CHROMSYMP. 1964

Relationship between the structure and retention of *n*-alkenes and *n*-alkynes on silicone phases

K. KUNINGAS*, S. RANG and T. KAILAS

Institute of Chemistry, Estonian Academy of Sciences, Tallinn (U.S.S.R.)

ABSTRACT

A comparative study of the elution behaviour of C_8–C_{14} *n*-alkenes and *n*-alkynes on OV-101, OV-17 and OV-225 was carried out. By means of the temperature and structure increments of retention indices, peculiarities of the sorbate–sorbent interactions in these systems have been considered. Advantages of the nitrile-containing phase OV-225 for separation of *cis*- and *trans*-isomers of *n*-alkenes were demonstrated. The equations obtained permit retention indices of higher homologues of these solute series to be predicted.

INTRODUCTION

The gas chromatographic behaviour of *n*-alkenes and *n*-alkynes has been widely investigated on capillary columns with stationary phases of various polarity [1–6]. However, only a few studies on the retention–structure relationship of these solutes on representative silicone stationary phases have been published. Several workers have determined retention parameters on OV-101 for *n*-alkenes: C_5–C_6 isomers [7], C_5–C_8 isomers [8], 1-heptene and 1-octene [9]. We have investigated the retention and thermodynamics of solution of linear alkenes on OV-101 [10] and thermodynamic functions of solution (relative molar enthalpies, entropies and free energies) of linear alkenes and alkynes on OV-101, OV-17 (50% phenyl) and OV-225 (25% phenyl, 25% nitrile) [11]. However, the structure–retention correlations necessary for solving separation and identification problems with high-boiling isomers of these series on OV-17 and OV-225 have not been discussed in the literature.

Considering the significance of OV-101, OV-17 and OV-225 as stationary phases in modern gas–liquid chromatography [12–14], we made a comparative study of the elution behaviour of all possible isomers of C_8–C_{14} *n*-alkenes and *n*-alkynes on these sorbents by using retention indices and their temperature increments ($\delta I/\delta T$) and structural increments (H, $\delta I^{c,t}$, δI^{mbi}), particularly with a view to discussing the role of structural features of sorbate molecules and the polarity of the stationary phase.

EXPERIMENTAL

Gas chromatographic measurements were performed on a Chrom-5 gas

chromatograph equipped with a flame ionization detector. The retention indices were measured on glass or stainless-steel capillary columns (50–60 m × 0.25 mm I.D.) at 40–140°C at 10°C intervals with a carrier gas (helium) linear velocity of 16–18 cm/s and splitting ratios of 1:200 to 1:400. The gas hold-up time was determined by extrapolation from the retention times of n-alkanes added to the mixture. The capacity factors of OV-101 and OV-225 glass capillary columns determined for n-tridecane at 110°C were 5.0 and 3.0, respectively, and the number of theoretical plates varied within the range 120 000–130 000 (at 130°C). The corresponding values for the stainless-steel capillary column coated with OV-17 were 12.5 and 30 000.

The reproducibility of retention index measurements expressed in terms of the standard deviation of an arithmetic mean of at least five measurements for each compound was 0.1–0.2 absolute index unit (i.u.). The retention indices on OV-101, OV-17 and OV-225 are given in Tables I–V; data for n-alkenes on OV-101 have been published previously [10]. The s_0 values [$s_0 = \sqrt{\Sigma(I_e - I_c)^2/(z - 1)}$, where I_e is the experimental retention index, I_c the calculated retention index and z the number of measurements] characterize the differences between the experimental and calculated

TABLE I

RETENTION INDICES OF C_9, C_{10} AND C_{12} n-ALKENES AT 110°C ($I_{110°}$), COEFFICIENTS A AND B FOR THE EQUATION $I = A + B/T$ AND $10(\delta I/\delta T)$ VALUES ON OV-17

Hydrocarbon	$I_{110°}$	A	B	s_0	$10(\delta I/\delta T)$
1-Nonene	908.2	910.0	−710	0.07	0.05
trans-2-Nonene	924.9	923.1	680	0.07	−0.05
cis-2-Nonene	936.8	951.3	−5550	0	0.40
trans-3-Nonene	916.5	911.0	2100	0	−0.15
cis-3-Nonene	920.4	936.7	−6260	0	0.45
trans-4-Nonene	913.4	917.1	−1390	0.07	0.10
cis-4-Nonene	918.9	942.5	−9030	0	0.65
1-Decene	1008.2	1011.7	−1280	0.12	0.09
trans-2-Decene	1025.1	1024.0	420	0.10	−0.03
cis-2-Decene	1036.7	1055.1	−6970	0.13	0.49
trans-3-Decene	1015.9	1014.9	450	0.15	−0.03
cis-3-Decene	1019.0	1036.6	−6710	0.12	0.47
trans-4-Decene	1012.6	1016.7	−1570	0.10	0.11
cis-4-Decene	1016.7	1037.7	−7970	0.14	0.56
trans-5-Decene	1013.1	1020.6	−2820	0.08	0.20
cis-5-Decene	1015.3	1037.8	−8550	0.16	0.60
1-Dodecene	1208.2	1215.2	−2710	0.10	0.17
trans-2-Dodecene	1224.9	1226.0	−440	0.08	0.03
cis-2-Dodecene	1236.1	1262.4	−10 110	0.10	0.65
trans-3-Dodecene	1215.1	1216.3	−480	0.06	0.03
cis-3-Dodecene	1217.1	1241.4	−9310	0.06	0.59
trans-4-Dodecene	1210.7	1221.8	−4270	0.08	0.27
cis-4-Dodecene	1213.4	1243.5	−11 540	0.08	0.73
trans-5-Dodecene	1210.3	1221.1	−4110	0.08	0.26
cis-5-Dodecene	1209.8	1241.5	12 140	0.08	0.77
trans-6-Dodecene	1210.2	1223.9	−5240	0.06	0.33
cis-6-Dodecene	1209.6	1244.3	−13 300	0.10	0.84

TABLE II

RETENTION INDICES OF C_8–C_{14} *n*-ALKENES AT 110°C ($I_{110°}$), COEFFICIENTS A AND B FOR THE EQUATION $I = A + B/T$ AND $10(\delta I/\delta T)$ VALUES ON OV-225

Hydrocarbon	$I_{110°}$	A	B	s_0	$10(\delta I/\delta T)$
1-Octene	828.4	841.6	−5040	0.08	0.47
trans-2-Octene	838.0	836.8	430	0.12	−0.04
cis-2-Octene	856.2	872.7	−6320	0.13	0.59
trans-3-Octene	826.0	822.0	1500	0.06	−0.14
cis-3-Octene	837.3	849.0	−4500	0.06	0.42
trans-4-Octene	822.1	822.3	−100	0.06	0.01
cis-4-Octene	837.2	852.8	−5990	0.16	0.56
1-Nonene	928.0	938.5	−4050	0.14	0.37
trans-2-Nonene	937.4	937.4	0	0	0
cis-2-Nonene	955.4	974.4	−7280	0.13	0.66
trans-3-Nonene	925.4	924.0	560	0.05	−0.05
cis-3-Nonene	936.3	953.5	−6600	0.17	0.60
trans-4-Nonene	922.0	923.7	−670	0.05	0.06
cis-4-Nonene	934.7	955.5	−7960	0.10	0.72
1-Decene	1028.8	1047.4	−7120	0.18	0.61
trans-2-Decene	1037.6	1038.5	−340	0.13	0.03
cis-2-Decene	1056.2	1081.5	−9710	0.13	0.83
trans-3-Decene	1025.0	1026.8	−700	0.09	0.06
cis-3-Decene	1035.4	1058.1	−8660	0.12	0.74
trans-4-Decene	1021.3	1028.1	−2610	0.07	0.22
cis-4-Decene	1032.6	1059.8	−10 420	0.15	0.89
trans-5-Decene	1022.0	1030.6	−3270	0.09	0.28
cis-5-Decene	1031.4	1059.1	−10 630	0.22	0.91
1-Undecene	1128.7	1147.1	−7080	0.10	0.54
trans-2-Undecene	1137.8	1140.8	−1190	0.07	0.09
cis-2-Undecene	1156.2	1186.9	−11 830	0.13	0.90
trans-3-Undecene	1124.3	1124.9	−260	0.07	0.02
cis-3-Undecene	1134.9	1161.3	−10 220	0.16	0.78
trans-4-Undecene	1120.4	1131.0	−4080	0.10	0.31
cis-4-Undecene	1131.0	1165.8	−13 390	0.16	1.00
trans-5-Undecene	1120.0	1129.0	−3450	0.12	0.26
cis-5-Undecene	1128.6	1164.1	−13 650	0.17	1.04
1-Dodecene	1228.6	1247.7	−7320	0.10	0.53
trans-2-Dodecene	1237.3	1239.1	−690	0.07	0.05
cis-2-Dodecene	1255.7	1289.6	−13 010	0.18	0.94
trans-3-Dodecene	1223.9	1227.2	−1250	0.07	0.09
cis-3-Dodecene	1233.6	1264.7	−11 900	0.17	0.86
trans-4-Dodecene	1219.0	1228.5	−3570	0.17	0.26
cis-4-Dodecene	1229.4	1263.6	−13 160	0.21	0.95
trans-5-Dodecene	1218.7	1232.7	−5370	0.10	0.39
cis-5-Dodecene	1225.6	1260.9	−13 560	0.15	0.98
trans-6-Dodecene	1218.2	1236.4	−6940	0	0.50
cis-6-Dodecene	1224.9	1264.7	−15 260	0.12	1.10
1-Tridecene	1328.7	1351.6	−8780	0.09	0.60
trans-2-Tridecene	1337.3	1342.9	−2160	0.10	0.15
cis-2-Tridecene	1355.2	1395.0	−15 160	0.23	1.04

TABLE II (continued)

Hydrocarbon	I_{110°	A	B	s_0	$10(\delta I/\delta T)$	
trans-3-Tridecene	1323.5	1325.4	−750	0	0.05	
cis-3-Tridecene	1333.1	1367.6	−13 190	0.12	0.90	
trans-4-Tridecene	1318.3	1330.9	−4830	0.05	0.33	
cis-4-Tridecene	1328.1	1369.4	−15 800	0.13	1.08	
trans-5-Tridecene	1316.9	1335.7	−7180	0.07	0.49	
cis-5-Tridecene	1323.7	1369.3	−17 420	0.10	1.19	
trans-6-Tridecene	1316.3	1339.6	−8900	0.07	0.61	
cis-6-Tridecene	1321.7	1369.3	−18 320	0.17	1.25	
1-Tetradecene	1428.8	1450.8	−8440	0.23	0.55	
trans-2-Tetradecene	1437.4	1442.9	−2130	0.09	0.14	
cis-2-Tetradecene	1455.9	1493.6	−14 440	0.19	0.94	
trans-3-Tetradecene	1423.4	1428.1	−1830	0.09	0.12	
cis-3-Tetradecene	1433.0	1469.9	−14 140	0.14	0.92	
trans-4-Tetradecene	1417.9	1433.2	−5860	0.09	0.38	
cis-4-Tetradecene	1427.7	1469.4	−16 000	0.19	1.04	
trans-5-Tetradecene	1416.5	1437.2	−7980	0.14	0.52	
cis-5-Tetradecene	1422.4	1468.1	−17 470	0.35	1.14	
trans-6-Tetradecene	1414.3	1440.0	−9830	0.16	0.64	
cis-6-Tetradecene	1419.2	1471.8	−20 110	0.28	1.31	
trans-7-Tetradecene	1414.1	1437.8	−9060	0.13	0.59	
cis-7-Tetradecene	1417.3	1470.5	−20 310	0.23	1.32	

TABLE III

RETENTION INDICES OF C_7–C_{14} n-ALKYNES AT 110°C (I_{110°), COEFFICIENTS A AND B FOR THE EQUATION $I = A + B/T$ AND $10(\delta I/\delta T)$ VALUES ON OV-101

Hydrocarbon	I_{110^c}	A	B	s_0	$10(\delta I/\delta T)$	
1-Heptyne	710.7	689.4	8150	0.10	−0.76	
2-Heptyne	765.8	741.2	9410	0.22	−0.88	
3-Heptyne	743.9	712.3	12 110	0.22	−1.13	
1-Octyne	811.5	795.3	6200	0.05	−0.56	
2-Octyne	865.1	841.1	9180	0.12	−0.83	
3-Octyne	842.8	813.6	11 180	0.13	−1.01	
4-Octyne	838.7	814.4	9300	0.05	−0.84	
1-Nonyne	911.7	895.3	6300	0.04	−0.55	
2-Nonyne	964.5	943.5	8060	0.09	−0.70	
3-Nonyne	940.3	911.8	10 940	0.08	−0.96	
4-Nonyne	935.7	912.5	8910	0.06	−0.78	
1-Decyne	1012.0	997.1	5720	0.19	−0.46	
2-Decyne	1064.2	1041.5	8710	0.09	−0.70	
3-Decyne	1039.2	1010.3	11 070	0.12	−0.89	
4-Decyne	1032.6	1011.3	8190	0.09	−0.66	
5-Decyne	1031.4	1010.5	7990	0.17	−0.64	

TABLE III (*continued*)

Hydrocarbon	$I_{110°}$	A	B	s_0	$10(\delta I/\delta T)$
1-Undecyne	1112.3	1099.3	4990	0.06	−0.37
2-Undecyne	1164.2	1145.1	7310	0.08	−0.54
3-Undecyne	1138.0	1109.1	11 070	0.08	−0.82
4-Undecyne	1131.0	1111.9	7300	0.06	−0.54
5-Undecyne	1127.4	1114.5	4990	0.08	−0.37
1-Dodecyne	1212.7	1203.2	3660	0.09	−0.25
2-Dodecyne	1264.3	1244.8	7450	0.13	−0.51
3-Dodecyne	1237.5	1211.1	10 070	0.16	−0.69
4-Dodecyne	1229.4	1212.6	6410	0.10	−0.44
5-Dodecyne	1225.3	1215.4	3820	0.09	−0.26
6-Dodecyne	1223.5	1214.5	3350	0.12	−0.23
1-Tridecyne	1312.7	1303.6	3560	0.15	−0.23
2-Tridecyne	1364.0	1345.4	7070	0.13	−0.46
3-Tridecyne	1337.1	1312.5	9390	0.14	−0.61
4-Tridecyne	1328.1	1316.3	4490	0.13	−0.29
5-Tridecyne	1322.9	1312.8	3800	0.11	−0.25
6-Tridecyne	1320.2	1315.8	1640	0.10	−0.11
1-Tetradecyne	1412.8	1408.2	1720	0.10	−0.11
2-Tetradecyne	1464.3	1444.3	7730	0.15	−0.49
3-Tetradecyne	1436.7	1409.6	10 420	0.18	−0.66
4-Tetradecyne	1427.2	1415.3	4550	0.20	−0.29
5-Tetradecyne	1421.2	1414.8	2460	0.12	−0.15
6-Tetradecyne	1417.4	1415.3	790	0	−0.05
7-Tetradecyne	1416.3	1433.6	−6610	0.08	0.41

TABLE IV

RETENTION INDICES OF C_8–C_{11} *n*-ALKYNES AT 110°C ($I_{110°}$), COEFFICIENTS A AND B FOR THE EQUATION $I = A + B/T$ AND $10(\delta I/\delta T)$ VALUES ON OV-17

Hydrocarbon	$I_{110°}$	A	B	s_0	$10(\delta I/\delta T)$
1-Octyne	875.6	855.5	7650	0.12	−0.55
2-Octyne	947.7	933.1	5580	0.10	−0.40
3-Octyne	919.5	888.5	11 840	0.12	−0.85
4-Octyne	912.3	886.9	9740	0	−0.70
1-Nonyne	976.0	957.4	7160	0.08	−0.50
2-Nonyne	1047.6	1041.4	2440	0.08	−0.17
3-Nonyne	1020.0	995.1	9560	0.06	−0.67
4-Nonyne	1012.3	994.9	6710	0.12	−0.47
1-Decyne	1076.2	1068.0	3170	0.12	−0.20
2-Decyne	1147.9	1149.1	−450	0	−0.03
3-Decyne	1119.2	1101.1	−6960	0.08	−0.44
4-Decyne	1111.4	1100.2	−4260	0.10	−0.27
5-Decyne	1111.0	1199.0	−4580	0.08	−0.29
1-Undecyne	1176.1	1168.7	−2860	0.08	−0.18
2-Undecyne	1248.1	1249.1	−450	0.12	−0.03
3-Undecyne	1218.6	1200.8	−6810	0	−0.43
4-Undecyne	1209.9	1202.9	−2690	0.08	−0.17
5-Undecyne	1208.9	1207.6	−500	0	−0.03

TABLE V

RETENTION INDICES OF C_7–C_{14} n-ALKYNES AT 110°C ($I_{110°}$), COEFFICIENTS A AND B FOR THE EQUATION $I = A + B/T$ AND $10(\delta I/\delta T)$ VALUES ON OV-225

Hydrocarbon	$I_{110°}$	A	B	s_0	$10(\delta I/\delta T)$
1-Heptyne	837.0	839.7	−1030	0.12	0.10
2-Heptyne	886.0	895.5	−3650	0	0.35
3-Heptyne	847.8	834.2	5220	0	−0.50
1-Octyne	938.8	948.6	−3730	0.16	0.34
2-Octyne	987.6	1000.2	−4850	0.10	0.44
3-Octyne	949.6	943.5	2330	0.07	−0.21
4-Octyne	942.1	938.0	1560	0.05	−0.14
1-Nonyne	1039.4	1048.1	−3320	0	0.30
2-Nonyne	1086.9	1100.2	−5090	0.05	0.46
3-Nonyne	1049.0	1043.5	2100	0.09	−0.19
4-Nonyne	1040.7	1040.2	220	0	−0.02
1-Decyne	1140.8	1157.5	−6430	0.15	0.52
2-Decyne	1188.0	1208.0	−7680	0.16	0.62
3-Decyne	1148.2	1146.6	620	0.07	−0.05
4-Decyne	1139.5	1143.7	−1620	0.05	0.13
5-Decyne	1138.7	1147.8	−3480	0.05	0.28
1-Undecyne	1241.1	1257.1	−6120	0.10	0.48
2-Undecyne	1288.2	1307.6	−7430	0.14	0.58
3-Undecyne	1247.3	1246.5	380	0	−0.03
4-Undecyne	1237.7	1245.8	−3080	0.08	0.27
5-Undecyne	1236.0	1249.3	−5120	0.08	0.40
1-Dodecyne	1342.7	1372.7	−11 570	0.17	0.81
2-Dodecyne	1389.1	1425.2	−13 790	0.15	0.97
3-Dodecyne	1348.0	1355.8	−3000	0.10	0.21
4-Dodecyne	1337.1	1352.9	−6000	0.06	0.42
5-Dodecyne	1334.6	1355.5	−8020	0.10	0.56
6-Dodecyne	1334.2	1358.5	−9310	0.08	0.65
1-Tridecyne	1443.1	1484.6	−15 950	0.21	1.06
2-Tridecyne	1489.0	1533.7	−17 100	0.24	1.14
3-Tridecyne	1447.6	1461.6	−5420	0.12	0.36
4-Tridecyne	1436.2	1466.6	−11 700	0.17	0.78
5-Tridecyne	1432.4	1460.8	−10 940	0.18	0.73
6-Tridecyne	1430.7	1464.8	−13 080	0.18	0.87
1-Tetradecyne	1543.8	1586.9	−16 490	0.10	1.04
2-Tetradecyne	1590.1	1633.0	−16 410	0.13	1.04
3-Tetradecyne	1548.5	1559.7	−4260	0.15	0.27
4-Tetradecyne	1535.7	1568.6	−12 630	0.12	0.80
5-Tetradecyne	1530.9	1572.6	−15 950	0.13	1.01
6-Tetradecyne	1528.6	1573.6	−17 250	0.08	1.09
7-Tetradecyne	1527.4	1578.6	−19 620	0.06	1.24

values of I, using the equation $I = A + B/T$ where A and B are constants and T is absolute temperature. These data have also been published previously [15] but the publication is not readily available.

Retention index increments (structural increment H, multiple bond increment δI^{mbi}, $\delta I^{c,t}$) were calculated as follows:

$$H = I(n\text{-alkene}/n\text{-alkyne}) - I(n\text{-alkane})$$
$$\delta I^{mbi} = I - I^{CH_3} - (n - 3)I^{CH_2} \text{ (terminal isomers)}$$
$$\delta I^{mbi} = I - 2I^{CH_3} - (n - 4)I^{CH_2} \text{ (internal isomers)}$$

where I^{CH_2}, I^{CH_3} are retention index increments of CH_2 and CH_3 groups, respectively, and $\delta I^{c,t} = I^{cis} - I^{trans}$.

All individual isomers of *n*-alkenes and *n*-alkynes were prepared in our laboratory.

RESULTS AND DISCUSSION

The coefficients of the equations describing the dependence of the retention index, I, on the number of carbon atoms, n, in the sorbate molecule are given in Tables VI and VII. The mean values of s_0 (0.39 and 0.22 for linear and non-linear equations, respectively) and regression coefficients (0.9999979 and 0.9999995) show that a better correlation is obtained with non-linear equations. The values of the coefficient b, which characterize the contribution of the energy of interaction of the CH_2 group of the sorbate with the stationary phase, vary in the range 90–100 i.u. These coefficients depend slightly on both the structure of the sorbate molecule and the polarity of the stationary phase. The coefficient a, which reflects mainly the specificity of interaction between the unsaturated group of the sorbate and the sorbent, is sensitive to the type

TABLE VI

COEFFICIENTS a AND b AND STANDARD DEVIATIONS, s_0, FOR THE EQUATION $I = a + bn$

Homologous series	OV-101			OV-225		
	a	b	s_0	a	b	s_0
1-Alkenes	− 10.58	99.95	0.14	27.63	100.09	0.22
trans-2-Alkenes	3.76	99.84	0.23	38.45	99.92	0.22
cis-2-Alkenes	14.52	99.71	0.31	56.54	99.94	0.41
trans-3-Alkenes	0.96	99.36	0.50	29.49	99.55	0.16
cis-3-Alkenes	4.69	99.21	0.28	43.09	99.25	0.30
trans-4-Alkenes	3.29	98.89	0.44	28.90	99.20	0.34
cis-4-Alkenes	9.69	98.45	0.65	49.17	98.40	0.67
trans-5-Alkenes	5.88	98.54	0.35	35.74	98.59	0.42
cis-5-Alkenes	15.39	97.66	0.52	53.82	97.71	0.56
trans-6-Alkenes	9.25	98.15	0.29	41.62	98.05	0.42
cis-6-Alkenes	20.17	97.10	0.41	58.98	97.15	0.17
1-Alkynes	9.05	100.29	0.19	130.93	100.94	0.34
2-Alkynes	66.53	99.81	0.32	182.80	100.51	0.43
3-Alkynes	50.50	98.95	0.77	149.38	99.89	0.71
4-Alkynes	52.60	98.11	0.89	150.36	98.91	0.41
5-Alkynes	55.52	97.51	0.61	157.56	98.08	0.29
6-Alkynes	60.63	96.90	0.12	167.57	97.20	0.41

TABLE VII

COEFFICIENTS a, b AND c AND STANDARD DEVIATIONS, s_0 FOR THE EQUATION $I = a + bn + cn^2$

Homologous series	OV-101				OV-225			
	a	b	c	s_0	a	b	c	s_0
1-Alkenes	−11.84	100.18	−0.011	0.12	26.24	100.35	−0.012	0.22
trans-2-Alkenes	9.89	98.69	0.052	0.15	40.01	99.62	0.013	0.19
cis-2-Alkenes	22.89	98.13	0.072	0.17	56.54	99.93	0.000	0.41
trans-3-Alkenes	14.75	96.77	0.118	0.20	33.82	98.73	0.037	0.11
cis-3-Alkenes	17.12	97.00	0.096	0.11	49.92	97.96	0.058	0.19
trans-4-Alkenes	14.26	96.82	0.094	0.25	25.43	99.86	−0.030	0.32
cis-4-Alkenes	40.14	93.03	0.235	0.13	69.38	94.60	0.173	0.12
trans-5-Alkenes	26.44	95.07	0.145	0.24	63.35	93.92	0.194	0.22
cis-5-Alkenes	55.09	90.95	0.280	0.07	95.49	90.67	0.293	0.20
1-Alkynes	5.29	101.04	−0.036	0.11	125.71	101.99	−0.050	0.30
2-Alkynes	73.20	98.48	0.064	0.11	183.01	100.46	0.002	0.43
3-Alkynes	65.93	95.86	0.147	0.30	151.13	99.54	0.017	0.70
4-Alkynes	79.75	93.00	0.232	0.19	162.17	96.70	0.100	0.19
5-Alkynes	99.23	90.12	0.308	0.28	173.89	95.32	0.115	0.22
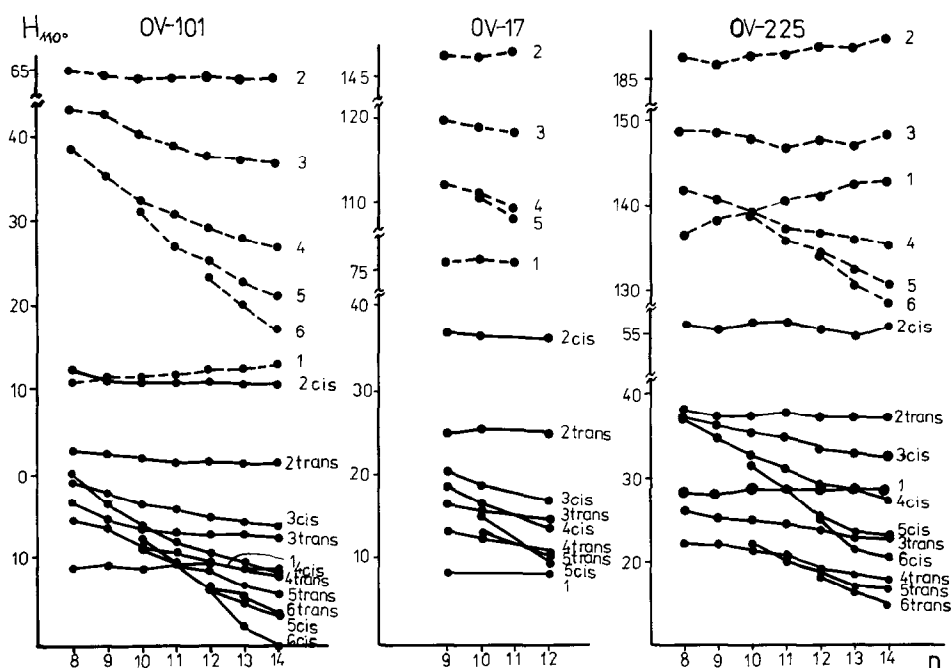
Fig. 1. Dependence of structure increment H on the number of carbon atoms n in the sorbate molecule. ——— = n-Alkenes; − − − − = n-alkynes. The numbers next to the plots indicate the position of the multiple bond.

and position of this group, and depends greatly on the polarity of the stationary phase. On going from non-polar OV-101 to the more polar OV-225, a characteristic increase in the values of the coefficient a is observed for each homologous series of isomers, which gives evidence for a regular increase in the specific intermolecular interaction between the sorbate and the sorbent.

The plots of H values *versus* n (Fig. 1) show characteristic curves with negative H values for n-alkenes (except for the 2-alkenes) on OV-101.

For the homologous series of 1- and 2-isomers (except 1- and 2-alkynes on OV-225), the H values are nearly independent of n. In the other series, the H values decrease with increasing n owing partly to a decrease in the relative contribution of the multiple bond to the interaction with lengthening alkyl chain in the molecule.

The H increments for internal isomers of identical chain length decrease as the
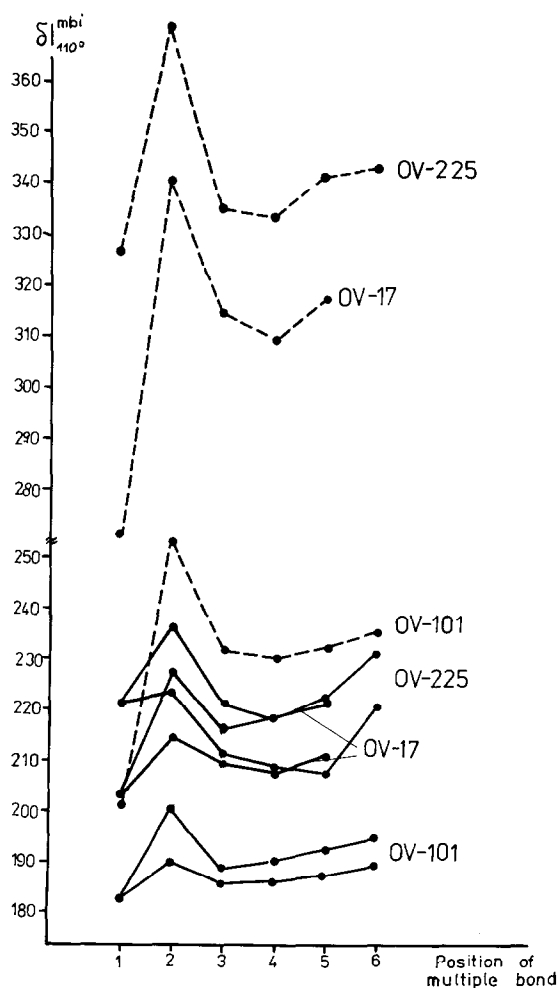
Fig. 2. Dependence of δH^{mbi} on the position of the multiple bond in the molecule. ——— = n-Alkenes; — — — = n-alkynes.

multiple bond shifts towards the centre of the molecule. This is in accordance with an increase in the shielding effect of alkyl groups on the interaction between the sorbate and sorbent molecules as the multiple bond shifts to the centre of the molecule.

The contribution of unsaturated groups ($CH_2 = CH-$, $-CH=CH-$, $CH\equiv C-$, $-C\equiv C-$) in the sorbate molecules to I (the multiple bond increment δI^{mbi}) depends markedly on the polarity of the stationary phase and increases in the order OV-101 < OV-17 < OV-225 (Fig. 2). Here the position of the multiple bond in internal isomers, starting from 3-alkenes and 3-alkynes, is of lesser importance. The lowest values of δI^{mbi} on OV-101 are explained by its capacity for mainly dispersive interactions with various sorbates. The increase in the I and δI^{mbi} values on OV-17 is caused by a stronger interaction between the π-electron system of the sorbate and the phenyl group in the sorbent. In addition, a specific donor–acceptor interaction of nitrile-containing OV-225 with unsaturated hydrocarbons accompanied by complex formation [12] leads to higher values of I and its structural increments on this sorbent. cis-2-Alkenes and 2-alkynes, where the methyl group is conjugated with the multiple bond, exhibit the strongest intermolecular interaction and the highest δI^{mbi}.

On OV-225 the complex formation of cis- and trans-isomers plays the most important role and the differences in their retention behaviour are the largest (Fig. 3). This results in better separations of cis- and trans-isomers of n-alkenes on OV-225 in comparison with OV-101 and OV-17. On all the silicone phases investigated, $\delta I^{c,t}$ decreases as the double bond shifts towards the centre of the molecule. This is explained by a decrease in differences in the sorbate–sorbent interactions as the shielding effect of alkyl substituents increases with their lengthening.

The temperature increments $10(\delta I/\delta T)$ for C_8–C_{14} n-alkenes and n-alkynes are comparatively small, varying within the ranges -1.0 to 1.1 (OV-101), -0.8 to 0.8
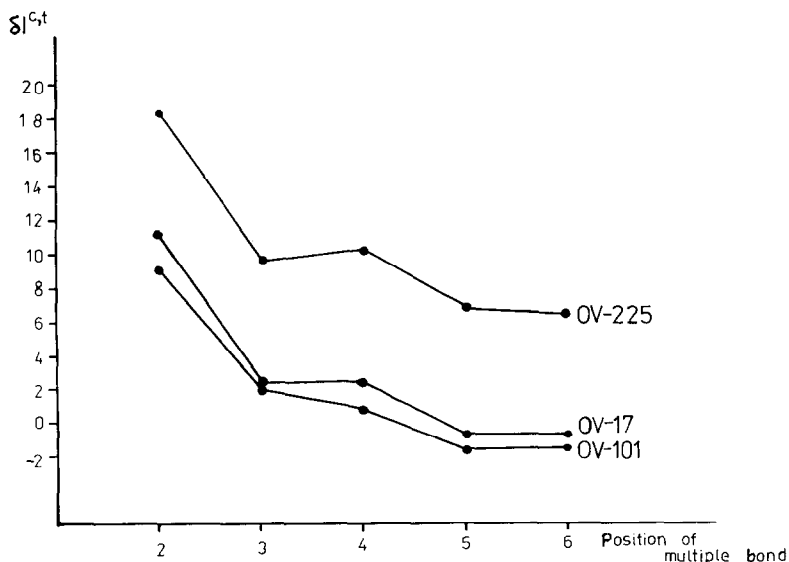

Fig. 3. Dependence of $\delta I^{c,t}$ on the position of the multiple bond for tridecenes.
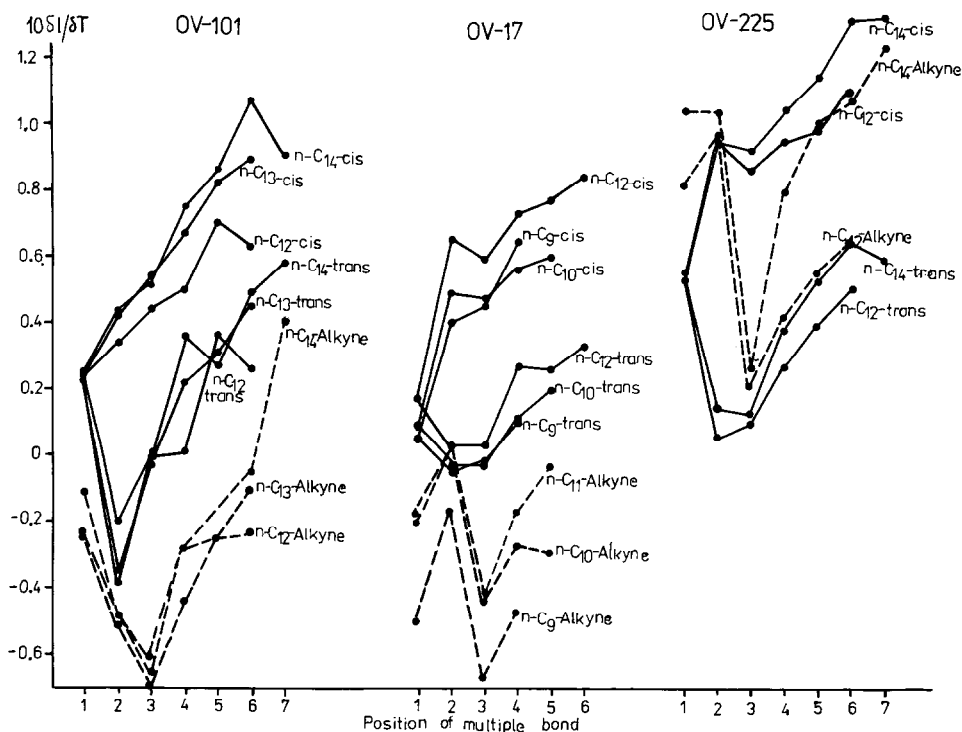
Fig. 4. Dependence of $\delta I/\delta T$ on the position of the multiple bond in the molecule.

(OV-17) and -0.2 to 1.5 (OV-225), depending on the polarity of the stationary phase (Fig. 4). With an increase in the latter the whole range of $10(\delta I/\delta T)$ values decrease from 2.1 (OV-101) to 1.5 (OV-225). This regularity results mainly from the complex formation between the sorbate and the sorbent on OV-225. On OV-101 *n*-alkynes (except 7-tetradecyne) reveal negative and on OV-225 positive $\delta I/\delta T$ values. The positive $\delta I/\delta T$ values of *cis*-alkenes on all the stationary phases investigated may be partly explained by a greater effect of temperature on the vapour pressure of their asymmetric molecules compared with more symmetrical *trans*-isomers. The $\delta I/\delta T$ values of the latter have an intermediate position between those of *n*-alkynes and *cis*-alkenes and reveal negative and positive $\delta I/\delta T$ values, depending on the chain length and double bond position.

CONCLUSIONS

Structure–retention correlations for *n*-alkenes and *n*-alkynes on OV-101, OV-17 and OV-225 have been derived using retention index increments H, $\delta I/\delta T$, $\delta I^{r,t}$ and δI^{mbi}.

Replacement of the methyl group in the silicone stationary phase by phenyl and nitrile groups leads to an increase in I, H, $\delta I^{r,t}$ and δI^{mbi}. This is caused by specific interactions between the π-electron system of the unsaturated bond and the phenyl

group (OV-17, OV-225) on the one hand and by the formation of a π-complex between the unsaturated bond and nitrile group (OV-225) on the other. The retention index multiple bond increment increases by about 20–23 and 30–40 i.u. in the alkene series and by 80 and 100–120 i.u. in the alkyne series on passing over from OV-101 to OV-17 and from OV-17 to OV-225, respectively.

REFERENCES

1 O. Eisen, A. Orav and S. Rang, *Chromatographia*, 5 (1972) 229.
2 L. Sojak, J. Hrivňák, P. Majer and J. Janák, *Anal. Chem.*, 45 (1973) 293.
3 S. Rang, K. Kuningas, A. Orav and O. Eisen, *J. Chromatogr.*, 119 (1976) 451.
4 S. Rang, K. Kuningas, A. Orav and O. Eisen, *Chromatographia*, 10 (1977) 55.
5 L. Soják, J. Krupčik and J. Janák, *J. Chromatogr.*, 195 (1980) 43.
6 L. Soják, P. Farkaš, J. Janák, S. Rang and O. Eisen, *J. Chromatogr.*, 287 (1984) 271.
7 C.-F. Chien, D. L. Furio, M. M. Kopečni and R. J. Laub, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 557 and 669.
8 S. Boneva and N. Dimov, *Chromatographia*, 21 (1986) 149.
9 V. Pacáková, K. Hoch and E. Smolková, *Chromatographia*, 6 (1973) 320.
10 S. Rang, K. Kuningas, T. Strenze and O. Eisen, *J. Chromatogr.*, 406 (1987) 75.
11 K. Kuningas, S. Rang and T. Kailas, *Chromatographia*, 27 (1989) 544.
12 J. K. Haken, *J. Chromatogr.*, 300 (1984) 1.
13 A. N. Korol, *Nepodvizhnye Fazy v Gazozhidgostnoi Khromatografii (Stationary Phases in Gas–Liquid Chromatography)*, Khimiya, Moscow, 1985.
14 Leibnitz and Struppe, *Rukovodstvo po Gazovoi Khromatografii (Handbuch der Gas-Chromatographie)*, Vol. II, Mir, Moscow, 1988.
15 S. A. Rang, A. E. Orav, K. R. Kuningas, A. E. Meister, T. V. Strenze and O. G. Eisen, *Gazokhromatograficheskie Kharakteristiki Nenasyshchennykh Uglevodorodov (Gas Chromatographic Characteristics of Unsaturated Hydrocarbons)*, Estonian Academy of Sciences, Tallinn, 1988.