Journal of Chromatography, 325 (1985) 367–378
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 610

CHROMATOGRAPHY OF MONOMERS

II*. GLASS CAPILLARY GAS CHROMATOGRAPHY OF C_1–C_{18} ALKYL ESTERS OF ACRYLIC AND METHACRYLIC ACIDS

ALEŠ HORNA* and JAN TÁBORSKÝ
Department of Analytical Chemistry, University of Chemical Technology, 532 10 Pardubice (Czechoslovakia)
OLDŘICH DUFKA and PAVEL MATOUŠEK
Research Institute for Synthetic Resins and Laquers, 532 07 Pardubice (Czechoslovakia)
and
JAROSLAV CHURÁČEK
Department of Analytical Chemistry, University of Chemical Technology, 532 10 Pardubice (Czechoslovakia)
(Received January 25th, 1985)

SUMMARY

Retention indices of 38 acrylate and methacrylate monomers at different column temperatures are reported. The temperature dependences of the retention indices and the incremental effects of the methylene group were determined on non-polar (OV-101, SE-54) and a polar (SP-1000) capillary column, operated isothermally between 80 and 200°C.

INTRODUCTION

Acrylic and methacrylic acid esters are produced on a large scale for a number of technological applications. However, these compounds have associated health hazards and environmental effects. The importance of chromatography, especially gas chromatography (GC), in the analysis of acrylates and methacrylates has grown considerably since the 1970's. Thus, GC is now the most frequently used method for the analysis of such monomers.

More than 100 papers have been published on the GC of individual aliphatic alkyl esters of acrylic and methacrylic acids. However, there are few reports dealing with the GC of long-chain alkyl acrylates and methacrylates[1]. Gas chromatographic studies of homologous series of C_1–C_6 alkyl esters of acrylic and methacrylic acids on packed columns have been published only by Haken and co-workers[2,3].

The present study concerns the effects on retention behaviour of both the col-

* For Part I, see ref. 4.

0021-9673/85/$03.30

umn temperature and the number of carbon atoms in the alkyl chain for C_1–C_{18} alkyl esters of acrylic and methacrylic acids on non-polar (OV-101, SE-54) and polar (SP-1000) capillary columns at temperatures between 80 and 200°C.

EXPERIMENTAL

The esters, either prepared in the laboratory or of commercial origin, were characterized as previously reported[4].GC analyses were carried out on a Varian Model 3700 instrument equipped with a flame ionization detector. The injector and detector temperatures were 200 and 250°C, respectively, for the higher alkyl esters. The glass capillary columns used were a laboratory-made OV-101 (19 m × 0.28 mm I.D.), 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). Nitrogen was used as carrier gas with a splitting ratio of *ca.* 1:100. The column temperatures used were 80 and 120°C with both injector and flame ionization detector operated at 200°C, and 170 and 200°C with injector and detector temperatures of 250°C, respectively, for analysis of higher alkyl esters.

Retention times were measured from the time of sample injection by a reporting integrator Autolab System IV (Spectra-Physics). The retention indices were calculated off-line using a TI-58C calculator, the dead time being first determined using the retention of methane. The average values of the retention indices presented were calculated from five to ten measurements.

RESULTS AND DISCUSSION

The retention indices of all 38 C_1–C_{18} alkyl esters of acrylic and methacrylic acids examined are summarized in Tables I–III. The retention indices were determined on non-polar OV-101 and SE-54 phases (Tables I and II) and on polar SP-1000 (Table III) at the following column temperatures: 80 and 120°C for C_1–C_6 *n*-alkyl and C_3–C_6 isoalkyl esters; 170 and 200°C for C_6–C_{10} *n*-alkyl and 2-ethylhexyl esters and at 200°C for C_{12}, C_{14}, C_{16} and C_{18} *n*-alkyl esters.

In addition to the retention indices (I) of the studied monomers, standard deviations are shown and the increments per methylene group, $\Delta I(CH_2)$, and temperature dependence of the retention indices expressed by $10(\Delta I/\Delta T)$ were calculated.

Generally, considering the data determined on all phases used, it can be stated that the retention indices of the studied acrylates and methacrylates are temperature dependent. However, it is evident that the magnitude of the shifts, due to a change in column temperature, strongly varies both with the individual ester and the polarity of the stationary phase.

On non-polar OV-101 (Table I) within the temperature range considered, the retention indices of C_1–C_6 alkyl esters of acrylic and methacrylic acids slightly decrease with increasing temperature. However, in the case of higher (C_6–C_{10}) alkyl acrylates and methacrylates, the temperature dependence of the retention indices can be considered to be insignificant within the precision of the measurements.

On SE-54 (Table II) the retention indices of C_1–C_4 *n*-alkyl acrylates increase strongly with increasing column temperature, although the retention indices of the other lower esters, with the exceptions of isohexyl acrylate and methacrylate, slightly decrease. The retention indices of higher (C_6–C_{10}) alkyl esters of acrylic acid seem to be more sensitive to temperature on SE-54 than those of the corresponding methacrylates.

On polar SP-1000 (Table III) the retention indices of all acrylates and methacrylates studied increase with increasing column temperature. The shifts in the retention indices of acrylates and methacrylates are more pronounced than those on the non-polar phases OV-101 and SE-54.

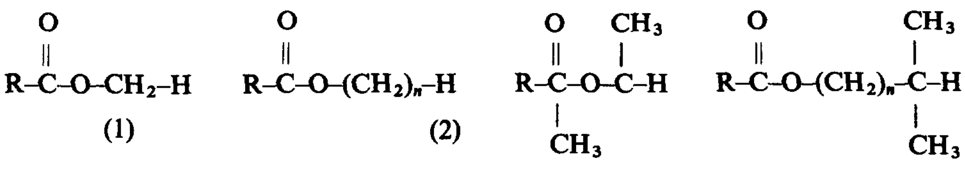
Considering the retention index contribution per methylene group (Tables I–III) in the alkyl chain of the esters, the correlation between retention and structure was examined. With higher (C_6–C_{18}) alkyl esters of acrylic and methacrylic acids the $\Delta I(CH_2)$ values, calculated as the difference between the retention indices of two successive members of the homologous series (Fig. 1), vary only slightly from the value of 100 on the non-polar phases OV-101 and SE-54 as well as on the polar SP-1000. These values are also comparable to the values of the slope of linear plots (Table IV) obtained by linear regression analysis of the dependence of the retention index on the number of carbon atoms in the alkyl chain.

The above patterns in retention behaviour are in agreement with the statement that "in any homologous series, the retention index of the higher members increases by 100 index units per methylene group introduced"[5]. However, considering the $\Delta I(CH_2)$ values for the short chain alkyl esters of acrylic and methacrylic acids (Tables I–III), the first members of the homologous series of both *n*-alkyl and isoalkyl esters exhibit considerably different values to the other higher members.

The increments per methylene group calculated as the difference between the retention indices of the ethyl and methyl esters do not exceed 80 retention index units. On the other hand, when calculated as the difference in retention indices between the isobutyl and isopropyl esters the $\Delta I(CH_2)$ values vary from 111.1 on OV-101 to 130.7 retention index units on polar SP-1000.

Table IV lists the equations $I = m + pC$ determined by linear regression analysis of plots of retention index *vs.* the number of carbon atoms in the alkyl chain, C, for the esters studied. The correlation coefficients of the individual data points in relation to the line fitted to these points are also shown. The positive deviation of the methyl esters and the negative deviation of the isopropyl esters from the plot for higher members of the homologous series is apparent (Fig. 2) on the non-polar phases as well as on the polar one. Similar behaviour occurs with homologous series of aliphatic esters of halogenated and/or unhalogenated acids[6,7]. It should be explained in terms of the electronic interactions and the steric hindrance[8]. However, trivial interpretations of the deviations of the methyl and isopropyl esters can be suggested by considering the number of C–H linkages of the α-carbon atom in the alkyl chain of the aliphatic esters.

The methyl (1), ethyl and higher *n*-alkyl (2), isopropyl (3), isobutyl and higher isoalkyl (4) esters are conveniently represented as



(1) (2) (3) (4)

TABLE I

RETENTION INDICES, THEIR STANDARD DEVIATIONS, RETENTION INCREMENTS PER METHYLENE GROUP AND TEMPERATURE DEPENDENCE FOR ACRYLATE AND METHACRYLATE ESTERS AT COLUMN TEMPERATURES FROM 80 TO 200°C ON OV-101

	$T = 80°C$		$T = 120°C$		$10(\Delta I/\Delta T)$ (80 vs. 120°C)	$T = 170°C$		$T = 200°C$		$10(\Delta I/\Delta T)$ (170 vs. 200°C)
	$I \pm S.D.$	$\Delta I(CH_2)$	$I \pm S.D.$	$\Delta I(CH_2)$		$I \pm S.D.$	$\Delta I(CH_2)$	$I \pm S.D.$	$\Delta I(CH_2)$	
Acrylate										
Methyl	602.3 ± 0.8	–	598.4 ± 1.0	–	–1.0					
Ethyl	680.7 ± 0.6	78.4	677.8 ± 1.2	79.4	–0.7					
Propyl	779.3 ± 0.7	98.6	776.6 ± 0.4	98.8	–0.2					
Butyl	878.4 ± 0.1	99.1	876.2 ± 0.7	99.6	–0.6					
Pentyl	978.3 ± 0.8	99.9	975.7 ± 0.5	99.5	–0.7					
Hexyl	1077.1 ± 0.6	98.8	1075.2 ± 0.3	99.5	–0.5	1073.0 ± 0.5	–	1072.6 ± 0.6	–	–0.1
Isopropyl	726.1 ± 0.5	–	725.2 ± 0.4	–	–0.2					
Isobutyl	838.5 ± 0.4	112.4	836.3 ± 0.5	111.1	–0.6					
Isopentyl	941.3 ± 0.3	102.8	939.5 ± 0.4	103.2	–0.5					
Isohexyl	1036.2 ± 0.3	94.9	1036.1 ± 0.7	96.6	0.0					
Heptyl						1173.4 ± 0.5	100.4	1173.2 ± 0.5	100.6	–0.1
Octyl						1273.3 ± 0.3	99.9	1273.2 ± 0.4	100.0	0.0
Nonyl						1373.3 ± 0.2	100.0	1374.0 ± 0.4	100.8	0.2
Decyl						1473.5 ± 0.2	100.2	1473.6 ± 0.2	99.6	0.0
Dodecyl						–	–	1674.7 ± 0.8	100.6	–
Tetradecyl						–	–	1875.8 ± 0.2	100.6	–
Hexadecyl						–	–	2076.8 ± 0.6	100.5	–
Octadecyl						–	–	2277.7 ± 0.5	100.5	–
2-Ethylhexyl						1214.3 ± 0.2	–	1215.7 ± 0.2	–	0.5

Methacrylate										
Methyl	699.5 ± 0.8	–	696.2 ± 1.1	–	−0.8					
Ethyl	772.7 ± 0.5	73.2	767.5 ± 1.1	71.3	−1.3					
Propyl	868.1 ± 0.6	95.4	864.5 ± 0.4	97.0	−0.9					
Butyl	966.9 ± 0.7	98.8	963.8 ± 0.4	99.3	−0.8					
Pentyl	1065.2 ± 0.7	98.3	1062.3 ± 0.4	98.5	−0.7					
Hexyl	1164.2 ± 1.0	99.0	1161.3 ± 0.5	99.0	−0.7	1158.0 ± 0.3	–	1157.9 ± 0.4	–	0.0
Isopropyl	811.3 ± 0.5	–	805.7 ± 0.5	–	−1.4					
Isobutyl	928.1 ± 0.5	116.8	925.1 ± 0.5	119.4	−0.8					
Isopentyl	1028.9 ± 0.7	100.8	1026.7 ± 0.7	101.6	−0.6					
Isohexyl	1123.2 ± 0.5	94.3	1122.1 ± 0.6	95.4	−0.3					
Heptyl						1257.2 ± 0.5	99.2	1257.3 ± 0.5	99.4	0.0
Octyl						1356.5 ± 0.3	99.3	1357.1 ± 0.2	99.8	0.2
Nonyl						1456.5 ± 0.2	100.0	1457.3 ± 0.3	100.2	0.3
Decyl						1556.0 ± 0.2	99.5	1556.6 ± 0.1	99.3	0.2
Dodecyl						–	–	1756.5 ± 0.1	100.0	–
Tetradecyl						–	–	1957.6 ± 0.3	100.6	–
Hexadecyl						–	–	2158.2 ± 0.3	100.3	–
Octadecyl						–	–	2358.6 ± 0.5	100.2	–
2-Ethylhexyl						1295.4 ± 0.2	–	1296.8 ± 0.3	–	0.5

TABLE II

RETENTION INDICES, THEIR STANDARD DEVIATIONS, RETENTION INCREMENTS PER METHYLENE GROUP AND TEMPERATURE DEPENDENCE FOR ACRYLATE AND METHACRYLATE ESTERS AT COLUMN TEMPERATURES FROM 80 TO 200°C ON SE-54

	T = 80°C		*T* = 120°C		$10(\Delta I/\Delta T)$ (80 vs. 120°C)	*T* = 170°C		*T* = 200°C		$10(\Delta I/\Delta T)$ (170 vs. 200°C)
	I ± *S.D.*	$\Delta I(CH_2)$	*I* ± *S.D.*	$\Delta I(CH_2)$		*I* ± *S.D.*	$\Delta I(CH_2)$	*I* ± *S.D.*	$\Delta I(CH_2)$	
Acrylate										
Methyl	622.2 ± 0.1	–	647.4 ± 0.1	–	6.3					
Ethyl	702.0 ± 0.8	79.8	721.6 ± 0.1	74.2	4.9					
Propyl	799.6 ± 0.7	97.6	814.1 ± 0.2	92.5	3.6					
Butyl	898.3 ± 0.7	98.7	905.0 ± 0.2	90.9	1.7					
Pentyl	996.0 ± 0.4	97.7	995.2 ± 0.2	90.2	−0.2					
Hexyl	1095.7 ± 0.6	99.7	1094.6 ± 0.1	99.4	−0.3	1095.3 ± 0.2	–	1098.5 ± 1.4	–	1.1
Isopropyl	744.9 ± 1.1	–	737.2 ± 0.7	–	−1.9					
Isobutyl	857.5 ± 0.4	112.6	853.7 ± 0.3	116.5	−1.0					
Isopentyl	959.3 ± 0.2	101.8	958.7 ± 0.1	105.0	−0.2					
Isohexyl	1053.7 ± 0.2	94.4	1055.4 ± 0.1	96.7	0.4					
Heptyl						1196.4 ± 0.6	101.1	1201.4 ± 0.7	102.9	1.7
Octyl						1296.8 ± 0.5	100.4	1302.2 ± 0.8	100.8	1.8
Nonyl						1396.7 ± 0.3	99.9	1400.9 ± 0.7	98.7	1.4
Decyl						1495.6 ± 0.3	98.9	1498.3 ± 1.0	97.4	0.9
Dodecyl						–	–	1695.7 ± 0.4	98.7	–
Tetradecyl						–	–	1898.5 ± 1.0	101.4	–
Hexadecyl						–	–	2099.0 ± 0.9	100.3	–
Octadecyl						–	–	2299.6 ± 0.7	100.3	–
2-Ethylhexyl						1232.7 ± 0.1	–	1233.2 ± 0.9	–	0.2

Methacrylate										
Methyl	714.0 ± 0.2	–	712.0 ± 1.0	–	−0.5					
Ethyl	786.3 ± 0.1	72.3	783.2 ± 0.6	71.2	−0.8					
Propyl	883.1 ± 0.3	96.8	880.7 ± 0.3	97.5	−0.6					
Butyl	981.5 ± 0.2	98.4	979.9 ± 0.1	99.2	−0.4					
Pentyl	1079.7 ± 0.2	98.2	1078.7 ± 0.1	98.8	−0.3					
Hexyl	1178.8 ± 0.2	99.1	1178.1 ± 0.2	99.4	−0.2	1177.6 ± 0.2	–	1179.8 ± 1.0	–	0.7
Isopropyl	822.2 ± 0.2	–	818.5 ± 0.1	–	−0.9					
Isobutyl	940.4 ± 0.1	118.2	939.6 ± 0.2	121.1	−0.2					
Isopentyl	1042.5 ± 0.2	102.1	1042.5 ± 0.3	102.9	0.0					
Isohexyl	1135.6 ± 0.2	93.1	1137.7 ± 0.1	95.2	0.5					
Heptyl						1277.0 ± 0.3	99.4	1277.0 ± 0.4	97.2	0.0
Octyl						1376.6 ± 0.2	99.6	1377.5 ± 0.2	100.5	0.3
Nonyl						1476.4 ± 0.2	99.8	1477.5 ± 0.4	100.0	0.4
Decyl						1575.8 ± 0.2	99.4	1576.4 ± 0.2	98.9	0.2
Dodecyl						–	–	1775.4 ± 0.3	99.5	–
Tetradecyl						–	–	1976.7 ± 0.7	100.7	–
Hexadecyl						–	–	2178.9 ± 0.2	101.1	–
Octadecyl						–	–	2378.3 ± 0.1	99.7	–
2-Ethylhexyl						1311.7 ± 0.0	–	1313.0 ± 0.2	–	0.4

TABLE III

RETENTION INDICES, THEIR STANDARD DEVIATIONS, RETENTION INCREMENTS PER METHYLENE GROUP AND TEMPERATURE DEPENDENCE FOR ACRYLATE AND METHACRYLATE ESTERS AT COLUMN TEMPERATURES FROM 80 TO 200°C ON SP-1000

	T = 80°C		*T* = 120°C		10(ΔI/ΔT) (80 vs. 120°C)	*T* = 170°C		*T* = 200°C		10 (ΔI/ΔT) (170 vs. 200°C)
	I ± *S.D.*	$\Delta I(CH_2)$	*I* ± *S.D.*	$\Delta I(CH_2)$		*I* ± *S.D.*	$\Delta I(CH_2)$	*I* ± *S.D.*	$\Delta I(CH_2)$	
Acrylate										
Methyl	936.8 ± 0.6	–	940.9 ± 1.1	–	1.0					
Ethyl	989.0 ± 0.3	52.2	993.3 ± 1.1	52.4	1.1					
Propyl	1073.9 ± 0.6	84.9	1080.2 ± 1.0	86.9	1.6					
Butyl	1169.1 ± 0.6	95.2	1177.6 ± 1.2	97.4	2.1					
Pentyl	1265.2 ± 0.7	96.1	1275.7 ± 1.4	98.1	2.6					
Hexyl	1361.6 ± 0.5	96.4	1373.9 ± 0.7	98.2	3.1	1387.8 ± 0.5	–	1392.2 ± 0.8	–	1.5
Isopropyl	993.7 ± 0.2	–	995.1 ± 0.0	–	0.4					
Isobutyl	1109.3 ± 0.1	115.6	1115.2 ± 0.1	120.1	1.5					
Isopentyl	1217.3 ± 0.1	108.0	1226.3 ± 0.5	111.1	2.3					
Isohexyl	1304.3 ± 0.1	87.0	1317.3 ± 0.3	91.0	3.3					
Heptyl						1488.9 ± 0.4	101.1	1494.9 ± 0.9	102.7	2.0
Octyl						1589.9 ± 0.7	101.0	1595.4 ± 0.8	100.5	1.8
Nonyl						1689.3 ± 0.6	99.4	1695.4 ± 0.6	100.0	2.0
Decyl						1788.9 ± 0.8	99.6	1794.7 ± 0.5	99.3	1.9
Dodecyl						–	–	1996.1 ± 0.5	100.7	–
Tetradecyl						–	–	2200.6 ± 0.7	102.3	–
Hexadecyl						–	–	2401.5 ± 0.7	100.5	–
Octadecyl						–	–	2601.9 ± 0.8	100.2	–
2-Ethylhexyl						1494.6 ± 0.3	–	1500.1 ± 0.7	–	1.8

Methacrylate										
Methyl	1002.0 ± 0.5	–	1010.1 ± 0.3	–	2.0					
Ethyl	1043.4 ± 0.7	41.4	1046.2 ± 0.5	36.1	0.7					
Propyl	1127.1 ± 0.5	83.7	1136.9 ± 0.7	90.7	2.5					
Butyl	1219.8 ± 0.5	92.7	1232.2 ± 0.8	95.3	3.1					
Pentyl	1313.8 ± 0.4	94.0	1327.7 ± 0.8	95.5	3.5					
Hexyl	1408.9 ± 0.4	95.1	1424.1 ± 0.8	96.4	3.8	1434.8 ± 0.1	–	1439.3 ± 1.0	–	1.5
Isopropyl	1039.1 ± 0.4	–	1042.6 ± 0.9	–	0.9					
Isobutyl	1162.4 ± 1.0	123.3	1173.3 ± 0.9	130.7	2.7					
Isopentyl	1266.3 ± 1.1	103.9	1280.8 ± 0.6	107.5	3.6					
Isohexyl	1351.8 ± 1.3	85.5	1369.6 ± 0.8	88.8	4.5					
Heptyl						1534.0 ± 0.5	99.2	1538.2 ± 0.6	98.9	1.4
Octyl						1632.2 ± 0.6	98.2	1639.1 ± 0.6	100.9	2.3
Nonyl						1732.1 ± 0.4	99.9	1739.7 ± 0.7	100.6	2.5
Decyl						1832.7 ± 0.4	100.6	1841.2 ± 0.4	101.5	2.8
Dodecyl						–	–	2042.3 ± 0.8	100.6	–
Tetradecyl						–	–	2244.8 ± 0.7	101.3	–
Hexadecyl						–	–	2446.5 ± 0.8	100.9	–
Octadecyl						–	–	2645.3 ± 0.4	99.4	–
2-Ethylhexyl						1540.5 ± 0.1	–	1546.2 ± 0.4	–	1.9

TABLE IV

REGRESSION EQUATIONS FOR PLOTS OF RETENTION OF *n*-ALKYL AND ISOALKYL ESTERS AGAINST THE NUMBER OF CARBON ATOMS IN THE ALKYL CHAIN, *C*

Ester series	*Phase*	*Column temperature (°C)*	*Regression eqn.*	*Correlation coefficient*
C_2–C_6 *n*-alkyl acrylates	OV-101	80	$I = 482.0 + 99.2\,C$	0.999998
		120	$I = 478.7 + 99.4\,C$	0.999999
	SE-54	80	$I = 504.8 + 98.4\,C$	0.999994
		120	$I = 535.3 + 92.7\,C$	0.9999
	SP-1000	80	$I = 797.2 + 93.7\,C$	0.9997
		120	$I = 797.5 + 95.7\,C$	0.9997
C_4–C_6 isoalkyl acrylates	OV-101	80	$I = 444.4 + 98.9\,C$	0.9997
		120	$I = 437.8 + 99.9\,C$	0.9998
	SE-54	80	$I = 466.3 + 98.1\,C$	0.9998
		120	$I = 451.7 + 100.9\,C$	0.9997
	SP-1000	80	$I = 722.8 + 97.5\,C$	0.9981
		120	$I = 714.4 + 101.1\,C$	0.9984
C_2–C_6 *n*-alkyl methacrylates	OV-101	80	$I = 575.4 + 98.0\,C$	0.99998
		120	$I = 569.7 + 98.5\,C$	0.99999
	SE-54	80	$I = 589.2 + 98.2\,C$	0.99999
		120	$I = 585.0 + 98.8\,C$	0.99999
	SP-1000	80	$I = 855.5 + 91.8\,C$	0.9997
		120	$I = 854.8 + 94.7\,C$	0.99994
C_4–C_6 isoalkyl methacrylates	OV-101	80	$I = 539.0 + 97.6\,C$	0.9998
		120	$I = 532.1 + 98.5\,C$	0.9998
	SE-54	80	$I = 551.5 + 97.6\,C$	0.9996
		120	$I = 544.7 + 99.1\,C$	0.9997
	SP-1000	80	$I = 786.7 + 94.7\,C$	0.9984
		120	$I = 783.8 + 98.2\,C$	0.9985
C_6–C_{18} *n*-alkyl acrylates	OV-101	200	$I = 470.0 + 100.4\,C$	0.9999998
	SE-54	200	$I = 501.0 + 99.9\,C$	0.99999
	SP-1000	200	$I = 788.2 + 100.8\,C$	0.999997
C_6–C_{10} *n*-alkyl acrylates	OV-101	170	$I = 472.6 + 100.1\,C$	0.9999997
	SE-54	170	$I = 495.4 + 100.1\,C$	0.99999
	SP-1000	170	$I = 786.9 + 100.3\,C$	0.999992
C_6–C_{18} *n*-alkyl methacrylates	OV-101	200	$I = 556.5 + 100.1\,C$	0.999999
	SE-54	200	$I = 577.5 + 100.0\,C$	0.99999
	SP-1000	200	$I = 834.0 + 100.7\,C$	0.999998
C_6–C_{10} *n*-alkyl methacrylates	OV-101	170	$I = 560.6 + 99.5\,C$	0.999999
	SE-54	170	$I = 580.0 + 99.6\,C$	0.9999998
	SP-1000	170	$I = 838.0 + 99.4\,C$	0.99999

where R is the acid chain and *n* 1,2,3,... the number of methylene groups. A comparison of structures 1 and 2 reveals that three hydrogen atoms are bonded to the α-carbon atom in methyl esters (1) but only two in the ethyl and higher *n*-alkyl esters (2). Similarly, one hydrogen atom is bonded to the α-carbon atom of isopropyl esters (3), but two in isobutyl and higher isoalkyl esters (4). Thus, the number of hydrogen

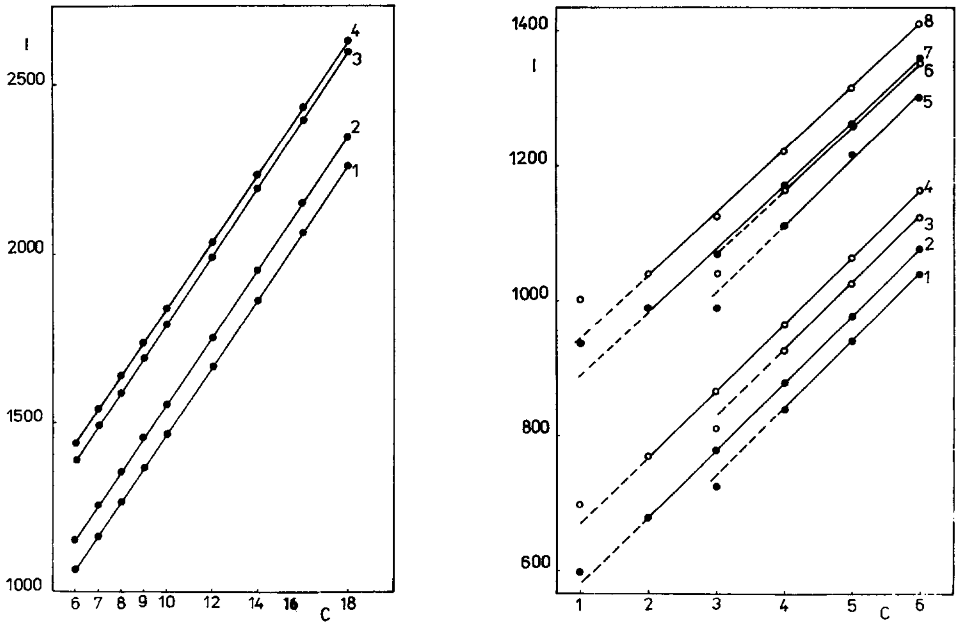


Fig. 1. Plots of the retention index, *I*, of higher alkyl esters of acrylic and methacrylic acids *versus* the number of carbon atoms, *C*, in the *n*-alkyl chains at a column temperature of 200°C on non-polar OV-101 and polar SP-1000 phases. Ester series: 1 = C_6–C_{18} *n*-alkyl acrylates on OV-101; 2 = C_6–C_{18} *n*-alkyl methacrylates on OV-101; 3 = C_6–C_{18} *n*-alkyl acrylates on SP-1000; 4 = C_6–C_{18} *n*-alkyl methacrylates on SP-1000.

Fig. 2. Plots of retention index, *I*, of lower alkyl esters of acrylic and methacrylic acids *versus* the number of carbon atoms, *C*, in the aliphatic chain at 80°C on non-polar OV-101 and polar SP-1000 phases. Homologous series: 1 = isoalkyl acrylates on OV-101; 2 = *n*-alkyl acrylates on OV-101; 3 = isoalkyl methacrylates on OV-101; 4 = *n*-alkyl methacrylates on OV-101; 5 = isoalkyl acrylates on SP-1000; 6 = isoalkyl methacrylates on SP-1000; 7 = *n*-alkyl acrylates on SP-1000; 8 = *n*-alkyl methacrylates on SP-1000.

atoms bonded to the α-carbon atom of the alkyl chain can be correlated with the deviations of the methyl and isopropyl esters from the retention behaviour exhibited by homologous series of aliphatic *n*-alkyl and isoalkyl esters.

CONCLUSIONS

The retention data summarized in this paper are useful for identification purposes in gas chromatography of the industrially important group of acrylate and methacrylate monomers under various operating conditions.

Having studied the relationship between the retention index and molecular structure in homologous series of C_1–C_{18} alkyl esters of acrylic and methacrylic acids, deviations were found to be exhibited by the methyl and isopropyl esters. This behaviour can be explained by the different configuration at the α-carbon atom of the alkyl chains of these esters compared to those in the higher *n*-alkyl and isoalkyl esters.

REFERENCES

1 M. Linkiewicz, A. Szocik and H. Smolik, *Chem. Anal. (Warsaw)*, 26 (1981) 153.
2 R. W. Germaine and J. K. Haken, *J. Chromatogr.*, 43 (1969) 43.
3 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 111 (1975) 171.
4 A. Horna, H. Pechová, A. Tůmová and J. Churáček, *J. Chromatogr.*, 288 (1984) 230.
5 E. Kováts, *Advan. Chromatogr.*, 1 (1965) 229.
6 K. Komárek, L. Hornová and J. Churáček, *J. Chromatogr.*, 244 (1982) 142.
7 K. Komárek, L. Hornová, A. Horna and J. Churáček, *J. Chromatogr.*, 262 (1983) 316.
8 J. K. Haken, H. N. T. Hartley (nee Dinh) and D. Srisukh, *Chromatographia*, 17 (1983) 589.