Journal of Chromatography, 348 (1985) 141–149
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 026

CHROMATOGRAPHY OF MONOMERS

IV. GAS–LIQUID CHROMATOGRAPHIC STUDIES OF C_1–C_6 *n*-ALKYL AND C_3–C_6 ISOALKYL ACRYLATES AND THEIR HYDROGEN HALIDE AND HALOGEN ADDITION DERIVATIVES

ALEŠ HORNA*, JAN TÁBORSKÝ and JAROSLAV CHURÁČEK*
Department of Analytical Chemistry, University of Chemical Technology, 532 10 Pardubice (Czechoslovakia)
and
OLDŘICH DUFKA
Research Institute for Synthetic Resins and Lacquers, 532 07 Pardubice (Czechoslovakia)
(Received June 26th, 1985)

SUMMARY

The retention behaviour of C_1–C_6 *n*-alkyl and C_3–C_6 isoalkyl acrylates and their mono- and dihalogen addition derivatives was examined isothermally at 100°C on squalane, OV-101, SE-54, UCON LB-550-X and SP-1000 capillary columns. The retention increments, showing the effect of derivation involving hydrogen halide and halogen addition in the acyl chain and the effect of methylene substitution in the alkyl chain, are presented.

INTRODUCTION

Acrylates are a major group of industrially produced monomers with unique properties in polymer synthesis but toxic to humans. The interest in halogenated carboxylic derivatives has increased owing to their important biochemical properties.

The homologous series of C_1–C_6 *n*-alkyl and C_3–C_5 isoalkyl acrylates have been extensively studied by Haken and co-workers[1–3] on packed columns with several polysiloxane stationary phases, and general relationships between the chemical structure and retention behaviour were presented. Recently, capillary column chromatography of C_1–C_{18} *n*-alkyl and C_3–C_6 isoalkyl acrylates and methacrylates was carried out to elucidate the effects of temperature and the structure of the alcohol chain on the retention increments on OV-101, SE-54 and SP-1000 stationary phases[4].

The gas chromatographic retention behaviour of C_1–C_{18} *n*-alkyl propanoates, 2-chloropropanoates and 3-chloropropanoates was examined on SE-30 and OV-351 capillary silica columns using temperature-programmed separation[5] and isothermally

* Present address: VÚSPL, S.K. Neumanna 1316, 532 07 Pardubice, Czechoslovakia.

0021-9673/85/$03.30

to elucidate the effects of methylene substitution in the alkyl chain an of monochloro substitution in the acyl chain[6]. The retention behaviour of the homologous series of 2-chloro-, 3-chloro-, 2-bromo- and 2,3-dichloropropanoates was studied by Komárek *et al.*[7] on OV-101 glass capillary column at 80 and 200°C, showing the effect of the halogen substituent in the acid moiety of the aliphatic esters.

The purpose of this work was to compare the retention behaviour of the homologous series of C_1–C_6 *n*-alkyl and C_3–C_6 isoalkyl acrylates with that of corresponding chlorinated and/or brominated propanoates on stationary phases of different polarity to show the incremental effects of adding hydrogen halide and/or halogen molecules, and to acquire a better understanding of the effects of the halogen substituent in the acyl group on the retention behaviour of homologous esters.

EXPERIMENTAL

Samples

The acrylates were commercially available monomers or were prepared by sulphuric acid-catalysed esterification of acrylic acid and commercial aliphatic alcohols.

2-Chloro-, 3-chloro- and 2-bromopropanoates were prepared as described earlier[7]. 2,3-Dibromopropanoates were prepared from the corresponding acrylates by addition of bromine as a chloroform solution. 3-Bromopropanoates were prepared from acrylates dissolved in hexane that had been treated with hydrogen bromide under ultraviolet irradiation at laboratory temperature. 2,3-Dichloropropanoates were prepared by addition of chlorine to acrylates as a carbon tetrachloride solution that had been treated with chlorine in the presence of $SbCl_5$ under ultraviolet irradiation. 3-Bromo-2-chloropropanoates were prepared as described[8].

The purities of all the samples were verified by gas chromatography–mass spectrometry and both electron impact and chemical ionization spectra were recorded.

Gas–liquid chromatography

A Varian Model 3700 gas chromatograph with a flame ionization detector was used for the analysis under the following operating conditions: injector and detector temperatures, 200 and 250°C, respectively, for the halogenated esters; nitrogen carrier gas flow-rate, 20–60 cm/s; splitting ratio, *ca.* 1:100; and chart speed 10 mm/min.

The glass capillary columns used were squalane (42 m × 0.30 mm I.D.), OV-101 (19 m × 0.28 mm I.D.) and UCON LB-550-X (26 m × 0.29 mm I.D.), all three laboratory made; SE-54 (30 m × 0.24 mm I.D.), supplied by Supelco (Bellefonte, PA, U.S.A.); and SP-1000 (46 m × 0.23 mm I.D.), supplied by SGE (North Melbourne, Australia). The columns were operated isothermally at 100°C.

A mixture of the esters and the alkane standards was injected. The retention times were measured from the time of sample injection by an Autolab System IV reporting integrator (Spectra-Physics, Mountain View, CA, U.S.A.). The retention indices were calculated off-line using a TI-57 calculator, the dead time being first determined by the retention of methane. The presented retention index values were calculated from 5–10 measurements with standard deviations varying from 0.1 to 0.6 retention index units (i.u.).

RESULTS AND DISCUSSION

The retention indices of C_1–C_6 *n*-alkyl and C_3–C_6 isoalkyl esters of acrylic, propionic, 2-chloro-, 3-chloro-, 2-bromo-, 3-bromo-, 2,3-dichloro-, 2,3-dibromo- and 3-bromo-2-chloropropionic acids on squalane, OV-101, SE-54, UCON LB-550-X and SP-1000 stationary phases at 100°C are summarized in Table I. Additionally, by comparing the retentions of alkyl propionates and/or halogenated propionates with those of corresponding acrylates, the retention index increments $\Delta I_{(X)}$ due to hydrogen, hydrogen chloride, hydrogen bromide, chlorine, bromine and bromine chloride additions were calculated.

It can be seen from the incremental data (Table I) that the alkyl chain length of both the *n*-alkyl and isoalkyl esters, except the methyl esters, only slightly affected the $\Delta I_{(X)}$, values which seem to fluctuate slightly or converge towards a constant value. Hence, having excluded the incremental values for methyl esters, the average $\Delta I_{(X)}$ values were calculated commonly for both the *n*-alkyl and isoalkyl ester series.

By plotting the average incremental values $\Delta I_{(X)}$ due to the addition of hydrogen, hydrogen chloride, hydrogen bromide, chlorine, bromine and bromine chloride to alkyl acrylates *versus* the polarity of squalane, OV-101, SE-54, UCON LB-550-X and SP-1000 stationary phase, expressed by the McReynolds constants 0, 229, 337, 996 and 2399 respectively, the plots in Fig. 1 were constructed. Table II shows the slopes, intercepts on the ordinate and correlation coefficients of the lines describing the incremental effects of hydrogen halides and halogens added to acrylates as a function of stationary phase polarity.

From both Table I and Fig. 1, it can be seen that the conversion of alkyl acrylates into propionates resulted in slightly increased retentions of approximately 10–17 i.u. on the non-polar stationary phases squalane, OV-101 and SE-54. However, on medium polarity UCON LB-550-X the effect of conversion of acrylates into propionates on retention behaviour is minimized owing to the very close retentions of the corresponding alkyl esters of acrylic and propionic acids, while the change in the elution sequence of the acrylate and propionate ester series is apparent. On highly polar SP-1000 stationary phase the separation between acrylates and propionates is maximized, with a pronounced elution order propionate < acrylate.

The addition of both hydrogen halides and halogens leads to a considerable elevation of the boiling points of alkyl acrylates. Hence a general enhancement of the retention of the series of halogenated esters was produced on all stationary phases used, as expected.

Considering hydrogen chloride and hydrogen bromide addition, 2-halo-3-hydrogen- and 3-halo-2-hydrogen derivatives are possible, so the incremental effects of adding a molecule will be strongly dependent on the resulting position of the halogen in the acyl chain of the ester. Thus, with 2-chloro-3-hydrogen addition (Fig. 1), the incremental effects of hydrogen chloride are 139, 155 and 161 i.u. on squalane, OV-101 and SE-54, respectively, and 178 and 219 i.u. on UCON LB-550-X and SP-1000, respectively. On the other hand, with 3-chloro-2-hydrogen addition, the incremental values increase substantially, to approximately 205, 223, 232, 277 and 371 i.u. on squalane, OV-101, SE-54, UCON LB-550-X and SP-1000, respectively. Similarly, on the non-polar phases squalane, OV-101 and SE-54, 2-bromo-3-hydrogen derivatives showed retention enhancements of approximately 214, 227 and 233

TABLE I

RETENTION INDICES OF C_1–C_6 *n*-ALKYL AND C_3–C_6 ISOALKYL ACRYLATES AND THE CORRESPONDING PROPIONATES AND HALOPROPIONATES WITH RETENTION INDEX INCREMENT $\Delta I_{(X)}$ DUE TO ADDITION OF HYDROGEN, HYDROGEN HALIDE AND HALOGEN MOLECULES TO ACRYLATES ON SQUALANE, OV-101, SE-54, UCON LB-550-X AND SP-1000 PHASES AT 100°C

Esters	*Squalane*		*OV-101*		*SE-54*		*UCON-LB-550-X*		*SP-1000*	
	I	$\Delta I_{(X)}$	I	$\Delta I_{(X)}$	I	$\Delta I_{(X)}$	I	$\Delta I_{(X)}$	I	$\Delta I_{(X)}$
Acrylates:										
Methyl	596.5	–	596.7	–	603.9	–	719.5	–	940.0	–
Ethyl	654.0	–	675.7	–	700.0	–	793.2	–	992.1	–
Propyl	733.2	–	775.0	–	797.2	–	884.6	–	1078.3	–
Butyl	835.2	–	875.2	–	895.1	–	983.3	–	1175.2	–
Pentyl	934.8	–	974.8	–	994.9	–	1082.7	–	1272.9	–
Hexyl	1033.6	–	1075.2	–	1095.3	–	1181.6	–	1370.3	–
Isopropyl	684.4	–	722.5	–	739.3	–	820.9	–	995.9	–
Isobutyl	794.5	–	835.5	–	854.7	–	936.0	–	1113.8	–
Isopentyl	899.8	–	939.0	–	958.8	–	1041.7	–	1223.2	–
Isohexyl	992.7	–	1035.4	–	1054.5	–	1132.8	–	1311.4	–
Propionates, X = H_2:										
Methyl	611.0	14.5	615.0	18.3	628.7	24.8	715.3	−4.2	904.6	−35.4
Ethyl	669.0	15.0	694.9	19.2	708.3	8.3	786.2	−7.0	954.4	−37.7
Propyl	748.1	14.9	794.1	19.1	807.2	10.0	880.1	−4.5	1041.7	−36.6
Butyl	841.9	6.7	892.2	17.0	905.5	10.4	979.0	−4.3	1138.3	−36.9
Pentyl	944.3	9.5	989.5	14.7	1005.4	10.5	1078.2	−4.5	1236.1	−36.8
Hexyl	1042.3	8.7	1086.5	11.3	1105.1	9.8	1176.9	−4.7	1332.6	−37.7
Isopropyl	688.1	3.7	739.4	16.9	750.2	10.9	814.0	−6.9	956.0	−39.9
Isobutyl	807.5	13.0	854.3	18.8	866.4	11.7	932.8	−3.2	1079.2	−34.6
Isopentyl	910.8	11.0	954.6	15.6	968.2	9.4	1037.2	−4.5	1186.4	−36.8
2-Chloropropionates, X = 2-Cl-3-H:										
Methyl	711.3	114.8	766.1	169.1	793.2	189.3	922.2	202.7	1197.8	257.8
Ethyl	789.3	135.3	847.8	172.1	873.7	173.7	978.8	185.6	1226.5	234.4
Propyl	878.2	145.0	932.1	157.1	958.5	161.3	1067.7	183.1	1303.9	225.6
Butyl	975.3	140.1	1029.0	153.8	1055.2	160.1	1161.9	178.6	1390.6	215.4
Pentyl	1072.7	137.9	1126.4	151.6	1152.9	158.0	1257.5	174.8	1483.5	210.6
Hexyl	1172.2	138.6	1225.1	149.9	1252.1	156.8	1356.2	174.6	1577.4	207.1
Isopropyl	820.5	136.1	875.6	153.1	899.0	159.7	997.1	176.2	1216.5	220.6
Isobutyl	937.2	142.7	989.1	153.6	1014.2	159.5	1114.0	178.0	1335.9	222.1
Isopentyl	1039.5	139.7	1090.0	151.0	1116.9	158.1	1218.1	176.4	1440.6	217.4
3-Chloropropionates, X = 3-Cl-2-H:										
Methyl	770.0	173.5	823.0	226.3	855.2	251.3	1007.7	288.2	1331.7	391.7
Ethyl	846.7	192.7	901.4	225.7	930.9	230.9	1071.5	278.3	1371.6	379.5
Propyl	944.4	211.2	1000.1	225.1	1029.6	232.4	1164.0	279.4	1454.2	375.9
Butyl	1042.7	207.5	1098.3	223.1	1127.8	232.7	1260.3	277.0	1544.5	369.3
Pentyl	1140.7	205.9	1195.8	221.0	1226.6	231.7	1358.3	275.6	1638.7	365.8
Hexyl	1239.3	205.7	1294.3	219.1	1326.1	230.8	1456.7	275.1	1734.7	364.4
Isopropyl	888.2	203.8	945.0	222.5	971.5	232.2	1095.9	275.0	1366.2	370.3
Isobutyl	1004.7	210.2	1059.6	224.1	1088.0	233.3	1213.0	277.0	1488.7	374.9
Isopentyl	1105.6	205.8	1160.1	221.1	1189.6	230.8	1316.8	275.1	1591.6	368.4
2,3-Dichloropropionates, X = Cl_2:										
Methyl	869.1	272.6	923.6	326.9	960.1	356.2	1130.8	411.3	1490.7	550.7
Ethyl	940.8	286.8	994.5	318.8	1028.0	328.0	1182.5	389.3	1512.1	520.0
Propyl	1036.1	302.9	1088.7	313.7	1122.6	325.4	1269.6	385.0	1585.4	507.1

TABLE I *(continued)*

Esters	*Squalane*		*OV-101*		*SE-54*		*UCON-LB-550-X*		*SP-1000*	
	I	$\Delta I_{(x)}$	*I*	$\Delta I_{(x)}$	*I*	$\Delta I_{(x)}$	*I*	$\Delta I_{(x)}$	*I*	$\Delta I_{(x)}$
Butyl	1131.5	296.3	1183.7	308.5	1218.4	323.3	1361.4	378.1	1669.0	493.8
Pentyl	1227.5	292.7	1279.8	305.0	1314.4	319.5	1457.3	374.6	1761.4	488.5
Hexyl	–	–	1378.1	302.9	1412.7	317.4	1554.8	373.2	–	–
Isopropyl	977.2	292.8	1032.0	309.5	1055.4	316.1	1198.6	377.7	1494.1	498.2
Isobutyl	1095.9	301.4	1145.3	309.8	1176.4	321.7	1315.5	379.5	1614.8	501.0
Isopentyl	1193.0	293.2	1243.0	304.0	1275.3	316.5	1414.6	372.9	1713.7	490.5
Isohexyl	–	–	–	–	1365.9	311.4	1499.0	366.2	–	–
2-Bromopropionates, X = 2-Br-3-H:										
Methyl	788.3	191.8	837.8	241.1	868.3	264.4	1000.0	280.5	1299.7	359.7
Ethyl	858.1	204.1	909.1	233.4	937.4	237.4	1056.1	262.9	1326.9	334.8
Propyl	953.5	220.3	1004.6	229.6	1032.6	235.4	1145.8	261.2	1405.3	327.0
Butyl	1050.4	215.2	1101.7	226.5	1129.2	234.1	1239.7	256.4	1493.5	318.3
Pentyl	1146.6	211.8	1198.5	223.7	1226.0	231.1	1335.7	253.0	1583.5	310.6
Hexyl	1245.8	212.2	1298.1	222.9	1325.7	230.4	1435.2	253.6	1681.1	310.8
Isopropyl	896.4	212.0	947.4	224.9	972.2	232.9	1075.3	254.4	1316.4	320.5
Isobutyl	1016.3	221.8	1062.8	227.3	1088.5	233.8	1192.6	256.6	1438.3	324.5
Isopentyl	1115.1	215.3	1162.9	223.9	1188.7	229.9	1292.2	250.5	1539.6	316.4
3-Bromopropionates, X = 3-Br-2-H:										
Methyl	852.4	255.9	901.7	305.0	937.1	333.2	1099.7	380.2	1435.2	495.2
Ethyl	928.3	274.3	978.5	302.8	1012.7	312.7	1160.0	366.8	1474.2	482.1
Propyl	1026.9	293.7	1076.9	301.9	1110.9	313.7	1251.3	366.7	1555.8	477.5
Butyl	1126.0	290.8	1175.3	300.1	1209.2	314.1	1346.9	363.6	1645.5	470.3
Pentyl	1223,7	288.9	1273.0	298.2	1307.3	312.4	1444.9	362.2	1739.7	466.8
Hexyl	1322.3	288.7	1373.2	298.0	1406.9	311.6	1545.2	363.6	–	–
Isopropyl	970.0	285.6	1021.1	298.6	1051.8	312.5	1183.6	362.7	1465.9	470.0
Isobutyl	1087.4	292.9	1135.5	300.0	1168.0	313.3	1300.0	364.0	1586.0	472.2
Isopentyl	1188.9	289.1	1235.9	296.9	1269.1	310.3	1396.7	355.0	1687.1	463.9
Isohexyl	1281.6	288.9	1330.4	295.0	1363.4	308.9	1493.0	360.2	1776.0	464.6
2,3-Dibromopropionates, X = Br_2:										
Methyl	1022.5	426.0	1070.1	473.4	1110.8	506.9	1288.0	568.5	–	–
Ethyl	1094.9	440.9	1139.7	464.0	1179.8	479.8	1341.9	548.7	–	–
Propyl	1171.4	438.2	1233.5	458.5	1272.3	475.1	1426.7	542.1	–	–
Butyl	1268.4	433.2	1327.1	451.9	1366.2	471.1	1516.0	532.7	–	–
Pentyl	–	–	1423.2	448.4	1461.3	466.4	1609.8	527.1	–	–
Hexyl	–	–	1521.0	445.8	1559.9	464.6	1707.5	525.9	–	–
Isopropyl	1133.3	448.9	1174.3	451.8	1210.4	471.1	1355.1	534.2	–	–
Isobutyl	1248.5	454.0	1288.0	452.5	1326.1	471.4	1469.5	533.5	–	–
Isopentyl	–	–	1383.8	444.8	1422.8	464.0	1565.2	523.5	–	–
Isohexyl	–	–	1474.1	438.-7	1512.4	457.9	1649.2	516.4	–	–
3-Bromo-2-chloropropionates, X = 3-Br-2-Cl:										
Methyl	–	–	1024.5	427.8	1031.6	427.7	1203.1	483.6	–	–
Ethyl	–	–	1070.1	394.4	1099.6	399.6	1254.4	461.2	–	–
Propyl	–	–	1158.5	383.5	1194.4	397.2	1342.3	457.7	–	–
Butyl	–	–	1252.9	377.7	1288.4	393.3	1433.3	450.0	–	–
Pentyl	–	–	1348.9	374.1	1383.6	388.7	1527.8	445.1	–	–
Hexyl	–	–	–	–	1481.1	385.8	1624.8	443.2	–	–
Isopropyl	–	–	1100.7	378.2	1133.4	394.1	1270.0	449.1	–	–
Isobutyl	–	–	1214.2	378.7	1249.1	394.4	1387.6	451.6	–	–
Isopentyl	–	–	1311.1	372.1	1345.1	386.3	1484.9	443.2	–	–
Isohexyl	–	–	1400.5	365.1	1435.3	380.8	1568.0	435.2	–	–

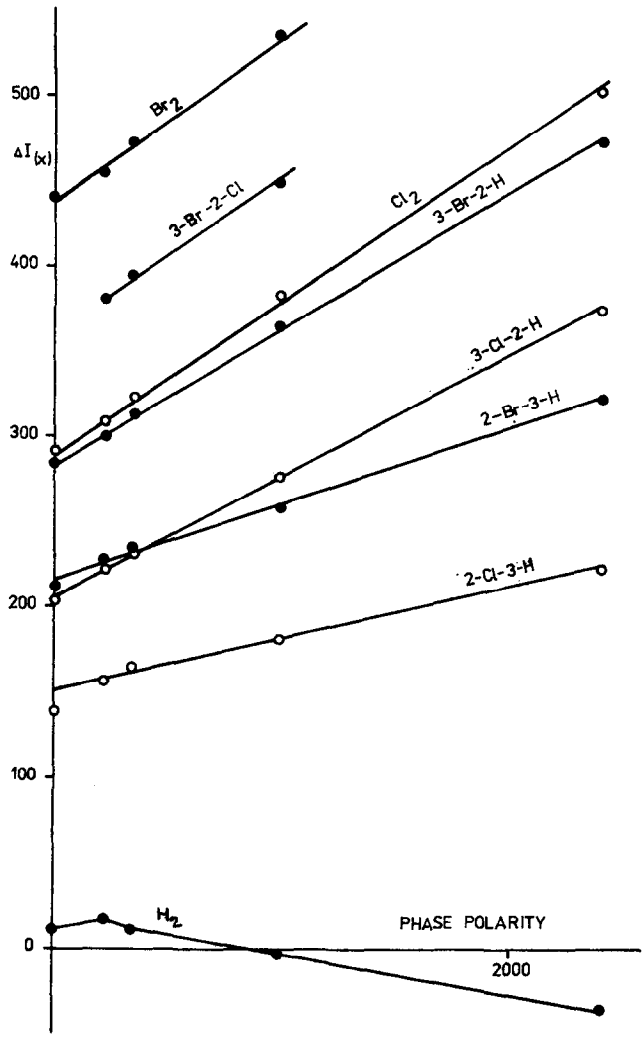

Fig. 1. Effect of the polarity of the stationary phase on the incremental values $\Delta I_{(X)}$ due to the addition of bromine (X = Br_2), bromine chloride (X = 3-Br-2-Cl), chlorine (X = Cl_2), hydrogen chloride (X = 3-Cl-2-H, 2-Cl-3-H), hydrogen bromide (X = 3-Br-2-H, 2-Br-3-H) and hydrogen (X = H_2) to C_1–C_6 alkyl acrylates.

i.u., respectively, compared with corresponding acrylates, whereas the 3-bromo-2-hydrogen derivatives showed increased retentions of 288, 299 and 312 i.u., respectively. With the UCON LB-550-X and SP-1000 stationary phases, the retention increments due to 2-bromo-3-hydrogen addition to acrylates were 256 and 320 i.u., respectively and those due to 3-bromo-2-hydrogen additions were 363 and 471 i.u., respectively.

From the incremental effects of adding chlorine, bromine and bromine chloride molecules, it is apparent that the last is close to the mean value calculated from the

TABLE II

LINEAR REGRESSION ANALYSES OF PLOTS OF INCREMENTAL $\Delta I_{(X)}$ VALUES *VERSUS* STATIONARY PHASE POLARITY

Halogenation	*Intercept on ordinate*	*Slope*	*Correlation coefficient*
2-Cl-3-H	146.0	0.031	0.9903
3-Cl-2-H	207.2	0.069	0.9998
Cl_2	291.7	0.087	0.9996
2-Br-3-H	215.7	0.043	0.9986
3-Br-2-H	285.4	0.077	0.9995
Br_2	437.2	0.093	0.9899
3-Br-2-Cl	358.9	0.090	0.9990

incremental values due to bromine and chlorine addition to acrylates (Fig. 1, Table I). In particular, the average incremental values due to the addition of halogen molecules on squalane, OV-101, SE-54, UCON LB-550-X and SP-1000 were calculated for the chlorine molecule to be 295, 309, 320, 377 and 500 i.u., respectively, and for the bromine molecule 443, 451, 469 and 532 i.u., respectively (not measured for SP-1000); with bromine chloride addition the calculated incremental values on OV-101, SE-54 and UCON LB-550-X were 378, 391 and 449 i.u., respectively.

The homologous series are particularly useful for the investigation of the retention mechanism, because they allow a differentiation between the non-specific contribution to retention caused by a regular increase in the length of the aliphatic chain and the specific contribution caused by the interactions of the acid part of the ester with the stationary phase. Hence, to acquire a better understanding of the retention behaviour of the studied aliphatic esters, linear regression analysis of plots of retention index *versus* number of carbon atoms in the alcohol chain was performed.

Table III lists the constants of the calculated linear plots ($I = a_0 + a_1 n_C$) together with the correlation coefficients indicating how closely the line approximates the collection of data points. Because of deviations exhibited by methyl and isopropyl esters[4], they were not included in the linear regression analyses. The slopes of the linear plots, a_1, represents the average value of the retention index increment per methylene group, $\Delta I_{(CH_2)}$, of the particular homologous series.

Overall, the effect of a halogen atom in the acyl chain of the ester has little influence on the alcohol chain length contributions. However, from the data in Tables I and III, it seems that with increase in both the number and weight of the halogen atoms in the acyl chain the incremental values per methylene group in the alcohol chain of the ester tends to be reduced (see a_1 values). This trend is more pronounced with the highly polar SP-1000 stationary phase, where the average values of the retention increment per methylene group in the alcohol chain of the halogenated ester series were reduced by 90 i.u.

On non-polar stationary phases, as expected, with aliphatic esters the boiling point has the greater effect on the order of elution. Considering the retention behaviour of the homologous series of esters, it can be seen (Table I) that on squalane, OV-101 and SE-54 acrylates have the lowest retention. Hence, the interesting feature

TABLE III

REGRESSION OF RETENTION PLOTS, $I = a_0 + a_1 n_c$, FOR *n*-ALKYL AND ISOALKYL ESTER SERIES AT 100°C

I = Retention index; n_c = number of carbon atoms in alcohol chain of esters; R = correlation coefficient.

Compounds	*Squalane*			*OV-101*			*SE-54*			*UCON LB-550-X*			*SP-1000*		
	a_0	a_1	R	a_0	a_1	R	a_0	a_1	R	a_0	a_1	R	a_0	a_1	R
*n-Alkyl esters**															
Acrylates	453.8	96.1	0.9991	475.7	99.9	0.999998	501.2	98.8	0.99997	595.1	97.5	0.9999	797.4	95.1	0.9997
Propionates	472.0	94.3	0.9989	500.0	97.9	0.99999	509.6	99.2	0.999995	588.3	98.0	0.99995	760.3	95.1	0.9998
2-Chloropropionates	593.4	96.0	0.9998	652.5	94.9	0.9996	678.0	95.1	0.9996	786.6	94.5	0.9998	1043.8	88.1	0.9992
3-Chloropropionates	650.2	98.2	0.999999	705.4	98.2	0.999998	733.2	98.7	0.999997	876.3	96.5	0.99992	1184.5	91.1	0.9996
2,3-Dichloropropionates	749.6	95.6	0.999999	801.6	95.8	0.99997	834.7	96.1	0.99998	992.2	93.2	0.9997	1341.0	83.2	0.9987
2-Bromopropionates	663.5	96.9	0.99998	713.6	97.2	0.99997	742.2	97.0	0.99997	863.3	94.8	0.9998	1143.4	88.7	0.9992
3-Bromopropionates	731.5	98.5	0.999998	781.2	98.6	0.999993	815.5	98.5	0.999996	964.1	96.4	0.9998	1293.6	88.6	0.9995
2,3-Dibromopropionates	918.0	86.8	0.9977	948.0	95.2	0.99995	988.2	94.9	0.99993	1154.7	91.4	0.9996	–	–	–
3-Bromo-2-chloropropionates	–	–	–	881.8	93.1	0.9998	908.5	95.2	0.99998	1066.0	92.6	0.9998	–	–	–
*Isoalkyl esters***															
Acrylates	400.2	99.1	0.9993	436.9	100.0	0.9998	456.5	99.9	0.9997	544.8	98.4	0.9991	722.1	98.8	0.9981
2,3-Dichloropropionates	–	–	–	–	–	–	798.8	94.8	0.9997	950.8	91.8	0.9989	–	–	–
3-Bromopropionates	700.5	97.1	0.9997	746.7	97.5	0.9998	778.3	97.7	0.9998	914.1	96.5	0.9999993	1208.0	95.0	0.9993
2,3-Dibromopropionates	–	–	–	916.7	93.1	0.9999	954.7	93.2	0.9998	1112.1	89.9	0.9993	–	–	–
3-Bromo-2-chloropropionates	–	–	–	842.9	93.2	0.9997	877.7	93.1	0.9998	1029.2	90.2	0.9990	–	–	–

* Methyl esters were not included.

** Isopropyl esters were not included.

of acrylates is their lower retention than those of the corresponding saturated propionates, although the boiling points of the two ester series are almost identical.

On squalane, OV-101 and SE-54 the sequence monochloropropionate < monobromopropionate is followed by dihalogenated esters; the highest retention occurs with 2,3-dibromopropionates, followed by 3-bromo-2-chloropropionates and 2,3-dichloropropionates. Further, 2-bromopropionates possess overall higher retentions than 3-chloropropionates on low-polarity phases; however, their separation is reduced with increase in the polarity of the stationary phase. Hence on SE-54 the retentions of 2-bromopropionates and the corresponding 3-chloropropionates are almost identical (Table I, Fig. 1). The use of a more polar stationary phase than SE-54 resulted in renewal of the separation, but the retention order was reversed. Thus on medium polarity UCON LB-550-X and on highly polar SP-1000, 2-bromopropionates eluted before the corresponding 3-chloropropionates. This may indicate that on polar stationary phases the position of the halogen substituent in the acyl chain of the esters is a more important factor than the different atomic weights of chlorine and bromine.

REFERENCES

1 R. W. Germaine and J. K. Haken, *J. Chromatogr.*, 43 (1969) 43.
2 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 111 (1975) 171.
3 J. K. Haken and D. Srisukh, *J. Chromatogr.*, 219 (1981) 45.
4 A. Horna, J. Táborský, O. Dufka, P. Matoušek and J. Churáček, *J. Chromatogr.*, 325 (1985) 367.
5 I. O. O. Korhonen, *J. Chromatogr.*, 268 (1983) 229.
6 J. K. Haken and I. O. O. Korhonen, *J. Chromatogr.*, 319 (1985) 131.
7 K. Komárek, L. Hornová, A. Horna and J. Churáček, *J. Chromatogr.*, 262 (1983) 316.
8 V. L. Heasley, D. W. Spaite, D. F. Shellhamer and G. E. Heasley, *J. Org. Chem.*, 44 (1979) 2608.