Inequality of temperature increments of *n*-alkane homologs as one of the reasons for the nonlinear variation of sorption parameters of substances in temperature-programmed gas chromatography

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GC behavior of C_6—C_{17} *n*-alkanes has been investigated at different temperatures of isothermal analysis and under temperature programming conditions using two capillary columns coated with OV—101 and OV—351 stationary phases. Temperature increments have been calculated for the homologs and their inequality has been demonstrated for each member of the *n*-alkane series. It was shown that the nonlinear individual temperature variation of the energy of dispersive interaction of *n*-alkane homologs with the stationary phase, which was observed under isothermal conditions, may be one of the main reasons for the nonlinear change in sorption parameters of *n*-alkanes in temperature-programmed gas chromatography.

Key words: temperature-programmed gas chromatography, temperature increments for *n*-alkanes.

Temperature-programmed gas chromatography (TPGC) is usually employed for the separation of multicomponent mixtures with a wide range of volatilities. Under TPGC conditions the individual retention indices are calculated from the emergence temperatures or from the retention times using the Van den Dool and Kratz[1] equation based on the assumption that the dependence of the retention parameters of *n*-alkane homologs on their molecular mass is linear, but this does not take into account the variation of the retention time of the non-sorbed gas ("dead time") with temperature programming. Previous studies[1,2] have shown that when the "dead time" of a column is taken into account not only do the individual retention parameters change but so does their ratio. It has also been shown that during TPGC on stationary phases with different polarities the relationship between the retention time (or temperature) and the number of C-atoms in the *n*-alkanes is nonlinear.[1,3,4] The TPGC retention parameters depend on the start temperature (T_0), programming rate (r), carrier gas flow rate, and on the variation of the energy of the intramolecular interactions with the analysis temperatures, which influences the temperature increments of substances dI/dT.[2,5,7]

The present paper studied the variation of the retention parameters of *n*-alkanes and their temperature increments with both the analysis temperature and the molecular mass (M) of the homologs under isothermal conditions and also with the programming parameters during TPGC.

Experimental

In this study C_6—C_{17} *n*-alkanes were investigated. GC analysis was carried out using a Micromat-412 (Nordion Instr., Finland) instrument with a flame ionization detector. Capillary columns 1) prepared by us using a high pressure static method[8] (glass, 50 m × 0.25 mm) and 2) produced by Nordion Instr. (fused silica film, 25m × 0.32 mm), coated, respectively, with stationary phases OV—101 and OV—351, were used. The thickness of OV—101 and OV—351 (d_f) were 0.25 and 0.20 μ, respectively.

The retention parameters of *n*-alkanes were determined under TPGC conditions at linear programming rates 2, 4, 8 K min^{-1} and start temperatures 70, 80, 100 °C and also isothermally at temperatures 70, 90, 110, 130, and 150 °C (Table 1). The temperatures of the injector and detector were 225 and 250 °C, respectively. The splitting of carrier gas (He) was 1:100. Mixtures of C_6—C_{12} and C_8—C_{17} *n*-alkanes were prepared by dissolving 1 μl of the individual alkane in pentane (1 mL). The size of the injected sample was 0.2—0.3 μl.

Programmed retention parameters were determined using the expression:

$$k' = t'_p / \sigma_0 , \qquad (1)$$

where $t'_p = t_p - \sigma_0$; t_p and t'_p are the retention time and corrected retention time, respectively, σ_0 is the retention time of non-sorbed gas (CH_4).

The σ_0 values were calculated with Eq. (2) using CH_4 retention times obtained isothermally

$$\sigma_0 = (t^{iso}{}_{0,T_0} + t^{iso}{}_{0,T_n})/2 , \qquad (2)$$

where $t^{iso}{}_{0,T_0}$ and $t^{iso}{}_{0,T_n}$ are the retention times of non-sorbed

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 642—645, April, 1994.

Table 1. The corrected retention times t' (s) of *n*-alkanes determined isothermally at different temperatures using capillary columns coated with OV—101 and OV—351

C_n	70 °C	90 °C	110 °C	130 °C	150 °C
			OV—101		
C_6	17.0	9.4	6.2	4.5	2.8
C_7	38.4	20.6	12.8	8.5	5.5
C_8	84.9	42.8	25.0	15.4	9.9
C_9	185.6	87.3	47.1	27.3	17.1
C_{10}	402.6	175.7	88.9	48.0	28.9
C_{11}	868.7	350.7	165.2	83.6	48.2
C_{12}		696.4	305.4	144.8	79.6
			OV—351		
C_8	13.0	5.6	3.3	1.9	0.7
C_9	27.0	11.1	6.5	3.9	2.0
C_{10}	56.0	21.3	12.1	7.2	4.0
C_{11}	115.5	40.2	21.7	12.6	7.2
C_{12}	238.2	75.0	38.3	21.3	12.1
C_{13}	491.3	139.0	66.9	35.6	19.8
C_{14}	1012.0	256.6	116.3	58.7	31.8
C_{15}	2096.3	473.6	201.3	96.5	50.4

gas determined, respectively, under two isothermal conditions, T_0 is the starting programming temperature, T_n is the emergence temperature of *n*-alkane under TPGC conditions.

Results and Discussion

Nonlinear variations of t' and the capacity factor k' were studied isothermally and under TPGC conditions.

Isothermal GC analysis. The variation of the retention parameter of a individual substance (*i*) with analysis temperature (T_{iso}) is usually described by the expression:

$$\lg t'_i = a_i + b_i/T_{\mathrm{iso}}\,, \qquad (3)$$

where a_i and b_i are coefficients for the substance *i*.

As was shown in the case of *n*-hexane and benzene[9] the following equation describes the relationship between the retention time of substances and the analysis temperatures more accurately.

$$\lg t' = a_i + b_i T_{\mathrm{iso}} + c_i \lg T_{\mathrm{iso}}\,. \qquad (4)$$

Table 2. Standard deviations (S/103) of lg t' determined for *n*-alkanes experimentally using capillary columns with different polarities and calculated with equations (3) and (4)

C_n	OV—101		C_n	OV—351	
	Calculated by (3)	Calculated by (4)		Calculated by (3)	Calculated by (4)
C_6	45	52	C_8	95	39
C_7	19	25	C_9	90	29
C_8	16	15	C_{10}	92	33
C_9	24	8	C_{11}	80	50
C_{10}	27	8	C_{12}	109	70
C_{11}	31	8	C_{13}	127	74
C_{12}	34	10	C_{14}	143	78
			C_{15}	160	83

Table 3. Coefficients of Eq. (4) for the calculation of lg t'_i for *n*-alkanes

C_n	a_i	b_i	c_i
		Phase OV—101	
C_6	98.94261	0.02531	17.95520
C_7	126.99760	0.03722	23.31889
C_8	153.25017	0.04747	28.28176
C_9	181.63951	0.05850	33.65771
C_{10}	199.71824	0.06392	36.94051
C_{11}	221.00493	0.07095	40.86802
C_{12}	234.88937	0.07412	43.30294
		Phase OV—351	
C_8	−64.01711	−0.07619	−15.86958
C_9	139.17918	0.03514	25.34959
C_{10}	226.51856	0.08040	42.84472
C_{11}	294.60156	0.11406	56.36079
C_{12}	347.93486	0.13896	66.83564
C_{13}	397.84234	0.16169	76.59697
C_{14}	444.55028	0.18247	85.69537
C_{15}	490.51343	0.20261	94.62796

To choose the best correlation of the corrected retention times of *n*-alkanes (Table 1) with T_{iso} we compared the values of lg t' calculated for series of C_6—C_{12} and C_8—C_{15} *n*-alkanes using Eq. (3) and (4) and columns with the OV—101 and the OV—351. Table 2 shows that Eq(4) is more accurate than Eq(3). Standard deviations of lg t' obtained with Eq. (4) using experimental data for all *n*-alkanes (Table 1) are within

Table 4. *n*-*A*lkane temperature increments, determined isothermally at different temperatures

C_n	70—90°C	90—110°C	110—130°C	130—150°C
		Phase OV—101		
C_6	0.2962	0.2081	0.1602	
C_7	0.3114	0.2371	0.2047	
C_8	0.3425	0.2688	0.2423	0.2209
C_9	0.3771	0.3085	0.2727	0.2339
C_{10}	0.4146	0.3406	0.3082	0.2537
C_{11}	0.4535	0.3764	0.3406	0.2753
C_{12}	0.4122	0.3731	0.2992	
		Phase OV—351		
C_8	0.4211	0.2644	0.2760	
C_9	0.4444	0.2676	0.2554	
C_{10}	0.4833	0.2828	0.2596	
C_{11}	0.5277	0.3083	0.2718	
C_{12}	0.5778	0.3360	0.2934	0.2828
C_{13}	0.6313	0.3656	0.3154	0.2933
C_{14}	0.6861	0.3957	0.3419	0.3065
C_{15}	0.7438	0.4278	0.3676	0.3248
	30—40°C	40—50°C	50—60°C	70—80°C
		Phase OV—101[12]		
C_5	0.3258	0.3056	0.2875	0.1275
C_6	0.3818	0.3592	0.3372	0.2998
C_7	0.4388	0.4117	0.3874	0.3438
C_8	0.4959	0.4649	0.4367	0.3885
C_9	0.5518	0.5186	0.4862	0.4324
C_{10}	0.6018	0.5708	0.5370	0.4769

experimental error (Table 2). Errors of Eq. (4) are 1.5—3 times lower then those of Eq. (3). Table 3 presents coefficients of Eq. (4) for the calculation of lg *t'* for all *n*-alkanes. These values depend both on the number of C-atoms in the *n*-alkane and the polarity of the stationary phase.

It is generally accepted,[5-7] that the temperature increment d(lg *t'*)/d*T* is a constant value for all members of a homologous series, but this is not the fact. Eq. (5) derived from Eq. (4) permits one to calculate this parameter for each homolog:

$$d(\lg t'_i)/dT_{iso} = b_i + c_i/T_{iso}, \quad (5)$$

where b_i, c_i are coefficients of Eq. (4). Their values depend both on the number of C-atoms in *n*-alkanes and the polarity of the stationary phase. (Table 3). This attests to the variability of *n*-alkane temperature increments. To illustrate this assumption we calculated the variations of d(lg *t'*)/10°C for *n*-alkanes under isothermal conditions using both data of Ref. 10 and our own data (Table 4). The values d(lg *t'*)/10°C calculated using the data of the Ref. 11 are also presented in table 4 for comparison. One can see that d(lg *t'*)/10°C increases with the molecular weight and decreases with the analysis temperature. For instance, for C_8 and C_{15} these values obtained at 70—90°C using the column coated with OV—351 are equal to 0.4211 and 0.7438, respectively. For C_{10} the variation of d(lg *t'*)/10°C from 0.4146 to 0.2537, determined at temperatures 70—150 °C using the column with OV—101 is nonlinear.

Thus, the variation of the temperature increments of *n*-alkanes with the number of C-atoms is nonlinear under isothermal conditions in the case of both polar and non-polar columns.

TPGC analysis. Considerable distinctions in the temperature increments of *n*-alkanes determined under isothermal conditions should influence their TPGC retention parameters.

The behavior of C_6—C_{17} *n*-alkanes was also investigated using columns coated with OV—101 and OV—351. The retention times were calculated with correction to the retention time of non-sorbed gas. The corrected retention times and the capacity factor were calculated using Eq. (1) and (2).

Table 5. Capacity factor (*k'*)determined at different PTGC initial temperatures and *r* = 4 K min^{-1} using polar and non-polar stationary phases.

C_n	OV—101			OV—351		
	70 °C	80 °C	100 °C	70 °C	80 °C	100 °C
C_6	0.16	0.12	0.09			
C_7	0.32	0.24	0.18			
C_8	0.63	0.47	0.33	0.13	0.12	0.06
C_9	1.12	0.85	0.59	0.25	0.24	0.14
C_{10}	1.83	1.41	1.00	0.50	0.48	0.26
C_{11}	2.70	2.15	1.58	0.97	0.92	0.49
C_{12}	3.63	2.99	2.29	1.77	1.67	0.87
C_{13}				3.02	2.86	1.51
C_{14}				4.76	4.52	2.49
C_{15}				6.88	6.58	3.87
C_{16}				9.19	8.84	5.58
C_{17}				11.59	11.20	7.56

Table 6. Capacity factor (*k'*) determined at different programming rates and T_0 = 70 °C using polar and non-polar stationary phases

C_n	OV—101		OV—351	
	2 K/min	8 K/min	2 K/min	8 K/min
C_6	0.16	0.15		
C_7	0.35	0.28		
C_8	0.72	0.51	0.12	0.11
C_9	1.38	0.95	0.26	0.23
C_{10}	2.43	1.28	0.53	0.46
C_{11}	3.85	1.76	1.05	0.85
C_{12}	5.53	2.26	2.00	1.45
C_{13}			3.62	2.30
C_{14}			6.13	3.32
C_{15}			9.54	4.45
C_{16}			13.57	5.60
C_{17}			18.00	6.73

When comparing the variation of *k'* and *t'* of *n*-alkanes with the initial programming temperature and programming rate *r* we found that the noted variation of *k'* and *t'* with T_0, *r* and increasing *M* are alike, which is confirmed by the data on *k'* variation presented in Tables 5 and 6. The data of Table 5 show that increasing T_0 results in a noticeable decrease in *k'* of *n*-alkanes. For instance, *k'* values determined at the initial programming temperature T_0 = 100 °C on phases OV—101 and OV—351 are, respectively, 52—63 % and 46—65 % of those, determined at T_0 = 70 °C.

The decrease of *k'* with increasing *r* depends on the *n*-alkane temperature increments. For example, on OV—351, raising *r* from 2 to 8 K min^{-1} results in a decrease in *k'* by 1.09 times for C_8 (Table 6) and by 2.14 for C_{15}, which possesses a greater isothermal temperature increment (Table 4). At a steady programming rate *r* the variation in *k'* with the number of C-atoms in a homologous series of *n*-alkanes is nonlinear. For example the difference between *k'* determined for C_9- and C_8-*n*-alkanes at a programming rate of 2 K min^{-1} using OV—351 is equal to 0.14, while it is 4.43 for C_{17}- and C_{16}-*n*-alkanes (Table 6). Thus, the nonlinearity of the variation of *k'* (or *t'*) with the number of C-atoms increases as both the programming rate and the molecular wieghts of the *n*-alkanes increase.

The present work was carried out with the financial support of the Russian Foundation for Basic Research (Grant 93-03-4969).

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Received June 26, 1993