Dependence of the relative retention of compounds on the average pressure of helium as a carrier gas in capillary GLC

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The dependence of retention factor k_i, relative retention time α_i, and retention index I_i of organic compounds on the average pressure (p_{av}) of the carrier gas (helium) was studied experimentally using a long narrow-bore capillary column with the SE-30 nonpolar phase at 120 °C. The linear dependences $k_i = f(p_{av})$, $\alpha_i = \psi(p_{av})$, and $I_i = \varphi(p_{av})$ obtained previously were found to be in good agreement with experimental data. Invariant relative retention values $k_{0,i}$, $\alpha_{0,i}$, and $I_{0,i}$, which do not depend on the helium pressure, were determined for some organic compounds of various chemical classes. The dependence of the relative retention on the carrier gas pressure needs to be taken into account in precision measurements and in experiments with narrow-bore capillary columns.

Key words: capillary gas-liquid chromatography, relative retention values, retention factor, relative retention time, retention index.

At present, capillary gas-liquid chromatography (GLC) is the main gas chromatography (GC) technique. Relative retention parameters are normally regarded in GLC as chromatographic constants and are widely used for identification of compounds (see, for example, Refs. 1—4). However, detailed studies[5] have shown that relative retention values depend linearly on the average pressure of the carrier gas (p_{av}) in the capillary column:

$$k_i = k_{0,i} + b_{k_i} \cdot p_{av}, \qquad (1)$$

$$\alpha_i = \alpha_{0,i} + b_{\alpha_i} \cdot p_{av}, \qquad (2)$$

$$I_i = I_{0,i} + b_{I_i} \cdot p_{av}, \qquad (3)$$

where k_i, α_i, and I_i are the retention factor, relative retention time, and retention index for an ith sorbate, respectively; b_{k_i}, b_{α_i}, b_{I_i} are constants for Eqs. (1)—(3); $k_{0,i}$, $\alpha_{0,i}$, $I_{0,i}$ are invariant retention values (retention factor, relative retention time, retention index) found by extrapolation of the corresponding dependences to the zero pressure.

Equations (1)—(3) describe adequately the experimental data obtained with H_2, N_2, and CO_2 used as carrier gases.[5] However, for helium, dependences of type (1)—(3) have not been studied. The necessity to investigate these dependences for helium is due to the following reasons: helium is the most "ideal" carrier gas, which is used most frequently in gas chromatography;[6—9] therefore, it can be suggested that for helium, the above dependences do not hold.

In this work, we studied the dependence of the relative retention on the average pressure of helium used as the carrier gas in a capillary column.

Since in recent years, considerable attention has been paid to GC on high-performance narrow-bore columns,[10] our experiments were carried out using a column of this type.

Experimental

Chromatographic studies were carried out on a modified LKhM-8MD gas chromatograph (the 5th modification) with a flame ionization detector (the "Chromatograph" plant, Moscow).

The retention times of sorbates were measured using a modified I-02 integrator (the "Mikroprovod" plant, Moldova) with a resolution of 0.1 s. A 75 m × 0.14 mm quartz capillary column with SE-30 as the stationary liquid phase was used in the experiments (the film of the stationary liquid phase (SLP) was ≈ 0.3 μm thick). Helium was used as the carrier gas. The carrier gas pressure at the inlet of the column was 2.5—25.0 atm, the carrier gas split ratio was 1 : 150, the columns and the detector were maintained at 120 °C, and the injector temperature was 275 °C. The sensitivity of the flame ionization detector was $1 \cdot 10^{-11}$ Afs.

The average carrier gas pressure in the column (p_{av}) was calculated from the known relation[11]

$$p_{av} = p_0 \frac{3}{4} \frac{(p_i/p_0)^4 - 1}{(p_i/p_0)^3 - 1}, \qquad (4)$$

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 314—316, February, 1998.

where p_i and p_0 are the inlet and outlet carrier gas pressures, respectively.

The mixture of test compounds contained 1—2% each of C(10)—C(12) *n*-alkanes, octan-1-ol, 2,6-dimethylphenol, 2,6-dimethylaniline, and naphthalene in *n*-hexane. Samples to be analyzed were injected with a microsyringe (1 μL). The sample size was 0.1—0.5 μL of a mixture of test compounds and 0.5 μL of methane. Each retention value was found as the average of five entries, and the mean square deviation normally did not exceed 0.2—0.3%.

Results and Discussion

Tables 1—3 present characteristics for the dependence of retention factors, relative retention times, and retention indices on the average pressure of the carrier gas (helium) in the capillary column.

Table 1. Parameters of the dependence of the retention factors of organic compounds on the average pressure of helium in a capillary column with SLP SE-30 (Eq. (1))

Sorbate	k_0	b_k	*R*	MV
n-Decane	1.413±0.007	−0.0025±0.0005	0.918	0.007
Octan-1-ol	1.932±0.009	−0.0034±0.0008	0.904	0.010
2,6-Dimethylphenol	2.363±0.012	−0.0048±0.0010	0.920	0.013
n-Undecane	2.504±0.012	−0.0043±0.0010	0.908	0.013
2,6-Dimethylaniline	3.300±0.018	−0.0067±0.0014	0.917	0.019
Naphthalene	3.860±0.020	−0.0079±0.0017	0.922	0.021
n-Dodecane	4.420±0.021	−0.0072±0.0017	0.901	0.022

Note. Here and in Tables 2 and 3, *R* is correlation coefficient, MV is multiple variance.

Table 2. Parameters of the dependence of relative retention of organic compounds on the average pressure of helium in a capillary column with SLP SE-30 (Eq. (2))

Sorbate	α_0	b_α	*R*	MV
Octan-1-ol	1.369±0.002	−0.0001±0.0000	0.955	0.0002
2,6-Dimethylphenol	1.674±0.001	−0.0008±0.0001	0.969	0.0009
n-Undecane	1.773±0.000	−0.0001±0.0000	0.969	0.0010
2,6-Dimethylaniline	2.339±0.002	−0.0011±0.0002	0.945	0.0019
Naphthalene	2.735±0.002	−0.0014±0.0002	0.968	0.0018
n-Dodecane	3.128±0.021	0.0005±0.0001	0.928	0.0013

Note. n-Decane was used as the standard.

Table 3. Parameters of the dependence of the retention indices of organic compounds on the average pressure of helium in a capillary column with SLP SE-30 (Eq. (3))

Sorbate	I_0	b_I	*R*	MV
Octan-1-ol	1054.61±0.03	0.0056±0.0022	0.869	0.022
2,6-Dimethylphenol	1090.07±0.11	−0.0825±0.0104	0.977	0.093
2,6-Dimethylaniline	1148.81±0.10	−0.0939±0.0103	0.982	0.092
Naphthalene	1176.40±0.07	−0.1032±0.0069	0.993	0.061

For all the organic compounds studied belonging to various classes, the above-mentioned relative values obey monotonic dependences on the average pressure of helium in the column. These dependences can be regarded as linear. The correlation coefficients and standard approximation errors[12] are also presented in Tables 2—4. These results indicate that the linear approximation of the dependences studied is quite satisfactory. The above results also imply that limiting (for $p_{av} \to 0$) retention values $k_{0,i}$, $\alpha_{0,i}$, and $I_{0,i}$ rather than the relative retention values used traditionally (see, for example, Ref. 13) should be regarded as true chromatographic constants.

If the rates of variation of the relative retention values as functions of the pressure (for example, for the retention factor, $dk_i/dp_{av} = b_{k_i}$) are compared with one another, it can be seen that in the case of helium, the dependence of the relative retention on the average carrier gas pressure is less pronounced than these dependences for other carrier gases (see Table 4). Note that, according to a previous publication,[14] the solubility of He in hexadecane at 25 °C is ~5 times lower than the solubility of N_2 (dissolved carrier gases change the properties of an SLP and have an effect on the distribution coefficients of the sorbates). This also made it possible to suggest that in the case of He, the dependence of the retention on the average pressure of the carrier gas in the column should be markedly less pronounced than for N_2, and this was confirmed experimentally.[5] The $I_i = \varphi(p_{av})$ dependence for He is much less clearly defined than those for H_2 and for the other gases (see Table 4). Comparison of our results with those reported in the study cited[5] leads to the conclusion that, in terms of the extent to which the relative retention depends on the pressure and on the nature of the carrier gas, the gases studied can be arranged in the following sequence: He < H_2 < N_2 < CO_2, because $b_{I_i}(\mathrm{He}) < b_{I_i}(\mathrm{H_2}) < b_{I_i}(\mathrm{CO_2})$.

By using known equations for the absolute retention values (see, for example, Refs. 15, 16) taking into account the fact that relative retention values are found as the ratios of the corresponding absolute values (see, for example, Refs. 1—3), we obtain

$$b_{\alpha_i} = \alpha_{i,0} \cdot \Delta\beta_{i,\mathrm{st}}, \tag{5}$$

$$\Delta\beta_{i,\mathrm{st}} = \beta_i - \beta_{\mathrm{st}}, \tag{6}$$

Table 4. Comparison of coefficients b_{I_i} (Eq. (3)) for three carrier gases: He, H_2, and N_2

Sorbate	b_{I_i}		
	He	H_2	N_2
Octan-1-ol	0.0056	0.091	0.203
2,6-Dimethylphenol	−0.0825	0.137	0.326
2,6-Dimethylaniline	−0.0939	0.155	0.364
Naphthalene	−0.1032	0.153	0.411

Note. The calculations for H_2 and N_2 were based on published data.[5]

$$\Delta\beta_{i,\mathrm{st}} = \frac{2(B_{i,\mathrm{m}} - B_{\mathrm{st,m}}) - (V_i^0 - V_{\mathrm{st}}^0)}{RT} + \lambda\left[\frac{\mathrm{d}\ln\gamma_{\mathrm{st}}^{\infty}}{\mathrm{d}X_{\mathrm{m}}} - \frac{\mathrm{d}\ln\gamma_i^{\infty}}{\mathrm{d}X_{\mathrm{m}}}\right], \quad (7)$$

where $B_{i,\mathrm{m}}$ and $B_{\mathrm{st,m}}$ are the second virial coefficients characterizing the interaction of the molecules of a substance (i) and a standard (st) with molecules of a carrier gas in the gas phase; V_i^0 and V_{st}^0 are molar volumes of the substance (i) and the standard (st); R is the gas constant; T is the absolute temperature; λ is the molar solubility of the carrier gas in the SLP; γ_i^{∞} and $\gamma_{\mathrm{st}}^{\infty}$ are the activity coefficients of the sorbate (i) and the standard (st) in the SLP; and X_{m} is the mole fraction of the carrier gas dissolved in the SLP.

It follows from Eqs. (5)—(7) that the magnitude of b_{α_i} (and its sign) are determined by the difference between the corresponding values (see Eq. (7)) characterizing the interaction of the compounds subjected to chromatography with the carrier gas and the change in the properties of the SLP caused by dissolution of the carrier gas in it.

The negative b_{I_i} coefficients found for some compounds merely indicate that the differences between the second virial coefficients of these compounds in He, on the one hand, and in H_2 and N_2, on the other hand, have opposite signs (see, for example, Ref. 5).

If the second virial coefficients are used as a measure of non-ideality of the gases under consideration,[17,18] then in order of increased non-ideality, these gases are also arranged in the above-presented sequence.

Thus, for helium, which is the most ideal gas, the relative retention also does depend somewhat on the average carrier gas pressure in the chromatographic column, although this dependence is less pronounced than those for other carrier gases. Nevertheless, these effects are significant and should be taken into account in high-precision measurements of retention values, especially those carried out at high carrier gas pressures.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 96-03-34451).

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Received June 30, 1997;
in revised form August 1, 1997