared with phenol. The strongly

TABLE IV
DISPERSION (I_M) AND SELECTIVITY (I^*) INDICES OF CHLORINATED PHENYL ACETATES
ON SE-30 AND OV-351 AT 160°C

Compound	I (SE-30)	I_M	I^* (SE-30)	I (OV-351)	I^* (OV-351)
Phenyl acetate	1008	956.3	51.7	1633	676.7
2-Chloro-	1173	1201.8	-28.8	1829	627.2
3-Chloro-	1198	1201.8	-3.8	1848	646.2
4-Chloro-	1203	1201.8	1.2	1870	668.2
2,6-Dichloro-	1296	1447.4	-151.4	1971	523.6
2,4 + 2,5-Dichloro-	1317	1447.4	-130.4	1986	538.6
3,5-Dichloro-	1334	1447.4	-113.4	1964	516.6
2,3-Dichloro-	1350	1447.4	-97.4	2052	604.6
3,4-Dichloro-	1377	1447.4	-70.4	2072	624.6
2,4,6-Trichloro-	1420	1693.0	-273.0	2035	342.0
2,3,6-Trichloro-	1463	1693.0	-230.0	2139	446.0
2,3,5-Trichloro-	1476	1693.0	-217.0	2117	424.0
2,4,5-Trichloro-	1481	1693.0	-212.0	2133	440.0
2,3,4-Trichloro-	1525	1693.0	-168.0	2233	540.0
3,4,5-Trichloro-	1543	1693.0	-150.0	2215	522.0
2,3,5,6-Tetrachloro-	1612	1938.5	-326.5	2225	286.5
2,3,4,6-Tetrachloro-	1617	1938.5	-321.5	2236	297.5
2,3,4,5-Tetrachloro-	1679	1938.5	-259.5	2233	394.5
2,3,4,5,6-Pentachloro-	1800	2184.1	-370.6	2401	216.9

polar hydroxy group adjacent to the halogen with screened electrons tends to reduce greatly the polar effects of the hydroxy group. However, chlorination in the 3- and 4-positions has little effect on the hydroxy group, as I^* is only slightly reduced. For these positions, the effect of the hydroxy group predominates.

Of the dichlorophenols, all four isomers with one chlorine atom adjacent to the hydroxy group exhibit I^* values that are greatly reduced, largely owing to the increased value of I_M . The 3,4- and 3,5-dichlorophenol isomers show considerably enhanced retentions and similarly I^* values. The I^* values of the 3,4- and 3,5-isomers are slightly reduced compared with those of the 3- and 4-chloro isomers, owing to the effect of the added chlorine substituent. The chlorine atom continues to have a dramatic effect when adjacent to the hydroxy group.

For the trichlorophenols, the additional chlorine atom in the isomers with a halogen adjacent to the hydroxy group has a considerable effect, and the I^* values are considerably reduced. 3,4,5-Trichlorophenol, with the halogens isolated from the hydroxy group, has considerably greater retention, and the I^* value is only slightly lower than those for 3,4- and 3,5-dichlorophenol. The reduction is again due to the small additional effect of the chlorine atom in this particular isomer.

For the tetra- and pentachlorophenols, the predominant effect of the additional halogen atoms is that due to the position of the groups, although one chlorine atom is adjacent to the hydroxy group.

TABLE V

DISPERSION (I_M) AND SELECTIVITY (I^*) INDICES OF PHENOL AND CHLORINATED PHENOLS ON SE-30 AND FFAP AT 160°C

Compound	I (SE-30)	I_M	I^* (SE-30)	I (FFAP)	I^* (FFAP)
Phenol	929	656.6	272.4	2000	1343.4
2-Chloro-	991	902.1	88.9	1866	963.9
3-Chloro-	1157	902.1	254.9	2371	1468.9
4-Chloro-	1157	902.1	254.9	2371	1468.9
2,3-Dichloro-	1180	1147.7	32.3	2160	1012.3
2,4-Dichloro-	1170	1147.7	22.3	2151	1003.3
2,5-Dichloro-	1170	1147.7	22.3	2160	1012.3
2,6-Dichloro-	1200	1147.7	52.3	2097	1049.3
3,4-Dichloro-	1378	1147.7	230.3	2731	1583.3
3,5-Dichloro-	1375	1147.7	227.3	2675	1527.3
2,3,4-Trichloro-	1363	1393.3	-30.3	2453	1059.7
2,3,5-Trichloro-	1327	1393.3	-66.3	2403	1009.7
2,3,6-Trichloro-	1354	1393.3	-39.3	2368	974.7
2,4,5-Trichloro-	1356	1393.3	-37.3	2458	1064.7
2,4,6-Trichloro-	1346	1393.3	-47.3	2301	907.7
3,4,5-Trichloro-	1587	1393.3	193.7	3028	1634.7
2,3,4,5-Tetrachloro-	1536	1638.8	-102.8	2730	1091.2
2,3,4,6-Tetrachloro-	1538	1638.8	-100.8	2554	915.2
2,3,5,6-Tetrachloro-	1530	1638.8	-108.8	2553	914.2
2,3,4,5,6-Pentachloro-	1720	1884.4	-164.4	2821	936.6

On the polar phase, the retentions of all isomers are much greater than those on SE-30 and, similarly, all of the I^* values are increased. Overall, the effect of the halogen atoms tends to predominate more strongly for the most sensitive isomers. The 3- and 4-chloro isomers, the 3,4- and 3,5-dichlorophenols and the 3,4,5-trichlorophenols have greater I^* values than phenol. The values for the tetra- and pentachlorophenols are much less reduced than for the same isomers on SE-30. On the polar phase, the elution pattern follows more closely the pattern proposed, so that 3,4-dichlorophenol is eluted after 3,5-dichlorophenol and 2,3,4,5-tetrachlorophenol after the other tetrachlorophenols.

Table VI shows the retention (I), dispersion (I_M) and selectivity (I^*) indices for the 2- and 4-hydroxybenzaldehydes and their chlorinated derivatives, and those for the parent compounds are shown in Table VII. In Table VII it is possible to compare the various indices of the parent compounds with those of compounds having one and two functional groups. On the low-polarity phase, the retention indices increase slightly from phenol to benzaldehyde and then more so with the two functional groups, the retention of the 2-hydroxy compound being appreciably lower than that of the 4-hydroxy compound. The strongly polar hydroxy group adjacent to the alde-

TABLE VI

DISPERSION (I_M) AND SELECTIVITY (I^*) INDICES OF CHLORINATED HYDROXYBENZALDEHYDES ON SE-30 AND OV-351 AT 160°C

<i>Compound</i>	<i>I</i> (SE-30)	I_M	I^* (SE-30)	<i>I</i> (OV-351)	I^* (OV-351)
Phenol	964	656.6	307.4		
Benzaldehyde	978	742.2	235.8		
4-Hydroxybenzaldehyde	1320	856.3	463.7		
2-Chloro-	1524	1101.8	422.2		
3-Chloro-	1291	1101.8	189.2		
2,3-Dichloro-	1463	1347.4	115.6		
2,5-Dichloro-	1449	1347.4	101.6		
2,6-Dichloro-	1753	1347.4	405.6		
3,5-Dichloro-	1465	1347.4	117.6		
2,3,5-Trichloro-	1632	1593.0	39.0		
2,3,6-Trichloro-	1651	1593.0	58.0		
Tetrachloro-	1820	1838.5	-18.5		
2-Hydroxybenzaldehyde	1062	856.3	205.7	1742	885.7
3-Chloro-	1264	1101.8	162.2	2082	980.2
4-Chloro-	1201	1101.8	99.2	1829	727.2
5-Chloro-	1206	1101.8	104.2	1966	864.2
6-Chloro-	1214	1101.8	112.2	1947	845.2
3,4-Dichloro-	1434	1347.4	86.6	2426	1078.6
3,5-Dichloro-	1388	1347.4	40.6	2314	966.6
3,6-Dichloro-	1387	1347.4	39.6	2160	812.6
4,5-Dichloro-	1358	1347.4	10.6	2036	688.6
4,6-Dichloro-	1326	1347.4	-21.4	1957	609.6
5,6-Dichloro-	1376	1347.4	38.6	2193	845.6
3,4,5-Trichloro-	1577	1593.0	-16.0		
3,4,6-Trichloro-	1529	1593.0	-67.0		
3,5,6-Trichloro-	1522	1593.0	-70.0		
4,5,6-Trichloro-	1510	1593.0	-82.0		
Tetrachloro-	1722	1838.5	-116.5		

hyde group causes a reduction, whereas separation of the groups considerably increases the values.

Chlorination of the two hydroxybenzaldehydes has opposite effects. Reduced I^* values occur in both series, but when the two substituents are together, *i.e.*, in 2-hydroxybenzaldehyde, chlorination has the least effect adjacent to the hydroxy group, *i.e.*, at the 3-, the 3,4- and the 3,4,5-positions. Mono-, di- and trichlorination

TABLE VII
RETENTION (*I*), DISPERSION (I_M) AND SELECTIVITY (I^*) INDICES OF CHLORINATED AROMATIC COMPOUNDS ON SE-30

Parameter	Compound	Benzaldehyde	<i>o</i> -Hydroxybenzaldehyde	<i>p</i> -Hydroxybenzaldehyde
<i>I</i>	Phenol	978	1062	1320
I_M	964	978	1062	1320
I^*	656.6	742.2	856.3	856.3
	307.4	235.8	205.7	463.7
Monochlorination I^* :				
Maximum	4-Chloro	—	3-Chloro-	2-Chloro-
Minimum	2-Chloro-	—	4-Chloro-	3-Chloro-
Dichlorination I^* :				
Maximum	3,5-Dichloro-	—	3,4-Dichloro-	2,6-Dichloro-
Minimum	2,4-Dichloro-	—	4,6-Dichloro-	2,5-Dichloro-
	2,5-Dichloro-	—		
Trichlorination I^* :				
Maximum	3,4,5-Trichloro-	—	3,4,5-Trichloro-	2,3,6-Trichloro-
Minimum	2,3,5-Trichloro-	—	4,5,6-Trichloro-	2,3,5-Trichloro-

of 4-hydroxybenzaldehyde gives a much greater selectivity value, with a smaller effect of the two separated groups. On chlorination, a smaller effect occurs adjacent to the aldehyde group, *i.e.*, 2-chloro-, 2,6-dichloro- and 2,3,6-trichlorohydroxy.

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REFERENCES

- 1 M. B. Evans, J. K. Haken and T. Tóth, *J. Chromatogr.*, 351 (1985) 155.
- 2 M. B. Evans and J. K. Haken, *J. Chromatogr.*, in press.
- 3 M. B. Evans and J. K. Haken, *J. Chromatogr.*, 462 (1989) 31.
- 4 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 265 (1983) 323.
- 5 I. O. O. Korhonen, *J. Chromatogr.*, 294 (1984) 99.
- 6 I. O. O. Korhonen, J. Knuutinen and R. Jääskeläinen, *J. Chromatogr.*, 287 (1984) 293.
- 7 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 257 (1982) 267.
- 8 I. O. O. Korhonen, *J. Chromatogr.*, 298 (1984) 101.
- 9 I. O. O. Korhonen and J. Knuutinen, *J. Chromatogr.*, 292 (1984) 345.
- 10 I. O. O. Korhonen, *J. Chromatogr.*, 315 (1984) 185.
- 11 I. O. O. Korhonen, *J. Chromatogr.*, 321 (1985) 467.