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CAPILLARY GAS CHROMATOGRAPHY OF C_6—C_{10} ISOALKENES ON POLYETHYLENE GLYCOL 20M

The retention behaviour of 18 selected isoalkenes was investigated on polyethylene glycol 20M (PEG 20M) to obtain data for the identification of compounds of this type in oligomers of ethylene and propylene. Detailed information about the composition of the oligomers is of importance in the petrochemical industry.

From the retention indices (I) measured structure-retention correlations and index increments, important from the viewpoint of characterization, were derived. Up to now literature data on isoolefins, mainly on the C_6—C_9 isomers, have been limited to the values of I on squalane (SQ), silicone stationary phases (OV-1, OV-101, OV-3, OV-7, OV-11, OV-17, OV-22, SE-30, SP-2100) and Citroflex A_4 (CF) [1—5], which are characterized by a lower selectivity with respect to the components of oligomers in comparison with PEG 20M.

Experimental

Gas chromatographic measurements were performed on a Chrom-5 gas chromatograph equipped with a flame ionization detector and a split-type sample injector. The PEG 20M column was prepared in our laboratory by the dynamic coating method using a stainless steel tube with an internal diameter of 0.25 mm and a length of 50 m, the film thickness of PEG 20M was about 0.24 μm. The retention indices were measured at 64, 70 and 75 °C with a carrier gas (helium) linear velocity of 5—6 cm/s and splitting ratio of ~1 : 150, the injector temperature was 250 °C. The gas hold-up time was determined by extrapolation from the retention times of the n-alkanes added to the mixture. The capacity factor determined for n-nonane was 0.42 and the number of theoretical plates was 57,000 (at 70 °C for n-nonane).

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 0.5 absolute index unit (i. u.).

The retention index values calculated from the experimental data are quite satisfactorily described by the following equations:

$$I = A + B/T \tag{1}$$
$$I = a + bn \tag{2}$$
$$I^{PEG} = c + dI^{SQ}, \tag{3}$$

where A, B, a, b, c and d are constants, T is the absolute temperature and n is the number of carbon atoms in a sorbate molecule. The s_0 values characterize the differences between the experimental and the calculated values of I:

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$$s_0 = \sqrt{\sum (I_e - I_c)^2/(z-1)},$$

where I_e is the experimental and I_c the calculated retention index, and z, the number of measurements.

Retention index increments were calculated as follows:

$$10(\delta I/\delta T) = I(75\,°C) - I(65\,°C)$$
$$H = I(\text{isoalkene}) - I(n\text{-alkane})$$
$$\Delta I^{\text{PEG–SQ}} = I(\text{PEG 20M}) - I(\text{SQ}).$$

Results and discussion

The results obtained by us on PEG 20M and the respective literature data [1, 6, 7] on the retention on squalane are summarized in Tables 1 and 2. It can be seen that the retention characteristics depend on the polarity of the liquid phase, the column temperature, the length, position and number of side chains, the position of the double bond in a sorbate molecule and the size of the molecule. The sorbate—liquid phase interaction (determined mainly by dispersion forces) is sensitive to the position of the side chain relative to the double bond. It decreases with the increasing degree of branching as the distance between the force centres of the linkages of the liquid phase and the branched molecule increases in comparison with the linear one. As a result, the energy of dispersion interaction and the retention indices decrease.

In the group of isomers with the same number of carbon atoms compounds with one or more side chains in positions α, β or γ to the double bond have the lowest values of I and H, e.g. 2,6-dimethyl-3-heptene, 2,3,3-trimethyl-1-butene, 2,4-dialkyl-1- and 2-alkenes (Fig. 1). Obviously, branching in these positions hinders most effectively the sorbate—sorbent intermolecular interaction. Branched chain sorbates have lower values

Table 1

Retention indices I, coefficients A, B, standard deviations s_A, s_B, s_0 for Eq. (1), increments $10(\delta I/\delta T)$ and H for isoalkenes at 70 °C on PEG 20M

Hydrocarbons	I	A	s_A	$10^3 B$	$10^3 s_B$	s_0	$10(\delta I/\delta T)$	H
2-Methyl-1-pentene	649.1	689.6	9.5	−13.9	3.2	0.11	1.2	49.1
2-Methyl-2-pentene	669.7	737.0	27.3	−22.9	9.3	0.42	2.2	69.7
2,3,3-Trimethyl-1-butene	689.4	753.6	28.7	−21.8	9.8	0.37	2.0	−10.6
2,4-Dimethyl-2-pentene	693.8	672.5	11.4	7.3	3.9	0.18	−0.7	− 6.2
5-Methyl-1-hexene	707.5	742.5	21.8	−12.2	7.5	0.26	0.8	7.5
2,3-Dimethyl-2-butene	713.8	764.1	9.3	−17.3	3.2	0.06	1.4	113.8
4-Methyl-1-hexene	717.3	757.3	9.8	−13.6	3.3	0.03	1.3	17.3
3-Ethyl-2-pentene	772.1	827.6	12.3	−19.0	4.2	0	1.7	72.1
2,3-Dimethyl-2-pentene	784.8	846.2	17.9	−20.9	6.1	0.21	1.9	84.8
6-Methyl-1-heptene	818.8	881.7	17.4	−21.7	5.9	0.22	1.8	18.8
2,6-Dimethyl-*trans*-3-heptene	834.1	840.4	12.4	− 2.1	4.3	0.06	0.05	−65.9
2-Ethyl-*trans*-2-hexene	843.4	917.9	12.9	−25.6	4.4	0.14	2.0	43.4
2-Methyl-1-heptene	843.7	886.5	18.1	−14.5	6.2	0.27	1.4	43.7
2-Ethyl-1-hexene	845.1	888.7	4.7	−15.0	1.6	0.06	1.3	45.1
2,4-Dimethyl-1-heptene	887.2	933.6	10.3	−15.9	3.5	0.10	1.4	−12.8
2,6-Dimethyl-1-heptene	898.3	916.9	9.9	− 6.4	3.4	0.04	0.6	− 1.7
2-Methyl-4-ethyl-1-hexene	900.7	937.1	20.7	−12.4	7.1	0.28	1.2	0.7
2-Methyl-1-nonene	1041.2	1100.3	—	−20.3	—	0.28	1.7	41.2

Table 2

Retention characteristics I, $10(\delta I/\delta T)$, H values on SQ at 70 °C and $\Delta I^{PEG-SQ}_{70\,°C}$ values for isoalkenes

| Hydrocarbon	I	$10(\delta I/\delta T)$	H	ΔI^{PEG-SQ}
2-Methyl-1-pentene	580.6	0.22	−19.4	68.5
2-Methyl-2-pentene	597.6	−0.11	− 2.4	72.1
2,3,3-Trimethyl-1-butene	630.7	1.12	−69.0	58.7
2,4-Dimethyl-2-pentene	640.0	−0.30	−60.0	53.8
5-Methyl-1-hexene	650.9	0.44	−49.1	56.6
2,3-Dimethyl-2-butene	625.7	0.26	25.7	88.1
4-Methyl-1-hexene	659.3	0.63	−40.7	58.0
2-Methyl-1-hexene	678.5		−21.5	
3-Ethyl-2-pentene	697.7	0.30	− 2.3	74.4
2,3-Dimethyl-2-pentene	704.2	0.38	4.2	80.6
6-Methyl-1-heptene	748.2*		−51.8	70.6
2-Methyl-1-heptene	776.4*		−23.6	67.3
2-Ethyl-1-hexene	779.3*		−20.7	65.8
2,4-Dimethyl-1-heptene	828**		−72	59.2
2,6-Dimethyl-1-heptene	835**		−65	63.3
2-Methyl-1-nonene	972		−28	69.2

* at 40 °C

** at 80 °C

of I in comparison with the corresponding linear compounds. Alkenes with branching at the double bond are the only exception (e.g. 2,3-dimethyl-2-alkenes). Their values of I and H are higher than those of the corresponding linear alkenes. This is obviously caused by an increase in the electrostatic interaction between the solute and the liquid phase molecules (an increase in the electron density on the double bond).

The temperature increments $10(\delta I/\delta T)$ for C_6-C_{10} isoalkenes on PEG 20M vary within the range of −0.7 to 2.2 i.u., they are higher than the corresponding values in nonpolar liquid phases, e.g. squalane. The variation in I with temperature is the largest for 2,3-dimethyl-2-alkenes and 2,3,3-trimethyl-1-butene (~2 i.u.), the lowest value of $10(\delta I/\delta T)$ was observed for 2,6-dimethyl-*trans*-3-heptene. On PEG 20M and SQ the I values of 2,4-dimethyl-2-pentene decrease with increasing temperature — the $10(\delta I/\delta T)$ values are −0.3 and −0.7 i.u., respectively (Table 3).

Fig. 1. Dependence of structural increments $H_{70\,°C}$ on the position of the side chain of isoheptenes on SQ (-----) and PEG 20M (————).

M, E — methyl and ethyl radicals.

D, T — number of side chains (di-, tri-).

Table 3
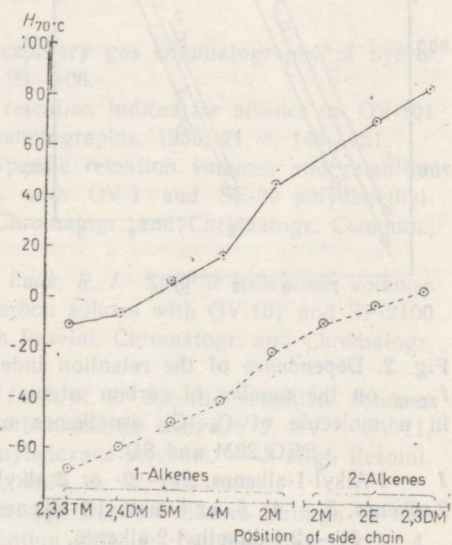
Retention index increments of homologous series of alkenes on PEG 20M and SQ at 70 °C

| Homologous series	$10(\delta I/\delta T)$		H		ΔI^{PEG-SQ}
	SQ	PEG 20M	SQ	PEG 20M	
2-Alkyl-1-alkenes	0.2	1.2...1.7	−19	41...49	68
4,5,6-Methyl-1-alkenes	0.4...0.6	0.8...1.8	−41...−49	7...19	57...58
2,4- and 2,6-Dialkyl-1-alkenes	—	0.6...1.4	—	−13...1	—
2,3,3-Trimethyl-1-alkenes	1.1	2.0	−69	−11	59
2- and 3-Alkyl-2-alkenes	−0.1...0.3	1.7...2.2	−2	43...72	72...74
2,3-Dimethyl-2-alkenes	0.3...0.4	1.4...1.9	4...26	85...114	81...88
2,4-Dimethyl-2-alkenes	−0.3	−0.7	−60	−6	54
2,6-Dimethyl-3-alkenes	—	0.1	—	−66	—
n-1-Alkenes*	0.2...0.3	0.6	−18	42...44	60...62
n-trans-2-Alkenes*	0.0...0.1	0.4	−3.3...−3.4	59...60	62...63
n-cis-2-Alkenes*	0.3...0.4	1.0	0.5...0.9	71...73	70...72
n-trans-3-Alkenes*	−0.03...0.1	0.4	−13.7...−15.7	41...42	55...56
n-cis-3-Alkenes*	0.4...0.5	0.9	−13.6...−15.3	46...48	61...62

* C_9—C_{10} alkenes [8].
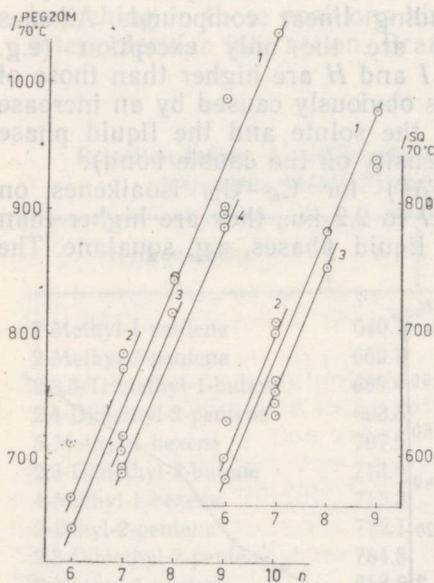
Fig. 2. Dependence of the retention index $I_{70°C}$ on the number of carbon atoms n in a molecule of C_6—C_{10} isoalkenes on PEG 20M and SQ.
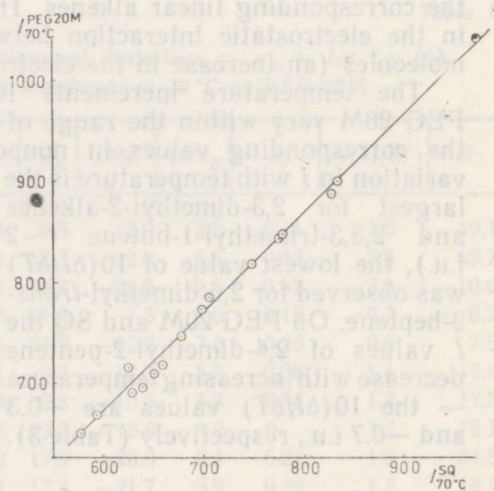1 — 1-Alkyl-1-alkenes, 2 — 2- or 3-alkyl-2-alkenes, 3 — 4-, 5- or 6-methyl-1-alkenes, 4 — 2,4-dimethyl-2-alkenes.

Fig. 3. Plots of I on PEG 20M versus I on SQ for isoalkenes at 70 °C.

The plots of I vs. n on PEG 20M and SQ are parallel straight lines for the homologous series of isoalkenes (Fig. 2). The data obtained can be presented by the following linear equation for 2-alkyl-1-alkenes on PEG 20M:

$$I^{PEG}_{70 °C} = (60.6 \pm 4.0) + (98.0 \pm 0.5)\,n, \quad s_0 = 0.79. \tag{2}$$

The I values of the isoalkenes studied on PEG 20M are by 54—88 i.u. higher than on SQ. This is caused by specific interaction forces between the sorbent and the polar liquid phase. This interaction is more strongly pronounced in 2,3-dimethyl-2-alkenes ($\Delta I = 81 - 88$ i.u.) and the weakest in 2,4-dimethyl-2-pentene ($\Delta I = 54$ i.u.) (Table 3).

The plots of I on PEG 20M versus I on SQ are straight lines for the homologous series of isoalkenes (Fig. 3) and can be presented by a linear equation for 2-alkyl-1- and 2-alkenes:

$$I^{PEG}_{70 °C} = (72.6 \pm 7.0) + (0.995 \pm 0.009)\,I^{SQ}_{70 °C}, \quad s_0 = 2.45. \tag{3}$$

Conclusions

Retention indices for C_6—C_{10} isoalkenes are determined on the PEG 20M capillary column. The I values of isoalkenes on PEG 20M are by 54—88 i.u. higher than on SQ. On PEG 20M isoalkenes with branching at the double bond (2,3-dimethyl-2-alkenes) have the highest retention values whereas isoalkenes with side chains in α, β or γ positions to the double bond (2,6-dimethyl-trans-3-heptene, 2,3,3-trimethyl-1-butene) reveal the lowest values of I.

The linear equations for relationships I vs. $1/T$, I vs. n and I^{PEG} vs. I^{SQ} are presented.

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C_6—C_{10} ISOALKEENIDE KAPILLAARGAASIKROMATOGRAAFIA POLÜETÜLEENGLÜKOOLIL 20M

On määratud 18 erineva struktuuriga C_6—C_{10} isoalkeeni retentsiooniindeksid (I), nende struktuuri- ja temperatuuriinkremendid (H, $10(\delta I/\delta T)$, ΔI^{PEG-SQ}) kapillaarkolonni PEG 20M abil 65, 70 ja 75 °C juures. Polaarse kolonni PEG 20M puhul on isoalkeenide I väärtused 54—88 indeksi ühiku võrra suuremad vastavatest suurustest kolonni SQ kasutamisel. Uuritud isoalkeenidest on suurimad karakteristikud ühendeil, mille külgahelad on kaksiksideme juures, väikseimad aga ühendeil, mille külgahelad asuvad α-, β- või γ-asendis kaksiksideme suhtes.

On arvutatud ka korrelatsioonivõrrandite $I=A+B/T$, $I=a+bn$ ja $I^{PEG}=c+d \cdot I^{SQ}$ koefitsiendid isoalkeenide puhul.

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КАПИЛЛЯРНАЯ ГАЗОВАЯ ХРОМАТОГРАФИЯ ИЗОАЛКЕНОВ C_6—C_{10} НА ПОЛИЭТИЛЕНГЛИКОЛЕ 20M

Изучено поведение 18 изоалкенов C_6—C_{10} на полиэтиленгликоле (ПЭГ) 20M с использованием индексов удерживания I, температурных и структурных инкрементов индексов — $10(\delta I/\delta T)$, H и $\Delta I^{ПЭГ-Ск}$. Величины I изоалкенов на полярном ПЭГ 20M на 54—88 единиц индекса выше, чем на сквалане. Более высокими параметрами удерживания обладают соединения с боковой цепью у двойной связи, более низкими — соединения с боковой цепью в α-, β- или γ-положениях по отношению к двойной связи.

Рассчитаны коэффициенты корреляционных уравнений $I=A+B/T$, $I=a+bn$ и $I^{ПЭГ}=c+d \cdot I^{Ск}$ для изоалкенов.