Investigation of the effect of the nature and pressure of a carrier gas on retention of organic compounds in capillary adsorption chromatography

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The dependence of capacity factors on the pressure of a carrier gas in capillary adsorption chromatography was studied theoretically and experimentally. The equation deduced theoretically satisfactorily conformed to experimental data.

Key words: capillary adsorption chromatography, carrier gas, capacity factor.

The nature of a carrier gas exerts an effect on retention of chromatographed compounds in adsorption chromatography (see, *e.g.*, Refs. 1 and 2). However, there are no systematic studies of the effect of the average pressure of a carrier gas in a column on retention of chromatographed compounds (for example, on capacity factors) in high efficiency capillary gas—solid state chromatography. These studies were performed for various carrier gases in the pressure range used in traditional capillary gas chromatography (at the inlet pressure were 1—5 atm). It is noteworthy that experimental factors that affect an increase in the retention value[4] become especially significant in capillary chromatography due to the increased resolution ability of open capillary columns. A change in the pressure of the carrier gas in the range of low pressures (1—5 atm) is a standard condition for analytical use of chromatography. For example, when the duration of an experiment decreases, the inlet pressure should be changed (and hence, the average pressure in the column in the pressure range mentioned above) to change the rate of the carrier gas in the column.

The purpose of this work is theoretical and experimental study of the dependence of retention (capacity factor) on the average pressure of a carrier gas in a capillary adsorption column. It is reasonable to emphasize some analogy between this study and the works (Refs. 5 and 6), where vapor-phase adsorption of one organic compound (for example, *n*-pentane, cyclohexane, benzene, or *n*-propanol) from the flow of an inert carrier gas also containing vapor of another substance (for example, *n*-hexane, *n*-propanol, or *n*-butanol) was studied by a pulse chromatographic method. In these experiments, a packed chromatographic column was filled with an active solid adsorbent (graphitized carbon black TG-10, thermal carbon black GTB, or Silochrom C-80). These studies were performed from an "adsorption" aspect rather than from a "chromatographic" one. A functional dependence between the capacity factor (retention value) and the pressure of a carrier gas in the column (experimental parameter) was not established, and mobile phases (a mixture of an inert carrier gas and vapor of an organic substance) were not actually used in the chromatography.

Experimental

An LChM-8MD chromatograph modified in our laboratory with a 50 m×0.32 mm capillary column (Crompack, Netherlands) (adsorbent Al_2O_3/KCl, 5-μm adsorbent layer, $\beta = 32.56$, temperature of the column 90 °C) was used. He, H_2, N_2, and CO_2 were used as carrier gases.

Results and Discussion

If the simplest model of adsorption of two volatiles **A** and **C** on a solid surface is considered and adsorption of **A** and **C** molecules is assumed to occur when they encounter one of the unoccupied adsorption sites on the surface of the solid adsorbent, the rate of desorption of these molecules being proportional to the surface area occupied by adsorbed molecules of compounds **A** and **C**, then the adsorption isotherm can be expressed by the following equation[7]:

$$a_{\mathrm{C}} = \frac{K_{\mathrm{C}}C_{\mathrm{C}}}{1 + K_{\mathrm{C}}C_{\mathrm{C}} + K_{\mathrm{A}}C_{\mathrm{A}}},$$

$$K_{\mathrm{AE}} = \frac{K_{\mathrm{A}}}{1 + K_{\mathrm{C}}C_{\mathrm{C}}}\frac{1}{\left[1 + K_{\mathrm{A}}C_{\mathrm{A}}(1 + K_{\mathrm{C}}C_{\mathrm{C}})^{-1}\right]^2},$$

where a_{A} and a_{C} are the concentrations of adsorbed compounds **A** and **C** (g g^{-1}); C_{A} and C_{C} are the concen-

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trations of compounds **A** and **C** in the gas phase (g L^{-1}); K_A and K_C are the adsorption coefficients of compounds **A** and **C**.

Let us consider **A** as a chromatographed substance and **C** as a carrier gas. As known (see, *e.g.*, Ref. 1), the capacity factor of the column for compound **A** is related to the adsorption coefficient (distribution constant) K_{AE} by the following equation:

$$k'/A = K_{AE}/\beta,$$

where β is the phase ratio (ratio of the volume of a gas phase in a column to the volume occupied by an adsorbent), K_{AE} is the adsorption coefficient of compound **A** at certain concentrations of the carrier gas (**C**) and the chromatographed substance (**A**).

It is known[1] that $K_{AE} = da_A/dC_A$, and hence,

$$K_{AE} = \frac{K_A}{1+K_C C_C}\,\frac{1}{\left[1+K_A C_A(1+K_C C_C)^{-1}\right]^2}.$$

Since the observed zones of chromatographed compounds are nearly symmetric, it can be assumed that $K_A C_A/(1 + K_C C_C) \ll 1$.

Under these conditions

$$K_{AE} = \frac{K_A}{1+K_C C_C},$$

and hence,

$$k'_A = \frac{K_A}{1+K_C C_C}\,\frac{1}{\beta}. \qquad (1)$$

It follows from Eq. (1) that the capacity factor of the chromatographed substance **A** depends on the concentration (and hence, pressure) of the carrier gas, and its value decreases as the pressure (concentration) of the carrier gas increases in the column.

In our experiments, we obtained the dependence of capacity factors on the average pressure of the carrier gas in the column (Table 1), which was determined from the known equation:

$$\bar{p} = p/j.$$

As follows from the results presented, capacity factors are almost independent of the average pressure in the column for He and H_2 carrier gases, while a slight dependence is observed for N_2 only for the "heaviest" chromatographed substance, 1-butene. The results obtained can be explained by the fact that He, H_2, and N_2 are grouped with permanent gases, and it should be expected that their adsorption on Al_2O_3 at 90 °C should be insignificant. The independence of capacity factors on pressure of the carrier gas should be observed under the condition that $K_C C_C$ is considerably lower than unity, and hence,

$$k'_A = K_A/\beta = \text{const.}$$

Table 1. Dependence of the capacity factor of hydrocarbon gases on the average pressure ($\bar{p}$) of the carrier gas in the capillary column

Compound	$\bar{p}$/atm				
	1.0	1.6	2.8	3.4	4.1
	Carrier gas — H_2				
Propylene	0.80	0.81	0.80	0.81	0.84
Butane	1.51	1.52	1.54	1.53	1.56
1-Butene	3.27	3.29	3.24	3.22	3.24
	Carrier gas — He				
Propylene	0.88	0.89	0.89	0.89	0.88
Butane	1.68	1.71	1.72	1.71	1.69
1-Butene	3.66	3.73	3.75	3.71	3.63
	Carrier gas — N_2				
Propylene	0.87	0.88	0.87	0.86	0.85
Butane	1.65	1.68	1.65	1.62	1.59
1-Butene	3.61	3.64	3.58	3.52	3.45
	Carrier gas — CO_2				
Propylene	0.64	0.59	0.54	0.49	0.44
Butane	1.17	1.08	0.95	0.88	0.80
1-Butene	2.46	2.24	1.91	1.71	1.58

When CO_2 is used as the carrier gas, the capacity factor of chromatographed compounds decreases as the average pressure in the column increases, which corresponds to Eq. (1). This means that under the conditions used the $K_C C_C$ value in this equation is significant compared to unity. Therefore, it is reasonable to use Eq. (1) for describing the dependence of the capacity factor of chromatographed compounds on the average pressure of CO_2 in the capillary column. To evaluate the correspondence of the experimental data to Eq. (1), let us present the latter in the following form:

$$\frac{1}{k'_A} = \frac{\beta}{K_A} + \frac{\beta K_C}{K_A} C_C = a + bC_C, \qquad (2)$$

where $a = \beta/K_A$ and $b = \beta K_C/K_A$ or $b = aK_C$. Since $C_C = g\bar{p}$, where g is the proportionality coefficient (g = 1.43 g $(L\ atm)^{-1}$), Eq. (2) can be expressed as follows:

$$1/k_A' = a + bg\bar{p} = a + b_m\bar{p}, \qquad (3)$$

where $b_m = bg$.

The concentration was calculated by the equation[8]:

$$C_C = G/V = \frac{(0.01605 \cdot 735.6)M}{273.2+T}\,\bar{p},$$

where G/g is the mass of the gas; V/dm^3 is the volume of the gas (under our conditions, 1 dm^3); M is the molecular weight; $\bar{p}$/atm is the average pressure of the carrier gas; T/°C is the temperature of the gas.

As follows from Fig. 1, which presents the $1/k' = f[C(\bar{p})]$ dependence, Eq. (2) satisfactorily describes the experimental data obtained. A similar treatment makes

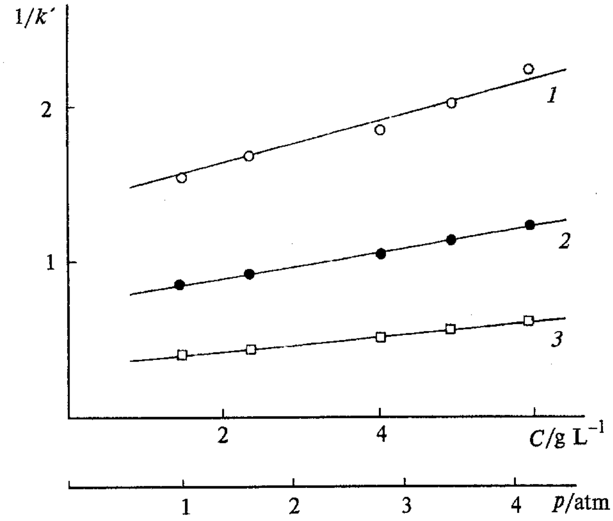

Fig. 1. Dependence $1/k' = f[C(\bar{p})]$: *1,* propylene; *2,* butane; *3,* 1-butene. Experimental conditions: column 50 m×0.32 mm, adsorbent Al_2O_3/KCl (5 μm), β = 32.56, *T* = 90 °C, carrier gas CO_2.

Table 2. Coefficients of Eq. (3) for various chromatographed compounds on an open capillary column with Al_2O_3/KCl (carrier gas CO_2)

Compound	a/g g^{-1}	b_m/atm^{-1}	K_A/L g^{-1}	K_C/L g^{-1}
Propylene	1.32	0.21	24.67	0.11
Butane	0.73	0.12	44.60	0.12
1-Butene	0.38	0.051	85.68	0.094

it possible to determine the values of coefficients in Eq. (3) (Table 2). Since the change in pressure of the carrier gas at the inlet of the column is also related to the change in its velocity, the dependence of the capacity factor on the velocity of the carrier gas will be manifested in the case considered.

In a conventional experiment, a change in pressure at the inlet of the column is unambiguously related to a change in the average velocity of the carrier gas used (Fig. 2). These parameters can be independent. For example, the pressure of the carrier gas can be independently changed with an almost unchanged optimum rate of the carrier gas, using the controlled resistance at the output of the column (more exactly, between the column and the detector).

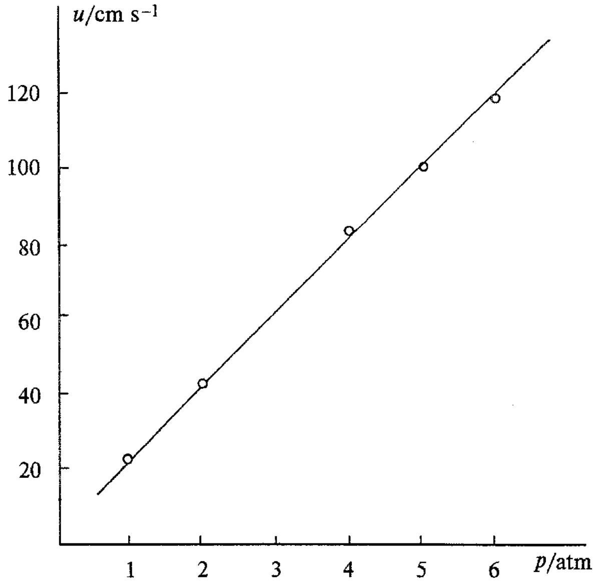

Fig. 2. Dependence of the mean linear rate of the carrier gas at the input of the open capillary adsorption column (for experimental conditions, see Fig. 1).

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