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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XX*. CAPILLARY COLUMN STUDIES OF ALKYL ACETATES, CHLOROACETATES, DICHLOROACETATES AND TRICHLOROACETATES

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SUMMARY

Isothermal capillary gas chromatography of C_1–C_8 *n*-alkyl acetates, chloroacetates, dichloroacetates and trichloroacetates has been studied using a low-polarity (SE-30) and a polar (OV-351) stationary phase at increasing temperatures from 100 to 160°C. The work extends recent studies of Komarek and co-workers and shows the effect of retention index increments on the methylene chain and of the various chlorine substituents in the individual homologous series.

INTRODUCTION

The retention behaviour of alkanoic and alkenoic esters has been extensively studied such that the relative incremental effects of the chain parameters are known to have a greater effect on retention when in the alkyl rather than the acyl chain[1,2].

Such systematic studies of homologous esters with other substituent groups have not been reported. Recently a series of studies[3] to maximize the separation of complex mixtures of various chlorinated esters with substitution in both the acyl and alkyl chains have been reported, using temperature programming and capillary columns coated with SE-30, OV-351 and Carbowax 20M.

The elution sequence of one series, *viz.* *n*-alkyl acetates with mono-, di- and trichlorination[3], on SE-30 and OV-351 has been reported by Korhonen[4] and the separation of the same series has recently been reported by Komarek *et al.*[5] using an OV-101-coated capillary column operated at 80 and 200°C for the C_1–C_5 and C_6–C_{16}

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esters, respectively. They showed the incremental effect of the methylene chain and of the various chlorine substituents.

This work extends that of Komarek *et al.*[5] by showing the retention indices and the effect of index increments of the same series of esters on a dimethyl polysiloxane-coated column (SE-30) at increasing temperatures from 100 to 160°C together with corresponding data obtained using the highly polar stationary phase OV-351.

EXPERIMENTAL

The analyses were performed using a Perkin-Elmer Sigma 3 instrument with the following operating conditions: injector and flame-ionization detector tempera-

TABLE I

RETENTION INDICES OF CHLORINATED ESTERS ON SE-30 AND OV-351

Compound	*SE-30*			*OV-351*			
	100°C	*140°C*	*180°C*	*100°C*	*120°C*	*140°C*	*160°C*
A1	560						
A2	642						
A3	729	651	647	1061	897	–	–
A4	818	755	716	1115	1042	1008	953
A5	912	863	853	1176	1165	1147	1100
A6	1006	978	972	1255	1274	1265	1230
A7	1099	1083	1083	1347	1377	1373	1294
A8	1194	1191	1195	1448	1479	1478	1453
C1	768	701	648	1251	1269	1265	1270
C2	832	768	771	1282	1307	1279	1305
C3	920	886	886	1355	1384	1379	1378
C4	1014	994	1000	1447	1479	1478	1472
C5	1106	1097	1106	1547	1578	1581	1575
C6	1200	1201	1216	1652	1676	1681	1668
C7	1296	1305	1319	1761	1774	1780	1769
C8	1394	1407	1420	1871	1874	1881	1866
D1	835	792	786	1337	1366	1365	1325
D2	904	871	876	1354	1382	1380	1378
D3	991	976	987	1425	1459	1460	1428
D4	1081	1072	1088	1514	1548	1551	1528
D5	1173	1175	1192	1614	1642	1648	1627
D6	1268	1278	1298	1719	1738	1745	1728
D7	1364	1380	1399	1827	1834	1843	1826
D8	1463	1481	1501	1937	1930	1941	1925
T1	912	897	896	1320	1352	1358	1320
T2	981	966	965	1333	1366	1365	1330
T3	1064	1063	1074	1396	1434	1441	1422
T4	1153	1161	1173	1480	1519	1528	1511
T5	1245	1260	1277	1573	1609	1620	1608
T6	1340	1359	1380	1674	1764	1715	1703
T7	1437	1478	1480	1781	1799	1812	1802
T8	1535	1558	1578	1889	1894	1910	1900

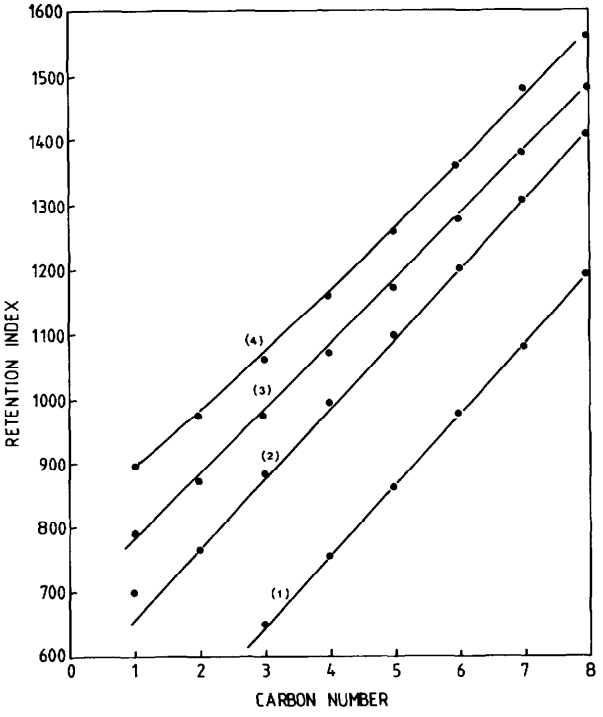

Fig. 1. Plots showing retention of the chlorinated esters on SE-30 at 100°C at 100°C. 1, *n*-Alkyl acetates; 2, chloroacetates; 3, dichloroacetates; 4, trichloroacetates.

tures, 230 and 250°C, respectively; hydrogen, air and nitrogen flow-rates, 40, 300 and 1 ml/min, respectively; splitting ratio, 1:25. The quartz capillary columns used were (1) vitreous silica (25 m × 0.22 mm I.D.) coated with SE-30, supplied by SGE (North Melbourne, Australia), and (2) fused silica (25 m × 0.32 mm I.D.) coated with OV-351, supplied by Orion Analytica (Espoo, Finland).

The retention times were measured from the time of injection and the retention indices were determined off-line using a Vector MZ microprocessor system, the dead volume first being determined by regression analysis from a series of *n*-alkanes using the procedure of Grobler and Balizs[6].

The C_1–C_8 *n*-alkyl acetates (A1–A8) were prepared in the laboratory as described previously[7]. Commercial chloroacetic and di- and trichloroacetic acids (Fluka, Buchs, Switzerland) were converted into the acid chlorides using thionyl chloride. C_1–C_8 *n*-alkyl chloroacetates (C1–C8), dichloroacetates (D1–D8) and trichloroacetates (T1–T8) were prepared from the acid chlorides using commercial alcohols (Fluka) by the method of Edvards *et al.*[8].

RESULTS AND DISCUSSION

Table I shows retention times and retention indices of the four ester series on the two columns at increasing temperatures; the C_1–C_8 alkyl esters are shown as A1–A8 and the appropriate mono-, di- and trichloro esters as C1–C8, D1–D8 and T1–T8,

TABLE II

RETENTION INCREMENTS FOR METHYLENE UNITS AND CHLORINE SUBSTITUENTS ON SE-30

Compound	*Data at 100°C*					*Data of Komarek et al.*[5] *at 80°C*				
	ΔI_{CH_2}	ΣI_{Cl}	ΔI_{1Cl}	ΔI_{2Cl}	ΔI_{3Cl}	ΔI_{CH_2}	ΣI_{Cl}	ΔI_{1Cl}	ΔI_{2Cl}	ΔI_{3Cl}
A1	–					–				
A2	82					70				
A3	81					100				
A4	89					101				
A5	94					100				
A6	94					100				
A7	93					–				
A8	95					–				
C1	–	208	208			–	204	204		
C2	64	190	190			77	211	211		
C3	88	191	191			96	207	207		
C4	94	196	196			99	205	205		
C5	92	194	194			99	204	204		
C6	94	194	194			101	204	204		
C7	96	197	197							
C8	98	200	200							
D1	–	275	208	67		–	286	204	82	
D2	69	262	190	72		70	287	211	76	
D3	87	262	191	71		92	273	205	68	
D5	92	261	194	67		97	270	204	66	
D6	95	262	194	68		100	270	204	66	
D7	96	265	197	69						
D8	99	269	200	69						
T1	–	352	208	67	77	–	370	204	82	84
T2	69	339	190	72	77	66	366	211	76	79
T3	83	345	191	71	83	90	355	207	72	77
T4	89	335	196	67	72	93	348	205	68	75
T5	92	333	194	67	72	96	344	204	66	73
T6	95	334	194	68	72	100	343	204	66	73
T7	97	338	197	69	72					
T8	98	342	200	69	73					

respectively. Dead volumes and retention indices were computed off-line by the same procedure normally used with our usual on-line operation.

Retention indices of the four series determined on the SE-30 column at 100°C are plotted in Fig. 1. A significant enhancement of retention compared with the simple ester (curve 1) is indicated by the addition of a chlorine atom (curve 2), while further but reduced enhancement is observed by the presence of a second (curve 3) and a third chlorine atom (curve 4).

The retention increments for the methylene unit and for the chlorine atoms

TABLE III

RETENTION INCREMENTS FOR METHYLENE UNITS AND CHLORINE SUBSTITUENTS ON SE-30 AT 140 AND 180°C

Compound	*Temperature (°C)*	*I*	ΔI_{CH_2}	ΣI_{Cl}	ΔI_{1Cl}	ΔI_{2Cl}	ΔI_{3Cl}
A1	140						
A2							
A3		651					
A4		755	104				
A5		863	108				
A6		978	115				
A7		1083	105				
A8		1191	98				
C1		701	–				
C2		768	67				
C3		886	106		235		
C4		994	103		239		
C5		1097	103		234		
C6		1201	104		223		
C7		1305	104		222		
C8		1407	102		216		
D1		792					
D2		871	79				
D3		976	105	325	235	90	
D4		1072	96	317	239	78	
D5		1175	103	312	234	78	
D6		1278	103	300	223	77	
D7		1380	102	303	222	81	
D8		1481	101	290	216	84	
T1		897	–				
T2		966	69				
T3		1063	97	412	235	90	107
T4		1161	98	406	239	78	89
T5		1260	99	397	234	78	85
T6		1359	99	381	233	77	71
T7		1478	119	395	222	81	92
T8		1558	120	367	216	84	67
A1	180						
A2							
A3		647					
A4		716	69				
A5		853	137				
A6		972	119				
A7		1083	111				
A8		1195	112				
C1		648	–				
C2		771	123				
C3		886	115		237		

(Continued on p. 226)

TABLE III *(continued)*

Compound	*Temperature (°C)*	*I*	ΔI_{CH_2}	ΣI_{Cl}	ΔI_{1Cl}	ΔI_{2Cl}	ΔI_{3Cl}
C4		1000	114		284		
C5		1106	106		253		
C6		1216	110		244		
C7		1319	103		236		
C8		1420	101		225		
D1		786					
D2		876	90				
D3		987	111	340	237	103	
D4		1088	101	372	284	88	
D5		1192	104	339	253	86	
D6		1298	106	326	244	82	
D7		1399	101	316	236	80	
D8		1501	102	306	225	81	
T1		896					
T2		965	69				
T3		1974	109	427	237	103	74
T4		1173	99	457	284	88	85
T5		1277	104	424	253	86	85
T6		1380	103	408	244	82	82
T7		1480	100	397	236	90	81
T8		1578	98	383	225	81	87

were calculated by considering the differences between the retention indices of the various series as shown below:

$$\begin{aligned}
\Delta I_{CH_2} &= I(A_{x+1}) - I(A_x) \\
&\quad I(C_x) - I(A_x) \\
\Sigma \Delta I_{Cl} &= I(D_x) - I(A_x) \\
&= I(C_x) - I(A_x) \\
\Delta I_{Cl} &= I(C_x) - I(A_x) \\
\Delta I_{2Cl} &= I(D_x) - I(C_x) \\
\Delta I_{3Cl} &= I(T_x) - I(D_x)
\end{aligned}$$

TABLE IV

SUMMARY OF RETENTION INCREMENTS OF METHYLENE UNITS AND CHLORINE SUBSTITUENTS ON SE-30 AT 80–200°C

Temperature (°C)	ΔI_{CH_2}	ΔI_{1Cl}	ΔI_{2Cl}	ΔI_{3Cl}	*Chain length*
80	70–108	204–211	66– 82	73– 84	C_1–C_6
100	69– 99	190–208	69– 77	72– 83	C_1–C_8
140	69–120	216–239	78– 90	67–107	C_1–C_8
180	69–137	225–284	80–103	74– 87	C_1–C_8
200	98–202	216–219	77– 78	78– 81	C_6–C_{16}

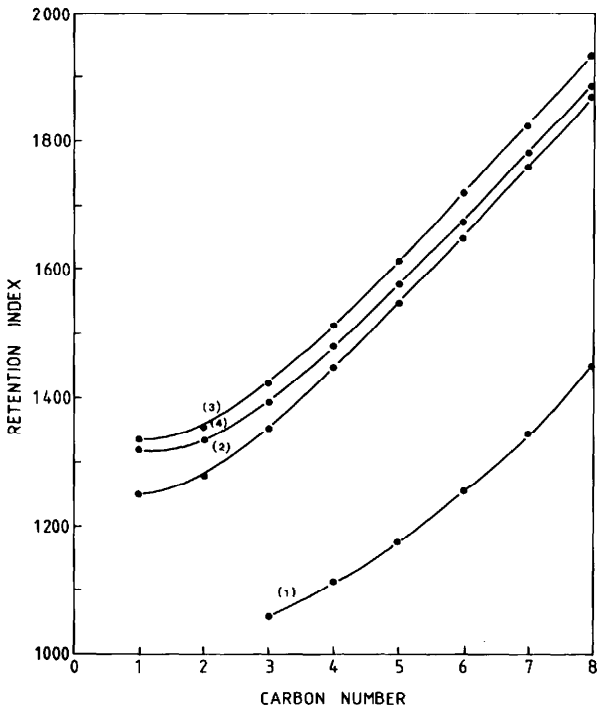

Fig. 2. Plots showing retention of the chlorinated esters on OV-351 at 100°C. Curves as in Fig. 1.

The values calculated in this manner are shown in Table II for data on SE-30 at 100°C and are compared with the data of Komarek *et al.*[5] produced at 80°C. The methylene increments are in the range 69–99 retention indices and are in reasonable agreement with the earlier work, *i.e.*, 70–108 units. The increment ranges for the first, second and third chlorine atoms are shown with the values of Komarek *et al.*[5] in parentheses: 190–208 (204–211), 67–69 (66–82) and 72–83 (73–84), respectively. This is exceptional agreement as some small temperature dependence of these values is shown. Also the dead volumes here were not determined in the same way as Komarek *et al.*[5] did by using the retention time of methane as the dead volume.

Table III shows the same increment differences on SE-30 determined at 140 and 180°C. A slight temperature dependence occurs and is more apparent from the summary shown in Table IV, where results of earlier work are included. An increase in all of the increments occurs with temperature, the values of the methylene increment being high at 180°C but not as high as the values near 200°C observed by Komarek *et al.*[5].

Monochlorination of the *n*-alkyl esters lead to a considerable elevation of the boiling point and, on a low-polarity stationary phase significantly increased retention, is expected. The addition of a second large group on the same carbon atom might be expected to provide some hindrance and shielding and reduced enhancement is not unexpected. The addition of the third chloride atom might, however, be expected to produce a smaller increase in retention than the second chlorine atom.

TABLE V

RETENTION INCREMENTS FOR METHYLENE UNITS AND CHLORINE SUBSTITUENTS ON OV-351 AT 100°C

Compound	*I*	ΔI_{CH_2}	ΣI_{Cl}	ΔI_{1Cl}	ΔI_{2Cl}	ΔI_{3Cl}
A1	–					
A2	–					
A3	1061					
A4	1115	64				
A5	1176	61				
A6	1255	79				
A7	1347	92				
A8	1448	101				
C1	1251					
C2	1282	31				
C3	1355	73		294		
C4	1447	92		332		
C5	1547	100		367		
C6	1652	105		397		
C7	1761	109		424		
C8	1871	110		423		
D1	1337	–				
D2	1354	17				
D3	1425	91	364	294	70	
D4	1514	89	399	332	67	
D5	1614	100	438	369	79	
D6	1719	105	464	397	67	
D7	1827	108	480	424	56	
D8	1937	110	489	423	66	
T1	1320					
T2	1333	13				
T3	1396	63	335	294	70	−29
T4	1480	84	365	332	67	−44
T5	1573	93	397	369	69	−42
T6	1675	102	420	397	67	−44
T7	1781	106	434	424	56	−46
T8	1889	108	441	423	66	−48

However, a minimal increase is observed. From studies of simple branched-chain esters some reduction might have been expected[9] in this situation.

Retention index plots for the four series determined on the OV-351 column are shown in Fig. 2. The general enhancement of the retention of all of the series on the more polar phase is as expected. The increased retention of the monochloro esters is greater than on SE-30 owing to the influence of the polar esters with the more polar stationary phase. The effect of the second chlorine substituent shows an increase in retention comparable to that on SE-30. The third chlorine substituent, however, shows a significant reduction in retention, the effect of this substituent being about equal to that due to the removal of a methylene group from the alkyl chain. Replacement of a hydrogen atom with a larger chlorine atom adjacent to the carbonyl group

TABLE VI

SUMMARY OF RETENTION INCREMENTS OF METHYLENE UNITS AND CHLORINE SUBSTITUENTS ON OV-351 AT 100–160°C

Temperature	ΔI_{CH_2}	ΔI_{1Cl}	ΔI_{2Cl}	ΔI_{3Cl}
100	13–110	294–324	56– 70	−29 to −48
120	14–109	395–437	59–104	−25 to −46
140	14–118	403–471	60– 76	−27 to −38
160	10–159	414–519	51– 60	−19 to −26

might be expected to produce an effect where the acceptor character of the halogen is minimized by the donor character of the carbonyl group, although the overall polar effect would be increased and retention increased on both stationary phases. Further substitution with the introduction of more polar groups would increase the polar effect although, as occurs with replacement of the hydrogen atoms of a methyl group, steric effects are introduced, as has been shown with hindered esters[10], the retention enhancement is reduced. This effect being accentuated with increasing stationary phase polarity and with complete substitution of all hydrogen atoms, the steric effects are of such significance that the observed reduction in retention occurs. The relative retention increments of the three chlorine atoms at 100°C are shown in Table V and the effect of temperature is summarized in Table VI. As with the low-polarity stationary phase, an increase in the incremental values is observed with increasing temperature.

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