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## DISPERSION AND SELECTIVITY INDICES IN GAS CHROMATOGRAPHY

### III\*. ALKYL, $\omega$ -CHLOROETHYL AND ALKENYL BENZOATE AND CHLOROBENZOATE ESTERS

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#### SUMMARY

The dispersion ( $I_M$ ) and selectivity ( $I^*$ ) indices of homologous alkyl,  $\omega$ -chloroethyl and alkenyl benzoate and monochlorobenzoate esters are presented as obtained on low polarity (SE-30) and polar (OV-351) capillary columns. The effects of alkyl chain length, unsaturation and the position of chlorination are discussed and the results compared with studies of aliphatic esters. The compounds considered allow a study of the effect upon retention of chlorination in both the aromatic ring and the alkyl group.

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#### INTRODUCTION

The division of the retention index of a solute in gas chromatography (GC) into a contribution due to apolar forces and related to molecular weight and a second contribution due to a summation of polar interactions and steric effects has been described recently<sup>1,2</sup>. The first communication dealt in general<sup>1</sup> with the development of the indices whilst the second detailed various homologous groups of carbonyl compounds. With the carboxyl compounds<sup>2</sup> the effects of substitution and branching in both constituent chains were considered together with carbonyl compounds, *i.e.* mono- and diketones and pyruvates, containing both a carboxyl and carbonyl functional group.

The present work considers both normal<sup>3</sup>,  $\omega$ -chloroethyl<sup>4</sup> and branched-chain<sup>5</sup> alkyl and alkenyl<sup>6</sup> benzoate esters and their isomeric monochlorinated derivatives examined isothermally at 160°C on low-polarity (SE-30) and polar (OV-351) capillary columns. The phase OV-351 is described as highly purified FFAP, reported to be the

\* For Part II, see ref. 2

TABLE I  
DISPERSION ( $I_m$ ) AND SELECTIVITY ( $P^*$ ) INDICES FOR ALKYL AND ALKENYL BENZOATE ESTERS AND THEIR MONOCHLORINATED  
DERIVATIVES ON SE-30 AND OV-351

Alkyl group	SE-30		OV-351		o-Chloro- benzoate esters		m-Chloro- benzoate esters		p-Chloro- benzoate esters	
	$I_m$	$P^*$	$I_m$	$P^*$	$I_m$	$P^*$	$I_m$	$P^*$	$I_m$	$P^*$
$n$ -C <sub>1</sub>	956.3	140.7	201.8	56.2	686.7	735.2	652.2	647.2	647.2	647.2
$n$ -C <sub>2</sub>	1056.3	107.7	1301.8	25.2	628.7	669.2	585.2	583.2	583.2	583.2
$n$ -C <sub>3</sub>	1156.3	107.7	1401.8	20.2	620.7	653.2	566.2	568.2	568.2	568.2
$n$ -C <sub>4</sub>	1256.3	103.7	1501.8	18.2	622.7	642.2	555.2	563.2	563.2	563.2
$n$ -C <sub>5</sub>	1356.3	101.7	1601.8	15.2	617.7	638.2	551.2	556.2	556.2	556.2
$n$ -C <sub>6</sub>	1456.3	101.7	1701.8	15.2	616.7	636.2	549.2	552.2	552.2	552.2
$n$ -C <sub>7</sub>	1556.3	100.7	1801.8	14.2	617.7	636.2	552.2	554.2	554.2	554.2
$n$ -C <sub>8</sub>	1656.3	99.7	1901.8	13.2	616.7	637.2	551.2	554.2	554.2	554.2
$n$ -C <sub>9</sub>	1756.3	99.7	2001.8	12.2	617.7	637.2	551.2	553.2	553.2	553.2
$n$ -C <sub>10</sub>	1856.3	98.7	2101.8	12.2	618.7	638.2	551.2	554.2	554.2	554.2
$n$ -C <sub>11</sub>	1956.3	98.7	2201.8	11.2	619.7	639.2	551.2	553.2	553.2	553.2
$n$ -C <sub>12</sub>	2056.3	98.7	2301.8	11.2	620.7	641.2	552.2	556.2	556.2	556.2
Methyl	1156.3	37.7	1301.8	26.6	526.7	556.4	481.4	482.4	482.4	482.4
1-Methylpropyl	1256.3	36.7	1501.8	41.8	517.7	539.2	454.2	456.2	456.2	456.2
2-Methylpropyl	1256.3	61.7	1501.8	-21.8	554.7	573.2	486.2	492.0	492.0	492.0
1,2-Dimethylpropyl	1356.3	10.7	1601.8	-73.3	476.7	499.7	403.7	410.6	410.6	410.6
1-Methylbutyl	1356.3	24.7	1601.8	-61.3	497.7	515.7	429.7	442.6	442.6	442.6
3-Methylbutyl	1356.3	68.7	1601.8	-23.3	568.7	576.7	498.7	503.6	503.6	503.6
2-Propenyl	1419	160.1	1387.5	22.6	694.4	716.6	632.5	631.5	631.5	631.5
2-Propenyl	1127.5	125.5	1373.1	46.9	889.5	924.9	833.9	830.9	830.9	830.9
3-Butenyl	1241.9	99.1	1487.5	17.5	675.1	698.5	613.5	614.5	614.5	614.5
1-Methyl-3-butenyl	1341.9	26.1	1587.5	-52.5	554.1	575.5	486.5	489.5	489.5	489.5
(E)-2-Butenyl	1241.9	131.1	1487.5	48.5	731.1	743.5	664.5	662.5	662.5	662.5
4-Pentenyl	1341.9	105.1	1387.5	19.5	686.1	702.5	620.5	623.5	623.5	623.5
(E)-3-Hexenyl	1441.9	102.1	1687.5	19.5	658.1	683.5	588.5	591.5	591.5	591.5
(Z)-3-Hexenyl	1441.9	111.1	1687.5	24.5	674.1	601.5	610.5	613.5	613.5	613.5

esterification product of Carbowax 20M and 2-nitroterephthalic acid<sup>7</sup>. Various studies of the esters of interest, particularly the parent esters, have been recently reported<sup>8</sup> and are not repeated in this work. The influence of the various structural parameters, particularly on the selectivity indices, are discussed and some comparisons are made with earlier studies of aliphatic carboxyl compounds.

## EXPERIMENTAL

The GC was conducted on a Perkin-Elmer Sigma 3 instrument using a vitreous silica SE-30 capillary column (25 m × 0.33 mm I.D.), (S.G.E., North Melbourne, Australia) and a fused-silica OV-351 column (25 m × 0.32 mm I.D.) (Orion Analytica, Espoo, Finland). The conditions were: injection and flame-ionisation detector temperature, 275°C; column temperature, 160°C; nitrogen carrier gas and a split ratio of 1:25. Retentions were measured as retention indices as previously reported<sup>3-6</sup>.

## RESULTS AND DISCUSSION

Table I shows dispersion ( $I_M$ ) and selectivity ( $I^*$ ) indices for the alkyl and alkenyl esters studied. The *n*-alkyl benzoate esters on the low-polarity phase show  $I^*$  values which tend to decrease slightly as the chain length is increased although the main decrease occurs with the lower alkyl esters. This is indicative of a significant methyl effect and formation of a homologous series where additional methylene groups have a truly additive effect. The values are, however, considerably higher than those of the corresponding alkyl esters, *i.e.* the *n*-alkyl hexanoates, due to the higher boiling points and the aromatic structure. As with alkyl- and alkenylbenzenes<sup>1</sup> an extension of the  $\pi$  bonding system greatly extends the selectivity.

Chlorination at all three positions on the ring produces equivalent and higher  $I_M$  values due to the increased molecular weight but lower values of  $I^*$  on the SE-30 stationary phase. It has been shown previously<sup>1</sup> with aliphatic compounds that the presence of polar functional groups tends toward positive  $I^*$  values whilst groups with screened electrons display strongly negative values. Here while the basic aromatic structure is of greater polarity, the addition of a halogen causes a considerable reduction.

The  $I^*$  values of the *ortho*, *meta* and *para* isomers are very similar, there being a slight decrease from *ortho* to *para* and a minimal further decrease from *para* to *meta*. The corresponding values of all compounds are greatly increased on the polar (OV-351) column. The substantial difference between the values of the parent esters and their derivatives is not evident now. The elution pattern is as demonstrated previously where maximization of the polar effects occurs with the *ortho* substituent<sup>3,6</sup>. This behaviour can be explained on the basis of electromerism<sup>6</sup>. The decrease in electron density occurring in the phenyl ring with *o*-substitution is more pronounced than that with *m*- and *p*-substitution, the increased interaction between this more electron-deficient ring and the electron-donating groups of the phase giving rise to the relatively higher retentions of the *o*-chloro isomers on OV-351. This effect with the *m*- and *p*-chloro isomers seems to be similar, *i.e.* the retention behaviour between the isomeric esters remains unchanged with increasing column polarity.

The effect of branching of the alkyl group is evident from Table I. Methyleneethyl

**TABLE II**  
DISPERSION ( $I_m$ ) AND SELECTIVITY ( $I^*$ ) INDICES FOR  $\omega$ -CHLOROETHYL BENZOATES AND THEIR MONOCHLORINATED DERIVATIVES ON SE-30 AND OV-351

Alkyl group	OV-351									
	SE-30	$I_m$	$I^*$	<i>o,m,p</i> - Chlorobenzoate esters	<i>o</i> -Chloro- benzoate esters	<i>m</i> -Chloro- benzoate esters	<i>p</i> -Chloro- benzoate esters	Benzoate esters	<i>o</i> -Chloro- benzoate esters	<i>m</i> -Chloro- benzoate esters
Ethyl	1056.3	107.7	1301.8	25.2	21.2	22.2	628.7	669.2	585.2	583.2
2-Chloroethyl	130.18	78.2	1547.4	1.6	5.4	3.4	821.2	850.6	756.6	777.6
2,2-Dichloroethyl	1547.4	77.4	1793.0	154.0	-166.0	-158.0	665.6	698.0	628.0	626.0
2,2,2-Trichloroethyl	1793.0	257.0	2038.5	330.5	-348.5	342.5	391.0	430.5	327.5	333.5

**TABLE III**  
REDUCTION IN SELECTIVITY ( $I^*$ ) WITH ADDITION OF INDIVIDUAL CHLORINE ATOMS IN ALKYL CHAIN AND AROMATIC RING

Alkyl substitution	SE-30			OV-351					
	$I^*$ Reduction	Ring substitution		$I^*$ Reduction	Ring substitution				
		<i>o</i> -	<i>m</i> -	<i>p</i> -	<i>o</i> -	<i>m</i> -	<i>p</i> -		
$C_2H_5 \rightarrow C_2H_4Cl$	29.5	23.6	26.6	25.6	$C_2H_5 \rightarrow C_2H_4Cl$	+192.5	+181.4	+171.4	194.4
$C_2H_4Cl \rightarrow C_2H_3Cl_2$	155.6	155.6	160.6	161.4	$C_2H_4Cl \rightarrow C_2H_3Cl_2$	156.5	152.6	138.6	151.6
$C_2H_3Cl_2 \rightarrow C_2H_2Cl_3$	179.6	176.5	182.5	184.5	$C_2H_3Cl_2 \rightarrow C_2H_2Cl_3$	274.6	267.5	300.5	292.5
$C_2H_5 \rightarrow C_2H_4Cl$	29.5	23.6	26.6	25.6	$C_2H_5 \rightarrow C_2H_4Cl$	+192.5	+181.4	+171.4	+194.4
$C_2H_5 \rightarrow C_2H_3Cl_2$	185.5	179.2	187.2	180.2	$C_2H_5 \rightarrow C_2H_3Cl_2$	+36.9	+29.8	+42.8	+42.8
$C_2H_5 \rightarrow C_2H_2Cl_3$	364.7	355.7	369.7	344.7	$C_2H_5 \rightarrow C_2H_2Cl_3$	237.7	238.7	257.7	249.7

benzoate on SE-30 has a considerably lower value of  $I^*$  than any of the *n*-alkyl benzoates, the effect of the methyl group in shielding the carbonyl being considerable as indicated previously<sup>2</sup>. The other five esters all follow a logical sequence, the 1-methylpropyl has a lower  $I^*$  value but this is greater than that of 2-methylpropyl ester where greater separation occurs. The 1,2-dimethylpropyl ester with further constraints has a lower  $I^*$  value. The 1-methylbutyl and 3-methylbutyl esters follow the corresponding propyl esters. With chlorination the greatest values of  $I^*$  are again shown with the *ortho* homologues, but the absolute values of  $I^*$  are very much lower than those for the saturated esters because branching on the carboxyl group reduces the polarity of this part of the compound and this in company with the aromatic moiety and the halogen atom has a marked effect.

On the polar phase the values of all four series are lower than for the straight chain esters but the trends are the same, namely

$$I^*_{o\text{-chloro}} < I^*_{\text{alkyl}} < I^*_{p\text{-chloro}} < I^*_{m\text{-chloro}}$$

The effect of unsaturation in the alkyl benzoates is evident firstly by comparison of 2-propenyl and *n*-propyl benzoate. On SE-30 slight enhancement of  $I^*$  occurs with the unsaturated ester while the three sets of chlorinated isomers have essentially equal  $I^*$  values. With increased phase polarity the  $I^*$  values of the unsaturated esters and of the chlorinated esters are expectedly increased. The 3-butenyl ester showed a reduced  $I^*$  value compared to the *n*-butyl ester on SF-30 but an increased value on OV-351. The 2-butenyl ester with closer proximity of the unsaturation to the carbonyl group shows further increased values of  $I^*$  in both phases. It is evident here as in the preceding work on alkyl esters that the 2-butenyl isomer shows greater relative  $I^*$  enhancement than the 2-propenyl ester, the significance of the terminal methyl group again being apparent. The 4-pentenyl ester shows increased values of  $I^*$  relative to the *n*-pentyl benzoates but the values are reduced compared to the shorter-chain unsaturated esters indicating further that transmission of polar effects along an alkyl chain is limited.

The ester (1-methyl-3-butenyl) with a pendant methyl group adjacent to the carboxyl group shows the lowest values of  $I^*$  of all the esters on both phases, and the effect relative to both the 3-butenyl and 4-pentenyl is quite dramatic. The moderating effect of a methyl group as a substituent adjacent to the carbonyl group has been observed previously with unsaturated aliphatic esters.

Table II shows dispersion ( $I_M$ ) and selectivity ( $I^*$ ) indices for the *o*-chloroethyl benzoates and their monochlorinated derivatives.

Monochlorination of the aromatic ring has been shown on the non-polar phase to produce a reduction in  $I^*$ . With ethyl benzoate, a reduction in  $I^*$  in excess of 80 is evident on monochlorination of the ring while similar chlorination of the ethyl group causes a reduction of about 30. The difference in the values are due to less interference of the  $\pi$  bonding system by the chlorine substituent. As expected, Table II shows that the selectivity index on the same phase is reduced both with chlorination of the ethyl group and of the ring.

Table III shows the effects of di- and trichlorination of the ethyl group where very much greater reductions in  $I^*$  are evident as expected, while similarly with ring chlorination comparably large reductions also occur. In common with the other series (Table I), the *ortho* compounds (Table II) exhibit greater retention and the highest  $I^*$

**TABLE IV**  
**ALTERNATIVE TABULATION OF REDUCTION IN SELECTIVITY ( $I^*$ ) INDICES WITH**  
 **$\omega$ -ETHYL AND RING CHLORINATION**

Compound chlorinated	Site of chlorination	$I^*$ Reduction	
		SE-30	OV-351
Ethyl benzoate	Alkyl group	29.5	192.5
	Aromatic ring	82.5, 85.5, 88.5*	40.5, 43.5, 45.5
Monochloroethyl benzoate	Alkyl group	155.6	155.6
	Aromatic ring	76.6, 83.6, 81.6	29.4, 64.6, 43.6
Dichloroethyl benzoate	Alkyl group	180.0	274.6
	Aromatic ring	76.6, 88.5, 80.6	39.5, 63.5, 57.5
Trichloroethyl benzoate	Aromatic ring	73.5, 91.8, 85.5	32.4, 37.6, 39.6

\* *o*-, *m*-, *p*- respectively

values of the three isomers. The actual variations in the  $I^*$  values are shown in Table III.

The increased difference in selectivity of monochloroethyl benzoate and dichloroethyl benzoate in comparison to ethyl benzoate and monochloroethyl benzoate is observed. However, a very similar reduction in  $I^*$  occurs with ring chlorination of the two species, and the same effect is apparent with all three series with  $I^*$  decreasing expectedly with increasing chlorine content. The effect of the addition of one, two or three chlorine atoms to ethyl benzoate is shown in the lower part of Table III.

With the polar stationary phase the same trends are evident but increased  $I^*$  values are initially experienced due to the predominant effects of the donor phase but are overcome with increased chlorine content.

The effects of ring chlorination are also shown in Table IV. The effect of chlorine introduction in the alkyl chain is as indicated in Table III. Introduction of a chlorine atom at any of the ring positions produces on SE-30 similar and possibly slightly lower reductions of  $I^*$  as the polarity or chlorine content of the parent compound is increased. With the polar stationary phase a significant increase in  $I^*$  is evident with the first alkyl chlorination and much less with ring chlorination of ethyl benzoate. The results for the three isomers are very variable with the monochloroethyl compound and only slightly less so with the dichloroethyl benzoate, but significantly lower with the trichlorobenzoate derivatives.

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