Dependence of retention of organic compounds on carrier gas pressure in capillary adsorption chromatography

Victor G. Berezkin*, Irina V. Malyukova, Victor R. Alishoev

Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky pr. 29, Moscow 117912, Russian Federation

Abstract

An equation for the dependence of the capacity factor of compounds on the carrier gas pressure in capillary adsorption chromatography was deduced for binary mixtures on the basis of an adsorption equation. The dependence of the capacity factors of hydrocarbon gases on the nature and pressure of the carrier gas was studied. The equation suggested conformed well with experimental data.

1. Introduction

Capillary gas chromatography is currently the main chromatographic variant [1]. The high efficiency of open-tubular capillary columns in principle allows an improvement in separation compared with packed column. The development of a reproducible method for obtaining open-tubular capillary columns with an adsorption layer on the inner walls and organization of their production were important stages in the successful development of gas–solid chromatography [2].

Investigation of the dependence of the capacity factor on carrier gas pressure is of theoretical and practical interest because on changing the average velocity of the carrier gas its pressure (column average pressure or inlet pressure) changes accordingly. The influence of the nature and pressure of the carrier gas on retention using packed columns has been studied for several

systems (e.g., for silica gel) [3,4]. However, the influence of the nature of the carrier gas on the retention of compounds in capillary adsorption chromatography does not appear to have been investigated. In view of the high resolution of open capillary columns, changes in retention are of special significance [5]. It should be noted that changes in the nature and pressure of the carrier gas (in the range of low pressures, 1–5 atm) are common in analytical chromatography. For example, to shorten the duration of an experiment by changing of the carrier gas velocity, the inlet pressure must be changed (and therefore the average column pressure in this pressure range).

The carrier gas pressure may influence the retention of analyte compounds as a result of (1) competition between the adsorption of the carrier gas and the adsorption of the analyte on the surface of the solid adsorbent and (2) a non-perfect state of the gas phase. In this paper, we consider the role of the former factor only, because deviations from the law of ideality are not great for carrier gas–hydrocarbon gas sys-

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* Corresponding author.

tems: at low pressures (less than 10 atm) [6] and can be neglected.

Preliminary experiments on the influence of carrier gas pressure on the capacity factors of C_1–C_4 hydrocarbon gases on a 50 m × 0.32 mm I.D. capillary column with SE-52 as the stationary liquid phase (SLP) (film thickness 1.2 μm) at ambient temperature confirmed our approach. The changes in the capacity factors of the C_1–C_4 hydrocarbons were within experimental error when the pressure was varied from 2.0 atm to 5.0 atm.

The purpose of this work was to carryout a theoretical and experimental investigation of the dependence of the retention on the average pressure of the carrier gas in a capillary adsorption column.

2. Theoretical analysis

First let us consider a physical model of the influence of the carrier gas pressure on the capacity factor. When examining a simple model for the adsorption of two volatile compounds A and C on a solid surface, assuming that their adsorption takes place when they collide with a free adsorption site on the surface of the solid adsorbent and that the desorption velocity of their molecules is proportional to the surface area that they occupy, it can be shown that the adsorption isotherm is given by the following equations [7]:

$$a_A = \frac{K_{Am}C_A}{1 + K_C C_C + K_{Am}C_A} \qquad (1)$$

$$a_C = \frac{K_C C_C}{1 + K_C C_C + K_{Am}C_A} \qquad (2)$$

where a_A and a_C are the concentrations of adsorbed compounds A and C (g/g), C_A and C_C are the concentrations of A and C in the gas phase (g/l) and K_{Am} and K_C are adsorption coefficients of Compounds A and C. It is then necessary to establish the relationship between the capacity factor and the parameters of the adsorption isotherm equation. We shall consider substance A to be the compound to be chro-

matographed and C to be the carrier gas in Eqs. 1 and 2. The capacity factor for substance A, k'_A, is connected with the adsorption coefficient by the following expression:

$$k'_A = K_{AE}(C_A, C_C)/\beta \qquad (3)$$

where β is the phase ratio (ratio of the gas-phase volume in the column to the volume occupied by the adsorbent) and K_{AE} is the adsorption coefficient for compound A at definite concentrations of the carrier gas (C) and chromatographed compound (A).

As

$$K_{AE}(C_A, C_C) = da_A/dC_A \qquad (4)$$

after differentiation of Eq. 1 we obtained

$$K_{AE} = \frac{K_{Am}}{1 + K_C C_C} \frac{1}{[1 + K_{Am}C_A(1 + K_C C_C)^{-1}]^2} \qquad (5)$$

As the observed zones of the chromatographed compounds are symmetrical, it could be assumed that $K_{Am}C_A/(1 + K_C C_C) \ll 1$. Taking into consideration the latter correlation, we can simplify Eq. 5:

$$K_{AE} \approx \frac{K_{Am}}{1 + K_C C_C} \qquad (6)$$

With Eq. 6, we can show that Eq. 3 gives

$$k'_A = \frac{K_{Am}}{1 + K_C C_C} (1/\beta) \qquad (7)$$

As follows from Eq. 7, the capacity factor of compound A in the general case depends on the carrier gas concentration (pressure) and its value decreases with increasing carrier gas pressure (concentration) in the column. At $K_C C_C \ll 1$ (when the carrier gas adsorption on the adsorbent surface is not high),

$$k'_A \approx K_{Am}(1/\beta) \qquad (8)$$

and in this case the capacity factor does not depend on the nature and pressure of the carrier gas.

In order to compare Eq. 7 with experimental data, it is necessary to present it in the following form:

$$\frac{1}{k'_A} = \frac{\beta}{K_{Am}} (1 + K_C C_C) \tag{9}$$

or

$$1/k'_A = \frac{\beta}{K_{Am}} + \frac{K_C \beta}{K_{Am}} \cdot C_C \tag{10}$$

As the concentration and pressure of the carrier gas in the range of low pressures are related with a linear dependence (with proportionality coefficient g) [8],

$$C_C = gP \tag{11}$$

where $g = 1.43$ g/l · atm, then

$$1/k'_A = \beta/K_{AM} + \frac{K_C \beta g}{K_{Am}} \cdot P \tag{12}$$

or

$$1/k'_A = A + BP \tag{13}$$

where

$$A = \beta/K_{Am} \tag{14}$$

and

$$B = K_C \beta g/K_{Am} \tag{15}$$

The dependence $1/k'_A = f(P)$ can be easily checked experimentally.

3. Experimental

Experiments were performed with an LKhM-8MD chromatograph developed in our laboratory (Khromatograf factory, Moscow, Russian Federation). It was fitted with a 50 m × 0.32 mm I.D. column (Chromapack, Middelburg, Netherlands), with Al_2O_3–KCl (5 μm) adsorbent, phase ratio = 32.56; the column temperature was 90°C. Helium, hydrogen, nitrogen and carbon dioxide were used as carrier gases.

4. Results and discussion

The dependence of the capacity factor on the average carrier gas pressure was obtained experimentally (see Table 1). The average pressure, $\bar{P}$, was determined in accordance with the known equation [1]

$$\bar{P} = P/j$$

where P = inlet pressure and j = compression correction factor.

As is evident from Table 1, the dependence of the capacity factor on the average pressure in the column is almost negligible for helium and hy-

Table 1
Dependence of capacity factors of hydrocarbon gases on average column pressure of the carrier gas in an adsorption capillary column

Carrier gas	Compound chromatographed	Average carrier gas pressure (atm)				
		1.0	1.6	2.8	3.4	4.1
Hydrogen	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
Helium	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
Nitrogen	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
Carbon dioxide	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

drogen slight for nitrogen with the "heavy" compound 1-butene. The results obtained are qualitatively clear because helium, hydrogen and nitrogen belong to the group of permanent gases. It would be expected that their adsorption on alumina would be insignificant at high temperature (90°C). The absence of a dependence of the capacity factor on carrier gas pressure should be observed under the condition $K_C C_C \ll 1$, and therefore

$$k_A' = K_{Am}/\beta = \text{constant}$$

Using carbon dioxide as the carrier gas, the capacity factors of the compounds chromatographed decreased with increase in average column pressure, corresponding to Eq. 13. This means that under our experimental conditions $K_C C_C$ is significant in comparison with unity (see Eqs. 7 and 10). Hence it is reasonable to use Eq. 13 for the description of the dependence of the capacity factors of the compounds chromatographed on the average pressure of carbon dioxide in the capillary adsorption column.
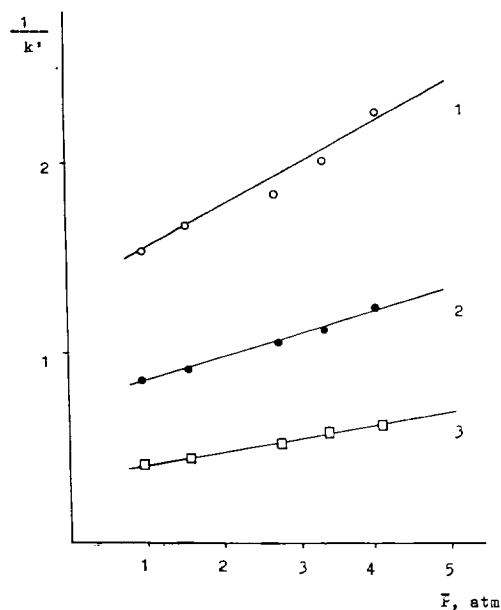
The dependence $1/k_A' = f(\bar{P})$ is shown in Fig.

Table 2
Coefficients of Eq. 12 for compounds chromatographed on an open capillary column with Al_2O_3–KCl and carbon dioxide as the carrier gas

Compound chromatographed	A	B (atm^{-1})	K_{Am}	K_C (l/g)
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

1. As can be seen, Eq. 13 fits the experimental data obtained well. Such a treatment allows the coefficients values in Eq. 12 to be determined (see Table 2). Hence the various compounds chromatographed are characterized by different dependences of the capacity factor on the nature of the carrier gas and its average pressure in the column.

It should be pointed out that in traditional experiments, changes in the inlet pressure are connected with changes in the average linear velocity of the carrier gas used (Fig. 2). Therefore, changes in the linear velocity of the carrier

Fig. 1. Dependence $1/k' = f(\bar{P})$ (Eq. 12). 1 = Propylene; 2 = butane; 3 = 1-butene. Experimental conditions: column, 50 m × 0.32 mm I.D.; adsorbent, Al_2O_3–KCl (5 μm); β = 32.56; column temperature, 90°C; carrier gas carbon dioxide.
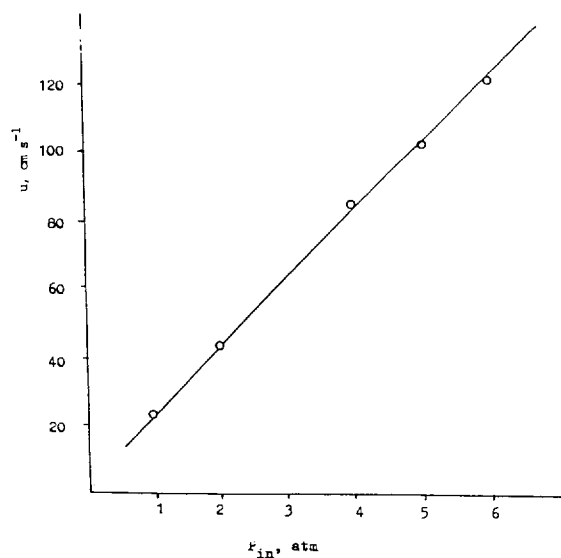

Fig. 2. Dependence of average linear velocity of the carrier gas on inlet pressure in an open adsorption capillary column. Experimental conditions: column, 50 mm × 0.32 mm I.D.; adsorbent, Al_2O_3–KCl (5 μm); β = 32.56; column temperature, 90°C; carrier gas, carbon dioxide.

gas in adsorption chromatography could result in changes in the retention values under definite experimental conditions. Such parameters could also be independent. Using a fine regulation valve at the column outlet (more exactly, between the column and the detector), the carrier gas pressure could be independently changed with the optimum velocity of the carrier gas.

Acknowledgement

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