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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XV. MOLECULAR RETENTION INDICES OF ALIPHATIC ESTERS*

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SUMMARY

Molecular retention indices (ΔMe) of aliphatic esters are examined for use in structure–retention relationships for tentative identification and contrasted with conclusions obtained from retention index plots and increments.

INTRODUCTION

The presentation of retention data as molecular retention indices (ΔMe) as an alternative to the use of retention indices (I) has been proposed by Evans and Smith. While the retention index is defined as the carbon number multiplied by one hundred of a hypothetical *n*-alkane having the same retention as the solute being considered, the molecular retention index considers the molecular weight of the same hypothetical alkane. This value, described as the effective molecular weight, is equivalent to the retention index. The difference between this value and the molecular weight of the compound is the molecular retention index (ΔMe). The relationships are shown in eqns. 1 and 2.

$$\begin{aligned} Me &= 14.026\, I' + 2.016 \\ &= 0.14026\, I + 2.016 \end{aligned} \qquad (1)$$

$$\Delta Me = Me - M \qquad (2)$$

where

$I = 100\, I'$

Me = effective molecular weight of the solute or of a hypothetical *n*-alkane with I' carbon atoms;

I' = number of carbon atoms in hypothetical *n*-alkane;

M = molecular weight of solute.

The early papers[1,2] suggested that ΔMe was a useful parameter for the correlation of chemical structure and chromatographic retention, and the the value was

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virtually constant within a homologous series. For a proposed structure, M is known and ΔMe for the various structural features could be obtained from correlation charts. Other aspects of the ΔMe scheme have been described by Evans *et al.*[3-5].

Evans and Smith demonstrated these proposals to a limited extent and more recently (6) work with *n*-alkanoates, *n*-alkanols, *n*-alkanones and *n*-alkanals has confirmed the constancy of ΔMe on columns of low (SE-30), medium (OV-25) and reasonably high polarity (SILAR 10C). It was further apparent that the constancy was little influenced by polarity, although the values with all series increased with the phase polarity.

The present work considers ΔMe values of homologous compounds of one functional class as these values have been suggested to be of value in facilitating identification of closely related compounds, such as might be experienced with reaction mixtures. Esters where structural variations occur in both the alcohol or alkyl chain (R′) or in the acid or acyl chain (R) and in the presence of unsaturation have been studied, as considerable information relating retention behaviour and molecular structure has been reported based on retention plots or index increments[7-13].

EXPERIMENTAL

The analyses were carried out using 12 ft. × 1/4 in. O.D. aluminium columns with 10% of the stationary phases on Chromosorb W AW DMCS with isothermal operation at 150°C.

To increase the speed and accuracy of the determination of retention data, a Hewlett-Packard 5750 research gas chromatograph was interfaced with 32 K PDP 11/40 digital computer. The chromatograph employed a splitter and individually operated detectors with injection by a Hewlett-Packard 7670A automatic sampler. Calculations of dead time and retention indices were conducted within the system.

RESULTS AND DISCUSSION

Structure–retention relationships with homologous esters, RCOOR′, based on retention plots and retention index increments, have shown:

(1) The slopes of plots representing homologous esters with the same number of carbon atoms in the acid chain (R) decrease as the value of R is increased; similarly for the same number of carbon atoms in the alcohol chain (R′) the slopes decrease as the value of R′ increases with the phases considered[7-9].

(2) Retention of methyl esters follows boiling point.

(3) On stationary phases containing highly polarizable substituent groups it was evident that a loss of linearity occurs with alcohol ester plots.

(4) The effect of isomerization in the alcohol chain was most apparent with isopropyl esters and to lesser extents with isobutyl and isopentyl esters[13].

(5) It is apparent that the methylene group has a greater effect on retention when in the alcohol chain (R′) than in the acid chain (R), this effect having also been observed with α-alkyl acrylic esters.

(6) Retention increments for the carboxyl group in *n*-alkyl esters indicated that the net retention of the group increased with increasing polar character of the phase.

(7) With unsaturated esters the boiling point was of importance but two fur-

ther effects were experienced. The presence of a double bond in an alkyl group tended to reduce retention on a non-polar phase, the decrease being accentuated where conjugation occurred[10–12].

(8) With increasing polar character of the stationary phase, retention as 2-alkanoates increased with respect to the corresponding branched chain series due to screening of the carboxyl group[10–12].

(9) With increased phase polarity the retention of *cis* isomers of unsaturated esters was affected more than that of *trans* isomers.

Table I shows retention indices, *Me* and *ΔMe* values for homologous esters of varying structure determined on columns of low (SE-30), medium (OV-25) and substantial (SILAR 10C) polar character, together with values for *n*-alkyl acetates extracted from our earlier report[6], the data being considered in terms of the conclusions enumerated above.

With the data determined on a non-polar column (SE-30) it is evident that the approximate degree of constancy previously observed[6] with the homologous acetate esters is maintained with series of increasing carbon number of the acid or acyl chain from propionates to hexanoates. The *ΔMe* values, however, cannot be constant as it would be necessary for esters of the same carbon number to have identical retention.

Table II shows that the *n*-alkyl and isoalkyl alkanoates on all three phases show a decreasing average *ΔMe* value as the chain length R is increased, retention of the series also decreasing; this is in agreement with the earlier reports[7–9]. The effect is less apparent on the non-polar SE-30 column as the separations are greatly enhanced with increased polarity of the phase. The same consideration from a study of R′ variation is not possible.

It has been reported previously that comparison of retention index increments of *n*-alkyl alkanoates has shown that the methylene group has a greater effect on retention when in the alkyl or alcohol chain (R′) than when in the acid or acyl chain (R)[7–9]. Consideration of the data in Table I does not allow such a conclusion to be made, although consideration of the *ΔMe* values of the isoalkyl esters indicates that the reverse effect is apparent, *i.e.* the retention is lower with the isoalkyl hexanoates where the effect of the particularly compact shape of the isopropyl group is minimised[13].

The constancy that exists with the *n*-alkyl alkanoates is not as apparent with the *n*-alkyl iso-esters, although the *ΔMe* values of these series are lower than those of the straight-chain series.

Branching in both the R and R′ chains has similarly been shown to lead to unexpectedly low retention. The *ΔMe* values would, as described above, indicate that reduced retention is experienced as the molecular size is increased. The constancy of the series with branching in both chains is less evident, although the *ΔMe* values are again lower, as would be expected (Table III).

With increasing phase polarity the *ΔMe* values of *n*-alkyl alkanoates increase, as with homologous series of other functional classes[6]. The constancy of the *ΔMe* values however is poorer on both the OV-25 and SILAR 10C phases. With homologous series with branched R′ with R and R and R′ both branched the constancy of the series is poor, although the general *ΔMe* values in all cases increase with phase polarity.

Table II shows retention indices and *ΔMe* values of two unsaturated series of

TABLE I

RETENTION INDICES, EFFECTIVE MOLECULAR WEIGHT (*Me*) AND MOLECULAR RETENTION INDICES (*ΔMe*) OF ALIPHATIC ESTERS

	SE-30			*OV-25*			*SILAR 10C*		
	I	*Me*	*ΔMe*	*I*	*Me*	*ΔMe*	*I*	*Me*	*ΔMe*
Acetates									
Propyl	581.69	83.61	−18.52	733.97	104.97	2.85	1143.18	162.37	60.24
Butyl	678.82	97.23	−18.93	831.29	118.62	2.46	1228.09	174.28	58.12
Amyl	785.37	112.18	−18.01	932.48	132.81	2.62	1326.90	188.14	57.95
Hexyl	878.41	125.23	−18.99	1035.25	147.23	3.01	1424.64	201.85	57.63
Proponates									
Methyl							1087.5	154.55	99.43
Ethyl	576.70	82.91	−19.22	727.60	104.08	1.95	1127.07	160.10	57.97
Propyl	678.49	97.19	−18.97	833.35	118.91	2.75	1224.83	173.81	57.65
Butyl	782.16	111.73	−18.46	934.12	133.05	2.85	1327.25	188.19	58.00
Amyl	885.25	126.19	−18.03	1033.59	147.00	2.78	1413.9	200.34	56.12
Hexyl	980.35	139.53	−18.71	1131.84	160.78	2.54			
Butyrates									
Methyl							1196.18	169.79	67.66
Ethyl	671.38	96.19	−19.97	833.06	118.87	2.71	1229.2	174.42	58.26
Propyl	785.37	112.18	−18.01	932.31	132.79	2.60	1309.52	185.69	56.57
Butyl	881.62	125.68	−18.54	1029.89	146.48	2.26	1405.75	199.19	54.97
Amyl	979.0	139.34	−18.90	1126.49	160.03	1.79	1511.8	214.08	55.84
Hexyl	1083.14	153.95	−18.32						
Valerates									
Ethyl	782.28	111.75	−18.44	928.81	132.30	2.11	1309.36	185.68	55.49
Propyl	888.40	126.63	−17.59	1024.13	145.67	1.45	1396.12	197.85	53.63
Butyl	985.20	140.21	−18.03	1124.79	159.79	1.55	1488.85	210.86	52.62
Amyl	1082.47	153.85	−18.42	1223.79	173.68	1.41	1586.47	224.55	52.28
Hexyl	1185.53	168.31	−18.00				1639.2	238.9	52.66
Hexoates									
Ethyl	882.50	125.80	−18.42	1030.26	146.58	2.31	1400.97	198.53	54.31
Propyl	984.75	140.15	−18.09	1127.78	160.21	1.97	1497.14	212.02	53.78
Butyl	1087.67	154.58	−17.69	1228.09	174.28	2.01	1591.25	225.22	52.95
Amyl	1181.99	167.81	−18.49	1327.25	188.19	1.89	1690.70	239.17	52.87
Hexyl	1286.02	182.41	−17.92	1427.63	202.27	1.94	1790.0	253.10	52.77

Propionates									
Isopropyl	649.71	93.15	−23.01	773.4	110.5	−5.66	1130.4	160.58	44.42
Isobutyl	736.04	105.26	−24.93	881.88	125.72	−4.47	1221.9	173.41	43.22
Isoamyl	832.90	118.85	−25.37	985.60	140.27	−3.95	1319.5	187.10	42.88
Butyrates									
Isopropyl	742.50	106.17	−24.02	851.37	121.44	−8.75	1260.55	178.83	48.64
Isobutyl	837.13	119.44	−24.78	959.58	136.61	−7.60	1346.05	190.81	46.59
Isoamyl	931.19	132.63	−25.61	1055.05	150.01	−8.23	1444.79	204.66	46.42
Valerates									
Isopropyl	835.76	119.25	−24.97	951.96	135.55	−8.67			
Isobutyl	932.50	132.81	−25.42	1047.76	148.99	−0.25	1423.3	201.66	43.42
Isoamyl	1030.49	146.56	−25.71	1146.94	162.9	−9.37	1521.41	215.42	43.15
Hexoates									
Isopropyl	938.99	133.73	−24.51	1039.15	147.78	−10.46	1452.51	205.76	47.52
Isobutyl	1042.45	148.24	−24.[illegible]	1148.81	163.16	−0.11	1527.23	216.24	43.97
Isoamyl	1142.88	162.33	−23.97	1246.34	176.84	−9.46	1627.53	230.31	44.01
Isobutyrates									
Isopropyl	703.94	100.76	−29.43	773.9	110.57	−19.62	1100.62	156.40	26.21
Isobutyl	801.10	114.39	−29.83	878.38	125.23	−18.99	1251.03	177.50	33.28
Isoamyl	895.49	127.63	−30.61	978.28	139.24	−19.00	1354.09	191.95	33.71
Isovalerates									
Isopropyl	794.1	113.40	−30.82	825.87	117.86	−26.36	1226.63	176.28	32.06
Isobutyl	889.95	126.85	−31.39	968.14	137.82	−20.42	1359.05	195.10	36.86
Isoamyl	990.3	140.93	−31.34	1069.81	152.08	−20.19	1456.73	208.97	36.70
4-Methyl pentanoates									
Isopropyl	887.61	126.52	−31.72	970.96	138.21	−20.03	1344.3	190.58	32.34
Isobutyl	979.4	139.40	−32.87	1108.26	157.47	−14.80	1514.99	214.52	42.25
Isoamyl	1074.3	152.71	−33.59	1212.37	172.08	−14.22	1613.41	228.33	42.03
Isobutyrates									
Butyl	831.47	118.65	−25.57	930.55	132.54	−11.68	1314.59	186.40	42.18
Amyl	929.5	132.40	−25.84	1022.39	145.43	−12.81	1499.72	198.35	40.11
Hexyl	1028.47	146.28	−25.99	1122.16	159.42	−12.85	1501.33	212.61	40.34

(Continued on p. 50)

TABLE I (*continued*)

	SE-30			*OV-25*			*SILAR 10C*		
	I	*Me*	*ΔMe*	*I*	*Me*	*ΔMe*	*I*	*Me*	*ΔMe*
Isovalerates									
Propyl	826.26	117.92	−27.30	937.91	133.58	−10.64	1324.95	190.25	46.03
Butyl	922.98	131.48	−26.76	1031.0	146.63	−11.61	1413.71	202.86	44.62
Amyl	1021.23	145.26	−27.01	1132.09	160.81	−11.46			
Hexyl	1119.79	159.09	−27.21	1231.58	174.77	−11.53			
2-Methyl pentanoates									
Methyl							1262.28	179.08	48.89
Ethyl	836.9	119.41	−24.81	909.89	129.65	−14.57	1291.61	183.19	38.97
Propyl	932.38	132.80	−25.44	1004.73	142.95	−15.29	1378.27	195.35	37.11
Butyl	1029.4	146.41	−25.86	1093.32	155.38	−16.89	1473.78	208.74	36.47
Amyl	1130.71	160.62	−25.68	1195.52	169.71	−16.59	1570.92	222.37	36.07
Hexyl	1228.24	174.30	−26.03				1671.9	236.53	36.20
4-Methyl pentanoates									
Propyl	956.64	136.20	−22.04	1070.20	152.13	−6.11	1448.22	205.16	46.92
Butyl	1051.9	149.57	−22.70	1167.19	165.74	−6.53	1624.95	229.95	57.68
Amyl	1149.3	163.22	−23.07	1267.99	179.88	−6.42	1726.7	244.22	57.92
Acrylates									
Propyl				843.59	120.35	6.21	1274.9	180.85	66.71
Butyl	878	125.17	−3.00	940.76	133.98	5.81	1369.9	194.17	66.00
Amyl	978	139.20	−3.01	1047.11	148.89	6.68	1470.1	208.23	66.02
Hexyl	1068	151.82	−4.43	1146.67	162.86	6.61	1573.2	222.69	66.44
Methacrylates									
Propyl	856	122.09	−6.08	902.51	128.61	0.44	1340.24	190.01	61.84
Butyl	962	136.96	−5.24	1005.04	142.99	0.79	1439.19	203.89	61.69
Amyl	1064	151.26	−4.98	1103.61	156.82	0.58	1537.46	217.68	61.44
Hexyl	1165	164.43	−4.85	1202.88	170.74	0.46	1640.2	232.09	61.81

TABLE II

AVERAGE ΔMe VALUES FOR HOMOLOGOUS ESTERS

	SE-30	*OV-25*	*SILAR 10C*
n-Alkyl acetates	−18.61	2.73	
n-Alkyl propionates	−18.66	2.57	57.43
n-Alkyl butyrates	−18.73	2.34	56.41
n-Alkyl valerates	−18.09	1.63	53.67
n-Alkyl hexanoates	−18.12		
Isoalkyl propionates	−24.44	−4.69	43.40
Isoalkyl butyrates	−24.47	−8.19	47.22
Isoalkyl valerates	−25.40	−9.09	43.28
Isoalkyl hexanoates	−24.17		
Isoalkyl isobutyrates	−29.92	−19.20	31.07
Isoalkyl isovalerates	−31.17	−22.32	32.93
4-Methyl pentanoates	−32.76	−16.34	42.14
n-Alkyl isobutyrates	−25.80	−12.44	40.88
n-Alkyl isovalerates	−26.82	−11.31	45.33
n-Alkyl 2-methyl pentanoates	−25.56	−15.84	36.93
n-Alkyl 4-methyl pentanoates	−22.78	−6.44	57.80
n.Alkyl acrylates	−3.48	6.33	66.29
n-Alkyl methacrylates	−5.28	0.55	61.69

esters, *i.e.* acrylates and methacrylates where, as expected, on a non-polar phase unsaturation leads to a reduction of both retention and ΔMe values. With increased polarity of the phase the effect of unsaturation becomes apparent, and substantial enhancement of both retention and ΔMe values occurs.

CONCLUSIONS

While the actual retention trends measured follow those of earlier reports the conclusions as outlined are largely not apparent from a study of the retention data expressed as molecular retention indices. It would seem that large or obvious reten-

TABLE III

MOLECULAR RETENTION INDICES AND DIFFERENCES OF BUTANOIC ESTERS

	Stationary phase		
	SE-30	*OV-25*	*SILAR 10C*
A *n*-Alkyl butanoates	−18.73	2.34	56.41
B Isoalkyl butanoates	−24.47	−8.19	47.22
C *n*-Alkyl isobutanoates	−25.80	−12.44	40.88
D Isoalkyl isobutanoates	−29.92	−19.20	31.07
Molecular retention index differences			
(A) − (B)	−5.74	10.53	9.19
(A) − (C)	−6.97	12.54	15.43
(A) − (D)	−11.19	21.54	25.34

tion variations are generally apparent, but that ΔMe values are less satisfactory than retention index values for use in the tentative identification of closely related or isomeric compounds.

The use of ΔMe values for assembly into a correlation chart for identification, as suggested by Evans and Smith[2], for use in tentative identification is unlikely, particularly for intra-laboratory studies, as the ΔMe values are particularly susceptible to stationary phase loading as demonstrated recently by Carmi and Evans[5]. This dependence might not be expected as both retention indices and molecular retention indices are dependent on the behaviour of *n*-alkanes, rather than an absolute value of retention.

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