Investigation of the role of the carrier gas in capillary gas-solid chromatography

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Nonideal interactions of the sorbate and the carrier gas and adsorption of the sorbate on the adsorbent surface in capillary gas-solid chromatography were studied. Chromatographic retention was found to be largely determined by adsorption processes. With respect to the retention coefficients (capacity factors) of a sorbate (k) with different carrier gases (P_1 and P_2), the correlation relationship $k(P_2) = A \cdot k(P_1) + B$ (A, B are parameters of the equation) is closely obeyed. The advantages of carbon dioxide as the carrier gas were analyzed; the use of carbon dioxide allows the efficiency of the column to be enhanced.

Key words: capillary gas-solid chromatography, separation of hydrocarbon gases, correlation equations for retention values.

For a long time carrier gas was considered to be just an inert participant in the chromatographic process.

Several cases in which the carrier gas had a noticeable effect on retention in gas-solid chromatography (GSC) have been reported in the chromatographic literature.[1-4] However, in our opinion, the role of carrier gas as an active participant in the chromatographic process has not been adequately studied.[5-8]

Table 1. Some physical properties of carrier gases in GC[10-12]

Properties	Carrier gas			
	Hydrogen	Helium	Nitrogen	Carbon dioxide
Molecular weight	2.016	4.002	28.016	44.01
Density with respect to hydrogen	1.00	1.99	13.9	21.99
Boiling point/°C	−252.90	−268.94	−195.76	−78.50
Critical temperature/°C	−239.9	−267.9	−147.1	31.1
Critical pressure/atm	12.80	2.26	33.50	73.00
Self-diffusion coefficient				
1) $cm^2\ s^{-1}$	1.280	1.620	0.170	0.097
2) rel. units	7.53	9.53	1.00	0.57
Viscosity				
1) 10^{-8} kg $cm^{-1}\ s^{-1}$ (at 50 °C)	938	2065	1883	1607
2) rel. units	0.498	1.097	1.00	0.85
Heat conductivity coefficient, 10^5 cal $cm^{-1}\ s^{-1}\ deg.^{-1}$ (at 100 °C)	49.94	39.85	7.18	5.06

In recent years, the number of studies dealing with GSC increased, mostly due to the adoption of its capillary version in practice (see, for example, the review[9]). However, in the published papers,[1-5,9] the investigation of the role of the carrier gas was limited to quasi-ideal permanent gases such as hydrogen, helium, and nitrogen; besides, the authors of these papers as a rule studied only the kinetic aspect of the effect of the carrier gas on the chromatographic characteristics of the compounds being analyzed. Therefore, in view of the high accuracy of the measurement of the equilibrium chromatographic values (capacity factor, relative retention time) in capillary gas chromatography (CGC), it seemed expedient to us to carry out a systematic study of the effect of the carrier gas on the characteristics of retention and band broadening in relation to both permanent gases (hydrogen, helium, nitrogen) and highly nonideal carbon dioxide.

The choice of carbon dioxide as the mobile phase is explained by the fact that it has a lower diffusion ability and a lower viscosity than other gases (like helium and nitrogen) and can be efficiently sorbed (Table 1).[10-12]

Experimental

Chromatographic measurements were carried out on a modified LKhM-8MD gas chromatograph with a flame ionization detector (produced at the "Khromatograf" plant, Moscow, Russia). A 50 m×0.32 mm capillary column of the "Chrompack" company (Netherlands) and Al_2O_3/KCl (5 μm) sorbent were used in the experiments. The rate of the carrier

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gas was determined from the retention time of methane and by direct measurement of the flow rate of the carrier gas. The values obtained coincided with an accuracy of ±5 %. Calculations were also carried out using the Flowcalc program of the Hewlett-Packard company. The phase ratio for adsorption columns $\beta = (V_g/g)$ (V_g is the volume of the gas phase in the column, and g is the mass of the adsorbent in the column[13]) was calculated based on the specific gravity of Al_2O_3, 2.47 g cm^{-3};[14] $\beta = 32.56$. Hydrogen, helium, nitrogen, and carbon dioxide were used as carrier gases. The pressures at the inlet of the column were: 0.7 atm for hydrogen, 1.05 atm for helium, 0.6 atm for nitrogen, and 0.55 atm for carbon dioxide. The ranges of pressure variation for attaining high velocities of gas flow (up to 100 cm s^{-1}) were the following: up to 1.9 atm for H_2, up to 4 atm for He, up to 3.7 atm for N_2, and up to 3.3 atm for CO_2. The oven temperature and the temperature of the detector were 90 °C. The temperature of the injector was 150 °C. The mixture of test compounds contained ~2 % each of methane, ethane, ethylene, propane, propylene, isobutane, butane, *trans*-2-butene, isobutylene, and *cis*-2-butene in helium. The volume of the sample being analyzed was 5 mL. The reproducibility of the capacity factor was no worse than 0.3 %.

Results and Discussion

1. Effect of the carrier gas on the retention values of chromatographic compounds

1.1. Adsorption mechanism of the effect of the carrier gas on the capacity factor. The effect of the nature of the carrier gas on the retention values results mostly from two factors: (1) modification of the surface of the adsorbent with molecules of the carrier gas and (2) nonideal interactions of molecules of the chromatographed compounds with the carrier gas molecules.

To evaluate the nonideal interactions occurring in the gas phase, we use the dependences of the capacity factors (capacity coefficients) for the compounds being chromatographed on the nature (and the pressure) of the carrier gas used, which have been obtained under the conditions of gas-liquid chromatography (GLC), when adsorption phenomena can be neglected and the whole effect can be explained by the effect of the nature of the carrier gas on the processes occurring in the gas and liquid phases.

The effect of the carrier gas on the capacity factor can be evaluated by using the ρ_g value:

$$\rho_g = \frac{k(G_1) - k(G_2)}{k(G_1)}, \qquad (1)$$

where $k(G_1)$ and $k(G_2)$ are capacity factors with two carrier gases G_1 and G_2 of various natures. Table 2 presents the relevant published data.[15,16] As follows from the Table, when one permanent gas is replaced by another permanent gas, the capacity factors of the C_5—C_7 hydrocarbons change, on the average, by no more than ~3 %, and when helium is replaced by carbon dioxide, the relative alteration of the capacity factor is ~4 %. Thus, the nonadsorption effect of the nature of the carrier gas on the mobile and stationary liquid phases is low; however, it exceeds the experimental error (according to Ref. 15, the reproducibility of the values for capacity factors is better than ±0.3 %).

In the present work the effect of the nature of the carrier gas on GSC was studied using the variation of the capacity factors of the C_1—C_4 hydrocarbon gases as an example.

Taking into account the facts that gaseous hydrocarbons are characterized by smaller second virial coefficient than liquid hydrocarbons and that with an increase in the temperature of the experiment, the nonideal interactions with the carrier gas are manifested to a lesser degree, one may assume that the change of the carrier gas should alter the capacity factors of gaseous hydrocarbons by no more than 1—2 %.

The above estimate of the role of nonideal interactions of hydrocarbon gases with the carrier gases under study should be taken into account in the interpretation of the data on the effect of the nature of carrier gases on the capacity factors of the chromatographed compounds.

Table 3 presents the capacity factors and the ρ_g values of hydrocarbon gases in an adsorption capillary column packed with Al_2O_3/KCl. It can be seen that the replacement of one permanent gas by another has an

Table 2. Effect of the nature of the carrier gas on the capacity factors (*k*) and the ρ_g^{max} values[a] of some hydrocarbons in capillary GLC (based on the data taken from Refs. 15 and 16)

Chromatographed compound	Conditions of the experiment[b]		Capacity factors						
	Stationary liquid phase[c]	Inlet pressure	Helium	Hydrogen	Nitrogen	Argon		Carbon dioxide	
						k	ρ_g^{max}	*k*	ρ_g^{max}
2,3-Dimethylbutane	Squalane	3.9	1.030	1.020	0.995	0.985	0.04	0.968	0.06
2,3-Dimethylpentane	»	3.9	2.153	2.121	2.063	2.040	0.05	1.994	0.07
3,3-Dimethylpentane	»	3.9	2.901	2.860	2.779	2.752	0.05	2.687	0.07
n-Pentane	1-Octadecene	2.1—2.5	0.680	—	—	0.660	0.03	0.680	0.00
n-Hexane	»	2.1—2.5	2.160	—	—	2.140	0.01	2.180	0.01
Methylcyclopentane	»	2.1—2.5	2.680	—	—	2.680	0.00	2.730	0.02

[a] ρ_g^{max} was calculated from Eq. (1), where G_1 is helium. [b] The temperature of the column was 25 °C. [c] The data for squalane were taken from Ref. 13, and those for 1-octadecene were taken from Ref. 14.

Table 3. Capacity factors (k) and ρ_g values of hydrocarbon gases for various carrier gases in an adsorption capillary column with Al_2O_3/KCl calculated from Eq. (1)

Chromatographed compound	Carrier gas						
	Hydrogen	Helium		Nitrogen		Carbon dioxide	
	k	k	ρ_g	k	ρ_g	k	ρ_g
Methane	0.089	0.087	0.02	0.075	0.16	0.068	0.24
Ethylene	0.16	0.15	0.06	0.14	0.12	0.12	0.25
Propane	0.39	0.39	0.00	0.33	0.15	0.29	0.26
Propylene	0.81	0.79	0.02	0.68	0.16	0.58	0.28
Isobutane	1.34	1.31	0.02	1.11	0.17	0.92	0.31
Butane	1.54	1.51	0.02	1.26	0.18	1.06	0.31
trans-2-Butene	2.88	2.79	0.03	2.31	0.20	1.89	0.34
Isobutylene	3.45	3.35	0.03	2.77	0.20	2.24	0.35
cis-2-Butene	3.86	3.74	0.03	3.08	0.20	2.50	0.35

effect on the retention values, the average variation of these values being 2—3 % for helium and 15—20 % for nitrogen. By comparing the data of Tables 2 and 3, one may conclude that the observed variations of the capacity factors of chromatographed compounds are due to the more effective adsorption of hydrocarbons in the presence of nitrogen.

When carbon dioxide is used, the relative variation of the capacity factors (with respect to those obtained with hydrogen) is 25—35 %. The mechanism of the effect of this carrier gas may be assumed to be mostly an adsorption mechanism, *i.e.*, carbon dioxide molecules are adsorbed on the surface of Al_2O_3/KCl, and thus displace the molecules of the compounds being chromatographed.

1.2. Regularities of the effect of the nature of the carrier gas on the capacity factors of the chromatographed compounds. In order to find out whether the Al_2O_3/KCl adsorbent used in the capillary column is selective with respect to the separation of saturated and unsaturated hydrocarbons, we used an approach that is well known in GLC (see, for example, Refs. 6 and 7) and involves representation of experimental data on retention as a linear dependence:

$$\lg Rt = a_R + b_R \cdot T_b, \cdot \qquad (2)$$

where Rt is a retention value (in our study, this is the capacity factor), T_b is the boiling point of the chromatographed compound, and a_R and b_R are constants.

In our study, this equation was used in the following form:

$$\log k = a_k + b_k \cdot T_b, \qquad (3)$$

where k is the capacity factor, and a_k and b_k are constants.

The sorbent used is selective if characteristic dependence (3) holds for each group of compounds studied. Fig. 1 shows the experimental data in the $\log k$—T_b coordinates. It can be seen from this Figure that saturated and unsaturated hydrocarbon gases separated on Al_2O_3/KCl are represented by various dependences of type (3). The selectivity of the separation can be estimated from the formula

$$\Delta a_{kij} = a_{ki} - a_{kj}, \qquad (4)$$

where a_{ki} and a_{kj} are the coefficients of Eq. (3) for two groups of compounds (in our case, the j index refers to unsaturated hydrocarbon gases and i refers to saturated hydrocarbon gases). The Δa_{kij} value determining the selectivity is rather high: $\Delta a_{kij} \approx 0.76$—$0.79$ (see Table 4).

The main parameters of relationships (3) for saturated and unsaturated hydrocarbons are listed in Table 4. As follows from this Table, Eq. (3) adequately describes the experimental data obtained both for saturated and unsaturated hydrocarbon gases, since the correlation coefficient R is rather high (0.994—0.997). Apparently, the nature of the carrier gas used has an effect on the

Table 4. Main characteristics of Eq. (3) used for description of experimental data obtained on a capillary column with Al_2O_3/KCl

Carrier gas	Saturated hydrocarbons			Unsaturated hydrocarbons		
	a_k	b_k	R	a_k	b_k	R
Hydrogen	−3.729	0.0146	0.997	−2.946	0.0128	0.994
Nitrogen	−3.773	0.0144	0.997	−2.995	0.0126	0.994
Helium	−3.753	0.0146	0.997	−2.990	0.0129	0.995
Carbon dioxide	−3.748	0.0140	0.997	−2.986	0.0122	0.995

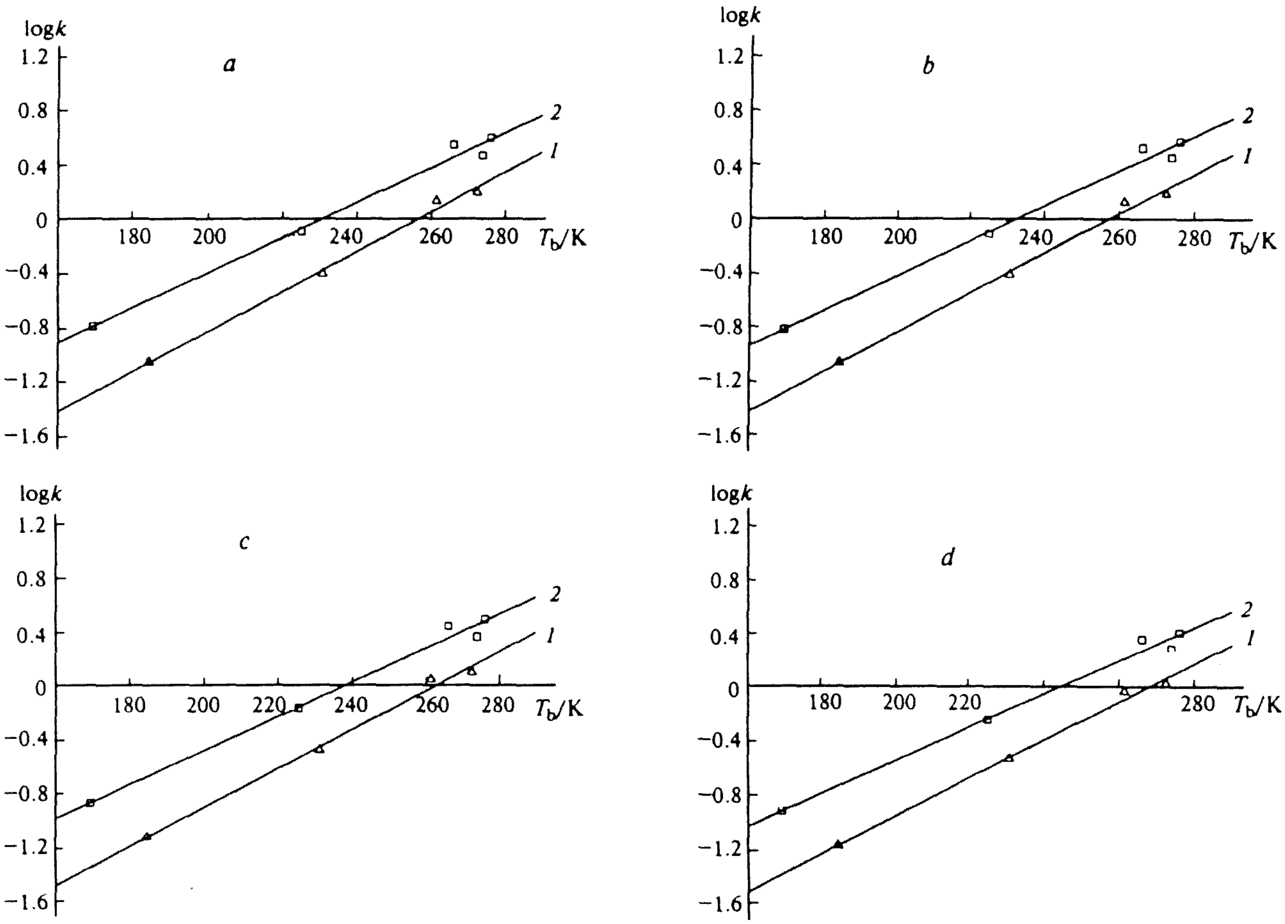

Fig. 1. Dependence of log*k* on the boiling points of saturated (*1*) and unsaturated (*2*) hydrocarbon gases. Experimental conditions: 50 m×0.32 mm column with Al_2O_3/KCl. Carrier gases: hydrogen (*a*), helium (*b*), nitrogen (*c*), carbon dioxide (*d*).

retention of the compounds being analyzed, because the a_k and b_k coefficients depend, among other factors, on the nature of the carrier gas.

Investigation of the variation of the capacity factors of hydrocarbon gases in capillary GSC on the replacement of one carrier gas by another may be regarded as a study of the functional dependence of a certain characteristic (the nature of the mobile phase) in the series of the compounds being analyzed at two values of a condition parameter (in our case, at two different carrier gases).

Functional dependences of this type have been surveyed most comprehensively in a monograph by Karapet'ants.[17] If we take the type of the carrier gas as the parameter of the separation conditions, and the capacity factor is taken as the characteristic studied, we can write down the following equation:

$$k(P_2) = A \cdot k(P_1) + B. \qquad (5)$$

Dependence (5) shown in Fig. 2 adequately describes the experimental results.

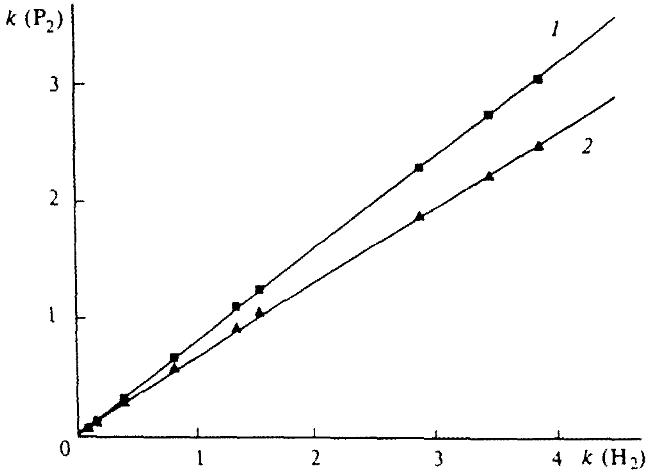

Fig. 2. Correlation plot (*5*) for various carrier gases: nitrogen (*1*), carbon dioxide (*2*).

Linear dependences have also been obtained when other carrier gases (see Table 5) were used. Dependence (5) describes the data on the retention of hydrocarbons

Table 5. Main characteristics of correlation equation (5)

Pair of carrier gases used for the correlation	*A*	*B*	*R* (correlation coefficient)
CO_2—H_2	0.0387	0.6416	0.9997
CO_2—N_2	0.0223	0.8057	0.9999
CO_2—He	0.0353	0.6622	0.9998
N_2—H_2	0.0228	0.7954	0.9999
N_2—He	0.0160	0.8219	0.9999
He—H_2	0.0059	0.9864	0.9999

of various natures (alkanes and alkenes) and, therefore, in the present case, the effect of carbon dioxide on the adsorption of hydrocarbon gases may apparently be considered to be nonspecific.

The correlation dependence (5) for GSC is also of practical interest. The use of this dependence makes it possible to pass from an array of the data obtained for one carrier gas to an array of the data obtained for another gas in the case where only limited data concerning the second carrier gas are available (these limited data are used to determine the coefficients of the linear dependence).

2. *Effect of the nature of the carrier gas on the efficiency of a capillary chromatographic column*

Using a column with Al_2O_3 as an example we studied the dependence of the H.E.T.P (height equivalent to a theoretical plate) on the linear velocity of the four carrier gases used most frequently in gas chromatography, *viz.*, hydrogen, helium, nitrogen, and carbon dioxide, for gaseous hydrocarbons with different capacity factors. The broadening of the chromatographic zone in an adsorption capillary column can be described by the Golay—Giddings equation.[18,19]

If we ignore the pressure differential along the column, we may write down

$$H = \frac{2D_g}{u} + \frac{(1+6k+11k^2)}{24(1+k)^2}\cdot\frac{r^2}{D_g}\cdot u + \frac{8k^2}{(k+1)^2}\cdot\frac{V_g\cdot\sigma}{\alpha\cdot\bar{c}\cdot A} = \frac{B}{u} + C_g\cdot u + C_A\cdot u\ , \quad (6)$$

$$B = 2D_g, \quad (7)$$

$$C_g = \frac{1+6k+11k^2}{24(1+k)^2}\cdot\frac{r^2}{D_g} = \frac{1+6k+11k^2}{24(1+k)^2}\cdot\bar{C}_g\ , \quad (8)$$

$$C_A = \frac{8k^2}{(1+k)^2}\cdot\frac{V_g\cdot\sigma}{\alpha\cdot\bar{c}\cdot A} = \frac{8k^2}{(1+k)^2}\cdot\bar{C}_A\ , \quad (9)$$

$$\bar{C}_g = \frac{r^2}{D_g}\ , \quad (10)$$

$$\bar{C}_A = \frac{V_g\cdot\sigma}{\alpha\cdot\bar{c}\cdot A}\ , \quad (11)$$

where u is the linear velocity of the carrier gas, D_g is the coefficient of diffusion of the chromatographed compound in the carrier gas under the conditions of the chromatographic experiment, k is the capacity factor, r is the radius of the capillary column, A is the surface area of the adsorbent in the column, α is the accommodation coefficient, $\bar{c}$ is the average velocity of the molecules of the compound being analyzed in the column, s is the heterogeneity factor, C_g is the coefficient of resistance to the mass transfer in the gas phase, C_A is the coefficient of resistance to the mass transfer in the adsorption layer, and $\bar{C}_g$ and $\bar{C}_A$ are sets of constant values not related to the capacity factor of the chromatographed compound. The agreement of experimental data with Eqs. (7)—(11) indicates that the effect of the carrier gas on the band broadening is mostly due to the variation of the capacity and diffusion coefficients on going from one carrier gas to another.

Previously the H—u dependence for the same type of adsorbent has been studied only for three carrier gases (hydrogen, helium, and nitrogen) and only one chromatographed compound (butadiene).[20] The application of the Golay—Giddings equation to the investigation of this problem in full measure is difficult, since this equation incorporates a number of variables that have not virtually been studied (for example, the heterogeneity factor) and the data on which (for example, on the accommodation coefficient) are very scarce. The theory of band broadening in capillary chromatography implies that the H.E.T.P values should depend on the capacity factors of the chromatographed compounds. Therefore, it has been of interest to study this dependence in relation to propylene, butane, and isobutylene and four carrier gases.

The results obtained are presented in Fig. 3 and in Table 6.

Table 6. Effect of the nature of the carrier gas on the variation of characteristics of an adsorption capillary column

Chromatographed compound	Carrier gas							
	Hydrogen		Helium		Nitrogen		Carbon dioxide	
	k	H_{min}/mm	*k*	H_{min}/mm	*k*	H_{min}/mm	*k*	H_{min}/mm
Propylene	0.81	0.60	0.79	0.43	0.68	0.29	0.58	0.25
Butane	1.54	0.48	1.51	0.41	1.26	0.31	1.06	0.29
Isobutylene	3.45	0.46	3.35	0.45	2.77	0.33	2.24	0.36

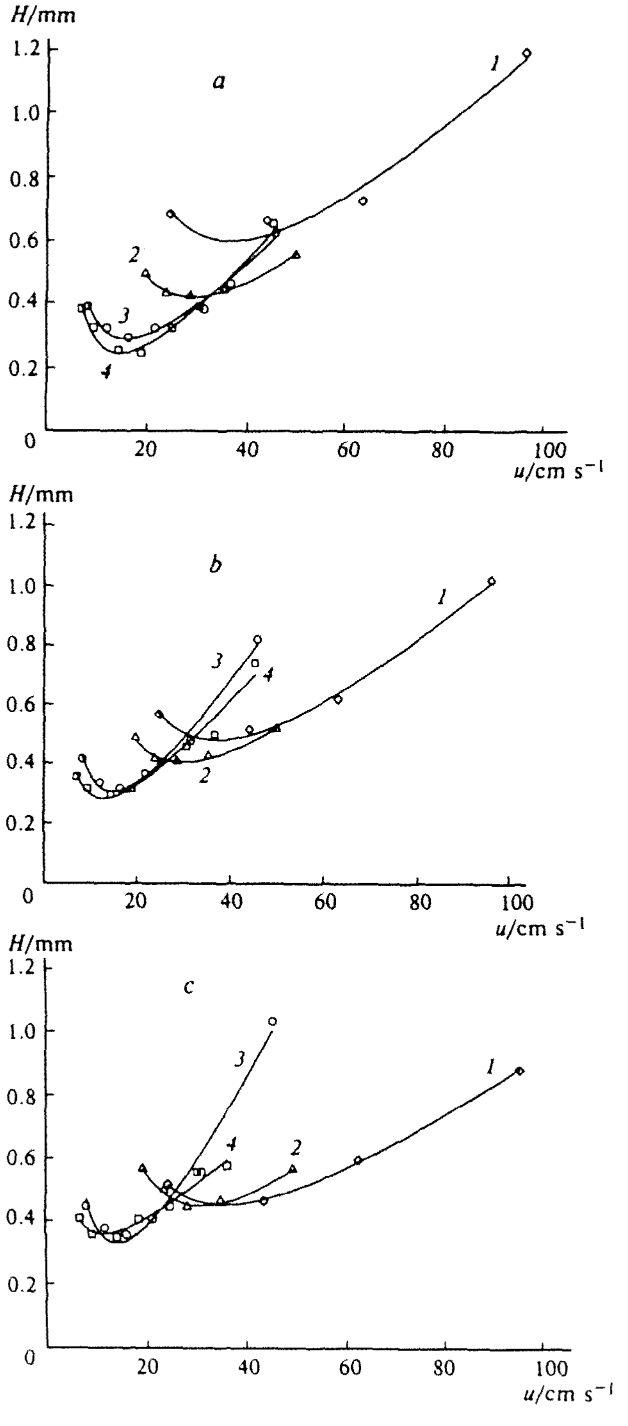

Fig. 3. Dependence of the H.E.T.P (H) on the linear velocity of the carrier gas (u) for some hydrocarbon gases characterized by different capacity factors: propylene (*a*), butane (*b*), isobutylene (*c*). Carrier gases: hydrogen (*1*); helium (*2*); nitrogen (*3*); carbon dioxide (*4*). Experimental conditions: 50 m×0.32 mm column with Al_2O_3/KCl, temperature 90 °C.

As a whole, they coincide with the data published for butylene.[20] The small distinctions are probably explained by both the differences in the characteristics of the Al_2O_3/KCl (50 m×0.32 mm) column and the sorbate used and the higher temperature of the experiment.

An analysis of the experimental data presented in Table 6 and Fig. 3 makes it possible to identify some characteristic features of the broadening of the chromatographic zone in capillary GSC.

1. The highest efficiency of a capillary column can be attained by using "heavy" carbon dioxide, the greatest gain in efficiency being observed with "light" chromatographed compounds. For example, in the sequence of the carrier gases studied, the overall efficiency of a column increases as follows: hydrogen (1.0), helium (1.6), nitrogen (2.2), and carbon dioxide (2.7). On going to "heavier" compounds the gain in efficiency decreases. For example, for isobutylene (k is 3.45 to 2.24), efficiency increases in the series of carrier gases in the following way: hydrogen (overall efficiency of the column 1.0), helium (1.14), nitrogen (1.32), and carbon dioxide (1.42). Thus, the maximum efficiency of a column for all sorbates studied increases in the following sequence of carrier gases: hydrogen < helium < nitrogen < carbon dioxide.

2. An important characteristic of the efficiency of separation is the h = (dH/du) slope tangent of the right branch of the $H = f(u)$ curve, which corresponds to high carrier gas velocities (see Fig. 3). The h values for carbon dioxide and nitrogen are similar for all the compounds (sorbates) studied; the h value is the smallest in the case of hydrogen and the greatest for carbon dioxide. This value characterizes the "sensitivity" of the H.E.T.P to the linear velocity of the carrier gas: the smaller the h value the lesser the degree to which the H.E.T.P depends on the velocity u. Thus, gases having the smallest h values can be used for a quick estimate of the efficiency of a column.

Note that according to the Golay—Giddings equation

$$h = \frac{dH}{du} = (C_g + C_A) - \frac{B}{u^2} \quad (12)$$

In the region of high velocities of a carrier gas

$$h \approx (C_g + C_A) = C_g^{exp} \quad (13)$$

The C_g^{exp} and C_g^{calc} values (see Eq. (8)) for some carrier gases are presented in Table 7. The D_g values were calculated from the Fuller—Schettler—Giddings equation.[21] The data listed in this Table indicate that when sorbates are separated under the conditions of approximate analysis, hydrogen is certainly preferred. Note that similar results have been obtained previously for GLC.[6,7] It also follows from the data obtained that the broadening of chromatographic zones occurs mostly in the gas phase.

3. Evaluation of the performance of carbon dioxide as a carrier gas

It has been shown above that with carbon dioxide the minimum H.E.T.P value for the compounds studied

Table 7. Coefficients of resistance to the mass transfer C_g^{exp} and C_g^{calc}

Compound	Carrier gas							
	Hydrogen				Carbon dioxide			
	k	D_g^{calc}/cm^2 s^{-1}	C_g^{calc}/s	C_g^{exp}/s	k	D_g^{calc}/cm^2 s^{-1}	C_g^{calc}/s	C_g^{exp}/s
Propylene	0.81	0.365	$0.47 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	0.58	0.081	$1.7 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$
Isobutylene	3.45	0.228	$1.40 \cdot 10^{-3}$	$0.8 \cdot 10^{-3}$	2.24	0.067	$4.2 \cdot 10^{-3}$	$2.8 \cdot 10^{-3}$

Note. Experimental conditions: a 50 m×0.32 mm column with Al_2O_3/KCl as the adsorbent, temperature 90 °C.

is much lower than with other carrier gases. Thus, by using carbon dioxide one can attain a substantially higher efficiency of separation in an adsorption capillary column. For this purpose, one should work under conditions of a small carrier gas pressure differential along the column, since an increase in the pressure differential is known to decrease the efficiency of the column.[6,7]

In view of the low viscosity of carbon dioxide, one may increase the length of the column without increasing the input pressure and thus increase the efficiency of the use of CO_2 to even a greater degree. However, the use of CO_2 for an express analysis in an isothermal experiment cannot be advised. This is due to the fact that coefficients of resistance to the mass transfer in the gas phase for carbon dioxide increase, since the coefficients of diffusion of the chromatographed compounds for CO_2 are lower than for hydrogen or helium.

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