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INFLUENCE OF MODIFICATION OF GLASS CAPILLARY COLUMN SURFACE WITH CARBON ON ITS ADSORPTION PROPERTIES IN GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

A comparative investigation of partition surface properties of PEG-1540 with non-modified and carbon-modified glass capillary columns was carried out. The adsorption contribution of compounds belonging to different classes was estimated on the basis of the dependence of the relative changes of their retention values on the film thickness of PEG-1540.

INTRODUCTION

During the last few years it has been shown that adsorption phenomena have a remarkable influence on retention values in capillary gas–liquid chromatography[1–4]. For this reason, it seemed appropriate to use previously developed methods[5,6] for the quantitative evaluation of widely used methods for modifying the inner walls of capillary columns.

This paper describes a comparative study of the role of adsorption effects in the retention of organic compounds on unmodified and carbon-modified glass capillary columns coated with PEG-1540[7].

Carbonization of the inner surface of the glass capillary column wall must improve the adhesion properties of the surface with respect to the liquid stationary phase. It usually leads to an improvement in the efficiency and lifetime of the column. The glass capillary columns with a carbonized surface obtained by us are usually characterized by a high efficiency (4000–5000 theoretical plates per metre). It was interesting to ascertain whether carbonization of the glass capillary column surface leads to an increase in its adsorption activity.

In order to elucidate the adsorption contribution to the relative retention value, it seemed appropriate to use the equation[5,6]

$$V_{ri} = \frac{K_{li}}{K_{lst}} + a_i \cdot \frac{1}{K_{st}} = V_{ri0} + a_{\lambda i} \cdot \frac{1}{K_{st}} \quad (1)$$

where V_{ri} = relative retention time, V_{ri0} = invariant retention value of the substance,

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TABLE I

CHANGES IN RELATIVE RETENTION VALUES DEPENDING ON RECIPROCAL OF THE CAPACITY FACTOR OF A STANDARD (*m*-XYLENE)

Compound	*Glass capillary column (unmodified)*				*Glass capillary column with carbonized surface*			
	$K_{st} = 0.85$	$K_{st} = 1.25$	$K_{st} = 2.10$	$k_{st} = 3.95$	$K_{st} = 0.93$	$K_{st} = 1.36$	$K_{st} = 1.86$	$K_{st} = 5.00$
Toluene	0.53	0.52	0.52	0.51	0.53	0.53	0.53	0.54
Propanol	0.61	0.60	0.61	0.60	0.61	0.60	0.62	0.61
Butyl acetate	0.67	0.67	0.65	0.64	0.68	0.69	0.71	0.72
Ethylbenzene	0.90	0.90	0.87	0.85	0.92	0.92	0.93	0.94
Butanol	1.27	1.25	1.25	1.22	1.27	1.27	1.27	1.26
Chlorobenzene	1.57	1.56	1.54	1.53	1.58	1.59	1.59	1.62
Pentanol	2.58	2.58	2.57	2.55	2.60	2.60	2.61	2.62
n-Decane	0.33	0.37	0.42	0.61	0.31	0.35	0.39	0.61
n-Undecane	0.64	0.72	0.87	1.22	0.63	0.69	0.78	1.28
n-Dodecane	1.28	1.46	1.79	2.58	1.25	1.41	1.59	2.69

$V_{ri0} = k_{li}/K_{lst}$, K_{li} and K_{lst} = distribution constants of the chromatographed substance between liquid stationary phase and the gaseous phase, a = adsorption coefficient that characterizes the adsorption contribution to the relative retention value and K_{st} = capacity factor of the standard substance, whose adsorption in the given chromatographic system can be neglected.

It follows that adsorption of the compounds being separated on the stationary phase–column wall interface (solid support) has a noticible influence on the retention of the sample compounds.

It should be noted that for a number of compounds the slope of the $V_{ri} = f(1/K_{st})$ dependence may be negative. A negative slope shows that adsorption of the standard substance is greater than that of the sample compound. It follows from ref. 5 that

$$V_{ri} = \frac{K_{li}}{K_{lst}} + \frac{K_{li}}{K_{lst}}(a_i - a_{st})\frac{1}{K_{st}}$$

$$= \frac{K_{li}}{K_{lst}} + A \cdot \frac{1}{K_{st}}$$

$$a_i = \frac{K_{gli}S_l + K_{li}K_{si}S_s}{K_{li}}$$

$$a_{st} = \frac{K_{glst}S_l + K_{lst}K_{sst}S_s}{K_{lst}}$$

$A > 0$ $\qquad$ $A < 0$

$a_i > a_{st}$ $\qquad$ $a_i < a_{st}$

EXPERIMENTAL

Measurements were carried out on an LKhM-8MD Model 5 chromatograph produced by Khromatograf (Moscow, U.S.S.R.) with a flame-ionization detector using glass capillary columns (25 m × 0.25 mm I.D.), polyethylene glycol PEG-1540 as the stationary phase, oven temperature 70°C, carrier gas nitrogen at a linear velocity of 8–15 cm/sec, splitting ratio 1:200 and liquid sample size 0.1 μl. The glass capillary columns were drawn from Pyrex glass tubes. The inner modified surfaces of the columns were washed with methanol and dried for 30 min at 280°C. Modification was carried out by pyrolysing methyl iodide during the capillary drawing process, *i.e.*, by a variant of Grob's method[7]. The glass capillary columns were coated by the static method[8] with PEG-1540 in methanol solution of different concentrations.

RESULTS AND DISCUSSION

Table I presents experimental data for relative retention values depending on the reciprocal of the capacity factor. These retention values were used as initial data for the calculation of V_{ri0} and a (see eqn. 1). The results obtained are presented in

TABLE II

INVARIANT VALUES OF RELATIVE RETENTIONS (V_{ri0}) AND ADSORPTION COEFFICIENTS (a) FOR A NUMBER OF ORGANIC COMPOUNDS OBTAINED ON UNMODIFIED AND MODIFIED GLASS CAPILLARY COLUMNS

Compound	*Glass capillary column (unmodified)*		*Glass capillary column with carbonized surface*	
	V_{ri0}	a_i	V_{ri0}	a_i
Toluene	0.53	−0.0055	0.53	0.0027
Propanol	0.61	−0.002	0.61	0.0005
Butyl acetate	0.68	−0.01	0.68	0.008
Ethylbenzene	0.92	−0.017	0.92	0.005
Butanol	1.27	−0.014	1.27	0.0027
Chlorobenzene	1.57	−0.012	1.57	0.0093
Pentanol	2.59	−0.01	2.59	0.005
n-Decane	0.25	0.09	0.25	0.07
n-Undecane	0.48	0.19	0.48	0.16
n-Dodecane	0.93	0.42	0.93	0.35

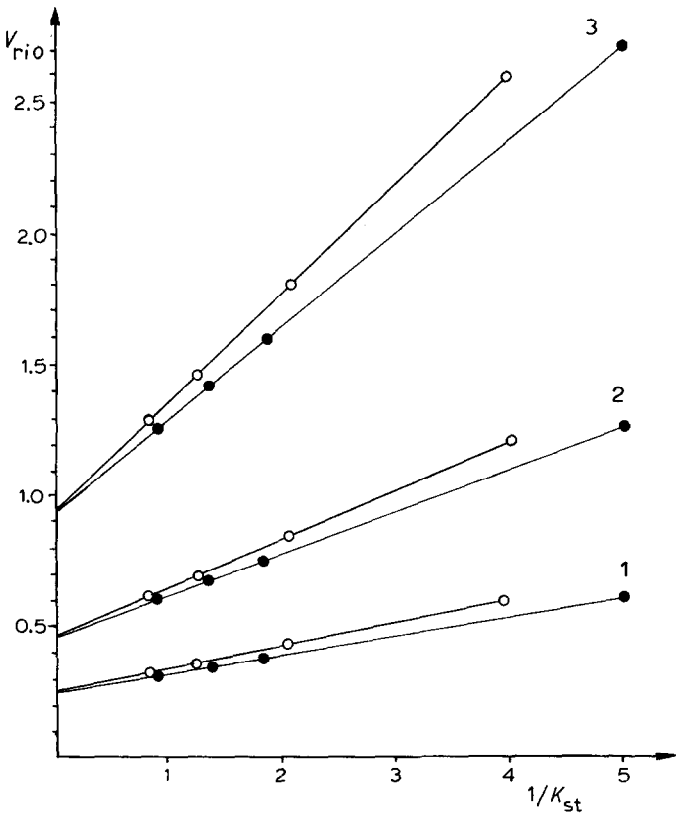

Fig. 1. Dependence of relative retention of *n*-alkanes on reciprocal of capacity factor of *m*-xylene (standard) obtained on 25 m × 0.25 „ I.D.columns coated with PEG 1540, temperature 70°C. ○, Unmodified glass capillary columns; ●, glass capillary column with carbonized surface. 1 = *n*-Decane; 2 = *n*-undecane; 3 = *n*-dodecane.

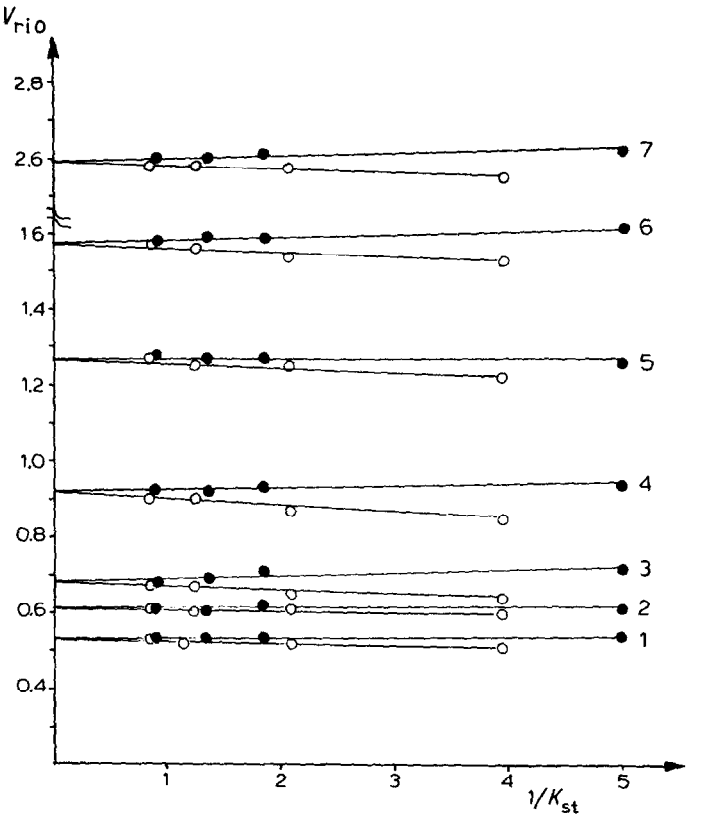

Fig. 2. Dependence of relative retention of organic compounds on reciprocal of capacity factor of *m*-xylene (standard) obtained on 25 m × 0.25 mm I.D. columns, coated with PEG 1540, temperature 70°C. ○, nmodified glass capillary column; ●, glass capillary column with carbonized surface. 1 = Toluene; 2 = propanol; 3 = butyl acetate; 4 = ethylbenzene; 5 = butanol; 6 = chlorobenzene; 7 = pentanol.

Table II. Experimentals results are also shown in Figs. 1 and 2 for a number of organic compounds.

It follows from Figs. 1 and 2 that the experimental data are in good agreement with the linear eqn. 1. In comparison with the initial unmodified capillary surface, carbonization leads to a decrease in the adsorption of organic compounds.

It should be mentioned here that according to the additive theory of retention values[6], limiting (invariant) retention values V_{ri0} do not depend on the nature of the capillary column surface. For both modified and unmodified glass capillary columns invariant retention values are close to each other.

CONCLUSION

For the determination of the adsorption capacity of modified glass capillary columns, it is appropriate to use a linear equation such as eqn. 1, which links relative retention values with the reciprocal of the capacity factor of a compound, whose retention is caused only by its solution in the stationary phase. It has been shown

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For the determination of the adsorption capacity of modified glass capillary columns, it is appropriate to use a linear equation such as eqn. 1, which links relative retention values with the reciprocal of the capacity factor of a compound, whose retention is caused only by its solution in the stationary phase. It has been shown that for the system solid–PEG 1540, the carbonized inner surface of a glass capillary column is characterized by a lower adsorption capacity than the initial unmodified glass surface.

REFERENCES

1 V. G. Berezkin and L. Soják, *Collect. Czech. Chem. Commun.*, 43 (1978) 1588.
2 L. Soják, V. G. Berezkin and J. Janák, *J. Chromatogr.*, 209 (1981) 15.
3 J. Krupčík, E. Matisová, J. Garaj, L. Soják and V. G. Berezkin, *Chromatographia*, 16 (1982) 166.
4 E. Matisová, J. Krupčík and J. Garaj, *Chromatographia*, 16 (1982) 169.
5 V. G. Berezkin, *J. Chromatogr.*, 98 (1974) 477.
6 V. G. Berezkin, V. P. Pachomov and K. I. Sakodynsky, *Solid Supports in Gas Chromatography*, Supelco, Bellefonte, PA, 1981.
7 K. Grob, *Helv. Chim. Acta*, 48 (1965) 1362.
8 E. L. Ilkova and E. A. Mistryukov, *J. Chromatogr. Sci.*, 9 (1971) 569.