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CAPILLARY GAS CHROMATOGRAPHY OF *n*-ALKYNES

II. VARIATION OF RETENTION INDICES WITH TEMPERATURE

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SUMMARY

The Kováts retention indices (I) of C_6–C_{14} *n*-alkynes on squalane (SQ), Apiezon L (ApL), polyphenyl ether (PFE) and polyethylene glycol 4000 (PEG) vary relatively slightly with temperature (T) in the range 60–190°C. On SQ the I values of internal *n*-alkynes decrease and on PEG and PFE they increase with increase in T, while 1- and 3-*n*-alkynes have negative temperature increments on PEG. On SQ the 3-isomers show the greatest change of I with T, and on PEG (C_{12}–C_{14} *n*-alkynes) and PFE the smallest change. Equations for calculating I based on column temperature are given.

INTRODUCTION

The variation of retention indices with temperature is related to structural features of compounds and is useful for the unambiguous identification of gas chromatographic peaks. Using results obtained earlier[1], the regularities in the variation of Kováts retention indices of C_6–C_{14} *n*-alkynes with column temperature on squalane (SQ), Apiezon L (ApL), polyphenyl ether (PFE) and polyethylene glycol 4000 (PEG) are considered in this paper.

Hively and Hinton[2] studied the variation of Kováts retention indices with temperature of C_3–C_7 *n*-alkynes on squalane at 27–86°C. Relatively large negative values of the temperature increments for internal C_5–C_7 *n*-alkynes on squalane were explained in terms of enhanced rigidity of *n*-alkyne molecules compared with the corresponding *n*-alkanes. This reflects the smaller minimum cross-sectional areas of *n*-alkyne molecules compared with *n*-alkanes and a decrease in the dispersion interaction between the molecules of *n*-alkynes and the liquid phase as the temperature increases. The effect of temperature on the retention indices of higher alkynes on squalane and on other liquid phases was not investigated.

RESULTS AND DISCUSSION

The earlier experimental results[1] were treated according to eqns. 1–4:

$$I = A + Bt \tag{1}$$

$$I = A' + \frac{B'}{t} \tag{2}$$

$$I = a' + \frac{b'}{T} \tag{3}$$

$$I = a + \frac{b}{c + T} \tag{4}$$

where t and T are the column temperature in °C and °K, respectively, and A, B, A', B', a, b, c, a' and b' are constants. To a first approximation, the dependence of I on temperature for homologous series of *n*-alkynes with identical positions of the triple bond is virtually linear (eqn. 1) in the range 20–60°C. The deviations of individual experimental points from the straight lines do not exceed $\pm$ 0.1–$\pm$ 0.8 index units (i.u.).

A better correlation (although very close to eqn. 1) was found with eqns. 2 and 3. Constants a' and b' for eqn. 3 are given in Table I. The mean differences between experimental and calculated I values using these constants are $\pm$ 0.1–$\pm$ 0.2 i.u. (0.3 i.u. on ApL at 130°C) with maximum deviations, observed in a few instances only, of 0.6–0.7 i.u. The linear relationships between I and $1/T$ for *n*-dodecynes are shown in Fig. 1. There is no better matching of our experimental data with the Antoine-type equation (eqn. 4) compared with eqn. 2 or 3.

The variations of I with temperature depend on the polarity of the liquid phase, on the number of carbon atoms and the position of the triple bond in the molecule. The temperature increments, $10(\delta I/\delta T)$, for the *n*-alkynes vary from −0.97 to +0.12 i.u. on SQ, from −0.61 to +0.63 i.u. on ApL, from −0.05 to +0.91 i.u. on PFE and from −1.93 to +0.73 i.u. on PEG (Table II).

On SQ the retention indices of internal *n*-alkynes decrease with increase in temperature, while on PEG they increase (except for C_6–C_{12} 3-alkynes and C_8–C_9 4-alkynes). Contrary to this, the retention indices of 1-alkynes on SQ increase and on PEG they decrease with increase in temperature. On PFE, the I values of *n*-alkynes increase as the column temperature increases. On ApL, in a similar manner to SQ, the retention indices of 1-alkynes increase, but those of most of the internal *n*-alkynes decrease with increase in column temperature.

The effect of chain length on the temperature increments depends on the character of the liquid phase and the position of the triple bond in the molecule. In general, on SQ and ApL lengthening of the carbon chain leads to a decrease in the absolute values of the temperature coefficients for internal *n*-alkynes. In many instances a change from negative to positive values or *vice versa* occurs, *e.g.*, at C_{12}–C_{13} for 2-, 5- and 6-alkynes on ApL and 3-alkynes on PEG ,and at C_9–C_{10} for 4-alkynes on PEG. The temperature increments for 1-alkynes on PFE, as well as those of 5- and 6-alkynes on PFE and PEG, increase gradually as the length of the carbon chain

TABLE I

CONSTANTS a' AND b' FOR THE EQUATION $I = a' + b'/T$ FOR C_6–C_{14} *n*-ALKYNES

Hydrocarbon	*SQ*		*ApL*		*PFE*		*PEG*	
	a'	b'	a'	b'	a'	b'	a'	b'
1-Hexyne	580.4	1312.7					761.8	25027.8
2-Hexyne	620.7	6995.3					837.3	8786.4
3-Hexyne	583.2	14289.0					782.8	16242.5
1-Heptyne	685.5	−434.9					871.8	21937.7
2-Heptyne	723.4	7196.3					970.2	−2060.4
3-Heptyne	689.3	10093.3					875.5	13338.8
1-Octyne	785.7	−727.7					991.8	14912.4
2-Octyne	822.7	7173.4					1077.7	−4907.9
3-Octyne	792.7	9088.1					1002.2	3634.0
4-Octyne	790.3	7609.1					980.2	6669.0
1-Nonyne	889.9	−2191.0			1013.7	−3964.9	1108.0	9515.9
2-Nonyne	926.8	5252.9			1086.4	−7272.8	1180.0	−6492.9
3-Nonyne	891.3	8914.8			1027.8	1823.0	1097.6	4253.3
4-Nonyne	892.5	6573.2			1035.6	−5060.2	1091.6	1332.7
1-Decyne	989.9	−2220.9	1021.4	−10186.1	1118.6	−5752.6	1209.4	9177.2
2-Decyne	1026.2	5522.6	1038.8	5137.7	1204.1	−13309.7	1285.2	−8333.2
3-Decyne	991.9	8156.3	994.9	9626.1	1133.7	−673.8	1203.2	1602.8
4-Decyne	991.3	5330.0	996.7	6014.7	1130.3	−3645.4	1192.9	−292.3
5-Decyne	998.0	3739.4	1008.2	2005.0	1129.5	−3255.0	1195.8	−1876.7
1-Undecyne	1089.9	−2206.8	1104.0	−3563.3	1228.8	−9881.4	1316.8	6364.5
2-Undecyne	1127.9	4723.2	1142.4	3569.1	1287.6	−7601.7	1388.2	−9692.6
3-Undecyne	1080.2	12375.6	1097.6	8255.9	1239.7	−3490.5	1299.3	2594.4
4-Undecyne	1086.5	7042.7	1105.1	2109.3	1238.5	−7402.0	1292.5	−1375.9
5-Undecyne	1091.9	4758.8	1106.3	1411.7	1231.1	−4824.1	1293.3	−2853.7
1-Dodecyne	1184.1	155.4	1222.9	−11506.5	1323.4	−7836.6	1420.8	5047.4
2-Dodecyne	1226.0	5331.2	1244.2	2706.9	1400.2	−12670.5	1487.6	−9200.8
3-Dodecyne	1186.1	9743.6	1190.1	11206.8	1337.2	−3028.8	1401.3	1650.7
4-Dodecyne	1184.9	7043.1	1209.6	−467.2	1343.3	−10288.0	1398.4	−4388.4
5-Dodecyne	1193.8	3004.8	1199.1	3654.8	1336.0	−7747.1	1395.0	−4622.4
6-Dodecyne	1197.8	912.8	1204.1	962.8	1330.8	−5790.4	1393.9	−4755.4
1-Tridecyne			1321.3	−10860.2	1424.2	−8306.4	1523.8	3665.6
2-Tridecyne			1350.9	−59.2	1495.2	−10662.1	1595.3	−12513.4
3-Tridecyne			1304.0	4940.2	1432.7	−1340.2	1509.2	−1724.4
4-Tridecyne			1301.4	2440.8	1430.7	−5846.5	1490.6	−1620.2
5-Tridecyne			1310.1	−1953.6	1430.6	−6367.1	1501.6	−8424.5
6-Tridecyne			1317.8	−6402.1	1441.6	−11239.1	1499.8	−8800.4
1-Tetradecyne			1426.0	−12789.1	1530.9	−11112.4	1632.5	133.8
2-Tetradecyne			1456.6	−2484.8	1588.2	−7645.1	1688.9	−9706.5
3-Tetradecyne			1410.1	2002.5	1528.9	76.3	1608.5	−1602.7
4-Tetradecyne			1404.3	1023.3	1529.6	−5519.3	1599.8	−5843.0
5-Tetradecyne			1417.6	−5346.0	1531.3	−7210.0	1599.6	−8311.6
6-Tetradecyne			1411.3	−4355.0	1540.1	−11749.1	1599.0	−9715.1
7-Tetradecyne			1405.9	−2425.9	1540.1	−12299.0	1602.4	−11816.0

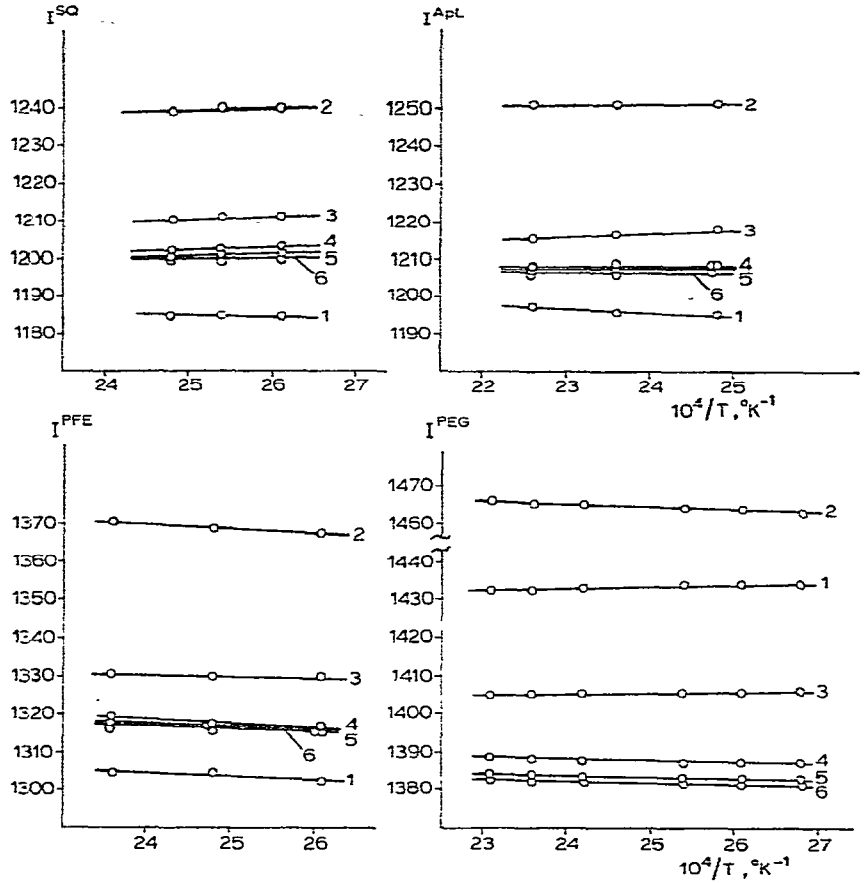

Fig. 1. Dependences of retention indices of *n*-dodecynes on the reciprocal of the absolute column temperature on SQ, ApL, PFE and PEG. The numbers on the lines indicate the position of the triple bond in the molecule.

increases. The variations of the $10(\delta I/\delta T)$ values of 1-alkynes on SQ and ApL, 2-, 3- and 4-alkynes on PFE and 2-alkynes ($>C_7$) on PEG do not show definite patterns with increasing chain length. In the last instance the change from negative to positive values is observed at C_6–C_7.

Plots of $10(\delta I/\delta T)$ values *versus* the position of the triple bond in a molecule are similar for SQ and ApL and for PFE and PEG (Fig. 2). On SQ and ApL the temperature increments grow more negative as the triple bond shifts from the first carbon atom to the third (*e.g.*, on SQ for *n*-dodecynes from −0.01 to −0.66 i.u.) and then increase as the triple bond shifts nearer the centre of the molecule. For the group of positional isomers with identical chain lengths on ApL and SQ, the decrease in I with T is greatest for 3-alkynes. Contrary to this, on PFE and PEG the change in I with increase in T for 3-alkynes is smallest [on PEG in the C_{12}–C_{14} region only, whereas in the range C_9–C_{11} the smallest $10(\delta I/\delta T)$ values occur for 4-alkynes]. Differently from *n*-alkynes, the temperature increments of *n*-alkenes are mostly positive on SQ[3,4] (Fig. 2). In their absolute values they do not differ markedly

TABLE II

TEMPERATURE INCREMENTS OF RETENTION INDICES, $10(\delta I/\delta T)$, FOR ISOMERIC C_6–C_{14} *n*-ALKYNES

Stationary phase	*Number of carbon atoms in molecule*	*Position of triple bond*							*Temperature range (°C)*
		1	*2*	*3*	*4*	*5*	*6*	*7*	
Squalane	6[1]	+0.20[1]	−0.41[1]	−0.80[1]					27– 86
	6	+0.10	−0.54	−0.97					90–130
	7[1]	0.31[1]	−0.27[1]	−0.80[1]					27– 86
	7	0.01	−0.51	−0.73					90–130
	8	0.01	−0.46	−0.57	−0.54				90–130
	9	0.10	−0.33	−0.53	−0.45				90–130
	10	0.12	−0.32	−0.50	−0.40	−0.30			90–130
	11	0.12	−0.34	−0.72	−0.40	−0.30			110–130
	12	−0.01	−0.34	−0.66	−0.44	−0.24	−0.08		110–130
Apiezon L	10	0.60	−0.33	−0.60	−0.33	−0.13			110–150
	11	0.22	−0.18	−0.45	−0.10	−0.10			110–170
	12	0.62	−0.10	−0.61	0.02	−0.20	−0.03		130–170
	13	0.55	0.00	−0.25	−0.13	0.10	0.18		150–190
	14	0.63	0.13	−0.10	−0.07	0.29	0.21	0.13	150–190
Polyphenyl ether	9	0.37	0.47	−0.05	0.29				90–130
	10	0.50	0.91	0.00	0.27	0.20			90–130
	11	0.56	0.50	0.19	0.43	0.34			90–150
	12	0.46	0.68	0.16	0.58	0.52	0.45		110–150
	13	0.55	0.64	0.02	0.35	0.40	0.66		110–170
	14	0.68	0.46	0.00	0.30	0.53	0.61	0.75	110–170
Polyethylene glycol 4000	6	−1.93	−0.51	−1.26					60– 80
	7	−1.68	0.20	−1.03					60– 80
	8	−1.17	0.41	−0.67	−0.49				60– 80
	9	−0.69	0.44	−0.27	−0.03				80–120
	10	−0.64	0.55	−0.13	0.02	0.12			80–120
	11	−0.39	0.58	−0.12	0.11	0.21			100–160
	12	−0.24	0.53	−0.08	0.21	0.22	0.26		100–160
	13	−0.15	0.73	0.05	0.19	0.33	0.52		120–160
	14	−0.07	0.45	0.05	0.29	0.49	0.55	0.64	120–160

for C_9–C_{12} 2-, 3- and 4-alkynes and for the corresponding *cis*-alkenes. On SQ the absolute $10(\delta I/\delta T)$ values for C_6–C_{12} 1-, *cis*-5- and *cis*-6-alkenes are greater than those for the corresponding *n*-alkynes. Contrary to this, the absolute $10(\delta I/\delta T)$ values for C_6–C_8 internal *n*-alkynes are greater than those for the corresponding *cis*-alkenes. On squalane[3] the minimum ($\delta I/\delta T = 0$ mostly) values are found for *trans*-2-alkenes (Fig. 2). These differences in the variation of $\delta I/\delta T$ values between *n*-alkenes and *n*-alkynes reflect their different electronic and geometrical structures. In these solute and solvent interactions, an important role is played by the high rigidity of *n*-alkyne molecules, as discussed by Hively and Hinton[2].

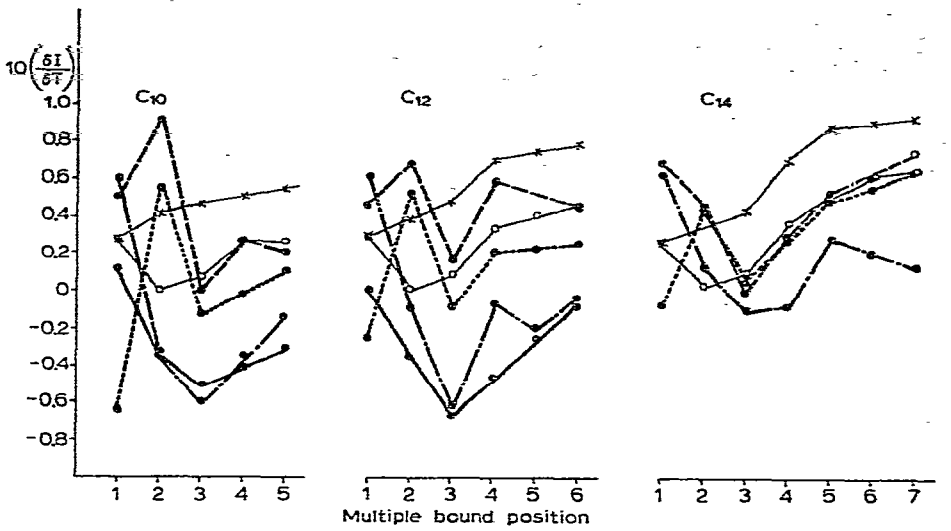

Fig. 2. Variation of $10(\delta I/\delta T)$ values with the position of the triple bond in the molecule for *n*-decynes, *n*-dodecynes and *n*-tetradecynes. Stationary phase: ———, squalane; ·—·—·, Apiezon L; — — —, polyphenyl ether; ·····, polyethylene glycol 4000. Other compounds: ○, *trans*-alkenes[3]; ×, *cis*-alkenes[3]; ⊗, 1-alkenes[3].

The $\delta I/\delta T$ values of 5-, 6- and 7-alkynes do not differ markedly from each other on PFE and PEG.

The *I–T* relationships permit *I* values of C_6–C_{14} *n*-alkynes to be calculated at various temperatures and the most suitable analysis temperature to be chosen; they can also be used for identification purposes and for the calculation of the thermodynamic functions of *n*-alkyne solutions.

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