

CHROMSYMP. 811

## RETENTION OF ORGANIC COMPOUNDS ON CARBON ADSORBENTS

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### SUMMARY

Liquid adsorption chromatography of organic compounds (aromatic hydrocarbons, acids, phenol, anisole, benzaldehyde and acetophenone) was studied at 293 K on two carbon stationary phases. Acetonitrile, acetonitrile-water (2:3) and *n*-heptane were used as mobile phases.

Capacity factors and Henry's constants of adsorption equilibrium of aromatic compounds were calculated from the values of their retention volumes. The influence of the chemical structure of organic compounds, the surface structure of the stationary phases and the nature of the mobile phases on retention parameters was established.

The differences in adsorption mechanism of organic compounds on hydroxylated and modified silica and carbon stationary phases are discussed.

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### INTRODUCTION

Carbon adsorbents with high chemical stability, mechanical strength and adsorption capacity and pre-determined particle size and pore distribution are finding wider use alongside traditional silica adsorbents in liquid chromatography<sup>1,2</sup>.

The retention and adsorption of aromatic compounds with different chemical structures on the surface of carbon adsorbents has been studied by liquid chromatography and the chromatographic properties of carbon and silica stationary phases have been compared.

### EXPERIMENTAL

Benzene, toluene, *o*-, *m*- and *p*-xylene, anisole, benzaldehyde, phenol, naphthalene and benzoic, salicylic, *o*-phthalic and anthranilic acids were used in adsorption studies. Chemical purity grade benzene, toluene, xylenes, anisole and benzaldehyde were purified by fractional distillation *in vacuo*; phenol, naphthalene and acids of chemical purity were recrystallized. The eluents were *n*-heptane, acetonitrile (both distilled, dried and stored over NaA zeolite) and acetonitrile-doubly distilled water (40:60, v/v).

CF-13 (C-1) carbon adsorbent was used. It was obtained by pyrolytic treat-

TABLE I  
CHARACTERISTICS OF THE ADSORBENTS

<i>Adsorbent</i>	<i>Specific surface area (m<sup>2</sup>/g)</i>	<i>Pore diameter (nm)</i>	<i>Pore volume (cm<sup>3</sup>/g)</i>
CF-13 (C-1)	770	20	1.9
C-80-U (SiO <sub>2</sub> + C)	80	50	1.3
Silasorb-600 (SiO <sub>2</sub> )	600	8	0.7

ment of silica gel impregnated with phenol-formaldehyde resin, followed by removal of the silica gel with an alkaline solution<sup>3</sup>. Other adsorbents were macroporous Silochrom C-80, coated with a monolayer carbon film (C-80-U) (SiO<sub>2</sub> + C), and Silasorb-600 (SiO<sub>2</sub>). Characteristics of the adsorbents are given in Table I.

Chromatographic investigations were carried out with a Tsvet-304 liquid chromatograph with a UV detector ( $\lambda = 254$ , cell volume 7  $\mu$ l). The eluent flow-rate was 1 ml/min and dose volumes were 1–10  $\mu$ l. The following columns were used: 20 cm  $\times$  0.4 cm I.D., packed with CF-13 adsorbent, particle size  $15 \pm 5$   $\mu$ m (HETP,  $H = 40$   $\mu$ m); 10 cm  $\times$  0.4 cm I.D., packed with C-80-U adsorbent, particle size  $10 \pm 2$   $\mu$ m ( $H = 40$   $\mu$ m); 10 cm  $\times$  0.4 cm I.D., packed with Silasorb-600 adsorbent, particle size  $7 \pm 2$   $\mu$ m ( $H = 30$   $\mu$ m). The columns were packed from solutions in *n*-heptane under a pressure of 400 atm. The working inlet column pressure was 60–80 atm. The adsorbents were pre-dried *in vacuo* at 393 K for 3 h.

Retention volumes,  $V_e$ , were determined for aromatic compounds according to the equation

$$V_e = V_R - V_0 \quad (1)$$

where  $V_R$  is the retention volume in cm<sup>3</sup> and  $V_0$  is the retention volume of the non-sorbed substance (hexane) in cm<sup>3</sup>. Capacity factors,  $k'$ , were calculated for aromatic compounds according to the equation

$$k' = (V_R - V_0)/V_0 \quad (2)$$

The absolute retention volume,  $V_A$ , was calculated as

$$V_A = V_e/mS \quad (3)$$

where  $m$  is mass of adsorbent in the column and  $S$  is the specific surface area of the adsorbent. In the theory of equilibrium chromatography,  $V_A = K_I$ , where  $K_I$  is Henry's constant.  $K_I$  represents the slope of the static adsorption isotherm at  $C \rightarrow 0$ , and can be calculated according to the equation<sup>4,5</sup>

$$K_I = \Gamma/C \quad (4)$$

at  $C \rightarrow 0$ , where  $\Gamma$  is the Gibbs's adsorption value and  $C$  is the molar concentration of the equilibrium solution.

## RESULTS AND DISCUSSION

Table II compares the  $k'$  and  $k'/k'_0$  (reduced to benzene) values of aromatic compounds on elution with *n*-heptane on various adsorbents. The retention order of aromatic compounds on the carbon adsorbent C-1 is naphthalene > benzaldehyde > anisole > benzene, whereas on SiO<sub>2</sub> + C and SiO<sub>2</sub> it is benzaldehyde > anisole > naphthalene > benzene. Moreover, the C-1 adsorbent has a higher adsorption capacity than SiO<sub>2</sub> + C and SiO<sub>2</sub> for aromatic hydrocarbons (benzene, naphthalene). Gradual replacement of the hydroxylated silica surface with a homogeneous carbon adsorbent surface decreases the contribution of specific interactions, while the contribution of dispersion interaction to the total sorption energy is increased. Thus, benzaldehyde is retained on SiO<sub>2</sub> 65.5 times, on SiO<sub>2</sub> + C 23 times and on C-1 only 1.9 times more strongly than benzene, while naphthalene is retained on SiO<sub>2</sub> 2.2 times, on SiO<sub>2</sub> + C 3.3 times and on C-1 as much as 5.6 times more strongly than benzene.

Table II shows that modification of silica by coating with a carbon monolayer makes the mechanism of retention of aromatic compound on this adsorbent similar to that on C-1; nevertheless, certain specific features of the SiO<sub>2</sub> + C surface remain, which is illustrated by the  $k'/k'_0$  values for anisole and benzaldehyde, and is explained by incomplete screening of hydroxyl groups on the SiO<sub>2</sub> surface with a carbon monolayer. Table III shows  $k'$  values for *o*-, *m*- and *p*-xylenes on elution with *n*-heptane using various adsorbents. In the process of their adsorption on SiO<sub>2</sub>, specific orientation interactions of molecules with the adsorbent surface predominate; the reten-

TABLE II  
 $k'$  AND  $k'/k'_0$  VALUES

Eluent: *n*-heptane.

Substance	SiO <sub>2</sub>		SiO <sub>2</sub> + C		C-1	
	$k'$	$k'/k'_0$	$k'$	$k'/k'_0$	$k'$	$k'/k'_0$
Benzene	0.16	1	0.17	1	1.8	1
Naphthalene	0.36	2.2	0.56	3.3	10.1	5.6
Anisole	1.87	12	0.63	3.7	2.0	1.1
Benzaldehyde	10.65	65.5	3.9	23	3.4	1.9

TABLE III  
 $k'$  VALUES OF XYLENES ON VARIOUS ADSORBENTS

Compound	<i>n</i> -Heptane			Acetonitrile:
	SiO <sub>2</sub>	SiO <sub>2</sub> + C	C-1	C-1
<i>o</i> -Xylene	0.27	0.10	1.40	1.27
<i>m</i> -Xylene	0.13	0.13	1.90	1.49
<i>p</i> -Xylene	0.10	0.17	2.00	1.53

TABLE IV  
EFFECT OF MOBILE PHASE ON  $k'$  ON A C-1 COLUMN

$V_0$  ( $C_6H_{14}$ ) = 4.5 ml.

Substance	$k'$		
	$n-C_7H_{16}$	$CH_3CN$	$CH_3CN-H_2O$ (40:60)
Benzene	1.80	0.7	10.1
Anisole	2.00	0.87	—
Phenol	5.65	0.56	5.6
Acetophenone	10.1	1.27	12.4

tion order of the xylenes is in fair correlation with their dipole moments: *o*-xylene ( $\mu = 0.52$ ), *m*-xylene ( $\mu = 0.37$ ) and *p*-xylene ( $\mu = 0.06$ ). A different retention order is observed on carbon adsorbents, determined by dispersion interactions of xylene molecules with the surface of the carbon adsorbent. Gradual replacement of *n*-heptane with a more polar eluent, acetonitrile, results in a slight reduction in the  $k'$  values for xylenes on C-1. The efficiency and selectivity of their separation on C-1 remain almost unchanged.

Hence the chemical nature of the adsorbent surface and modification-induced changes thereto have considerable effects on the mechanism, retention order, efficiency and selectivity of separation of the studied aromatic compounds on elution with *n*-heptane.

In addition to the chemical nature of the adsorbent surface, a large influence on the retention of aromatic compounds is also exerted by the nature of the mobile phase. Table IV gives  $k'$  values of aromatic compounds on C-1 column on elution with various solvents. On replacement of *n*-heptane with polar acetonitrile, the  $k'$  values of aromatic compounds decrease, particularly those of polar molecules (phenol, acetophenone), which experience a roughly 10-fold decrease. In contrast, introduction of a more polar substance (water) into acetonitrile results in an abrupt increase in retention on C-1; interactions that take place in the mobile phase are probably the reason behind the stronger interaction between the eluted aromatic com-

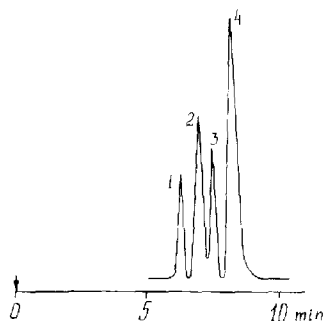


Fig. 1. Chromatogram of a mixture of aromatic acids (1 = benzoic, 2 = salicylic, 3 = anthranilic, 4 = phthalic acid) on a C-1 column (20 cm  $\times$  0.4 cm I.D.) at 295 K. Eluent: acetonitrile-water mixture (40:60); flow-rate, 1 ml/min.

TABLE V

 $k'$  VALUES WITH ACETONITRILE-WATER (40:60) AS ELUENT ON DIFFERENT ADSORBENTS

Substances	C-1	Carbon <sup>6</sup>	LiChrosorb RP-8 <sup>7</sup>
Acetophenone	12.4	3.25	2.0
Benzene	10.1	1.3	4.7
Phenol	5.6	0.4	3.9
Benzoic acid	0.45	—	0.3

pounds and the surface of C-1. Elution with acetonitrile-water (40:60) on a C-1 column gave the highest efficiency and selectivity in the separation of aromatic acids; the analysis time was less than 10 min (Fig. 1).

Table V compares the results obtained on C-1 adsorbent with reference data<sup>6,7</sup>; the orders in which aromatic compounds are observed in the C-1 and the carbon column are identical, whereas  $k'$  values obtained for each compound are greater on the C-1 than on the carbon column<sup>6</sup>, which is probably due to different parameters of the columns. A different retention order is observed on the LiChrosorb RP-8 column, decreasing in the sequence benzene, phenol, acetophenone, benzoic acid, indicating different retention mechanisms for LiChrosorb RP-8 and carbon adsorbents.

A comparison of the  $K_1$  values of aromatic compounds obtained from the chromatograms and calculated according to eqn. 4 from the slopes of the static sorption isotherms is also of interest. Adsorption was carried out from solutions in *n*-heptane in the region of low equilibrium concentrations on carbon black<sup>8</sup> and SiO<sub>2</sub><sup>9</sup> surface. Table VI gives the results of this comparative study, and shows that in terms of  $K_1$  values, the C-1 adsorbent occupies an intermediate position between carbon black and SiO<sub>2</sub> with respect to the sorption of aromatic compounds from solutions in *n*-heptane, indicating an increasing polarity in this adsorbent series. It is also worth mentioning that, as opposed to SiO<sub>2</sub>, the solvent itself exhibits a strong interaction with the adsorbent surface, thereby weakening the adsorption of aromatic compounds from solutions in *n*-heptane on the surface of C-1 and carbon black.

TABLE VI

 $K_1$  VALUES OF AROMATIC COMPOUNDS ON DIFFERENT ADSORBENTS WITH *n*-HEPTANE AS ELUENT

Substances	$K_1$ ( $\text{mm}^3/\text{m}^2$ )		
	C-1	Carbon black <sup>8</sup>	SiO <sub>2</sub> <sup>9</sup>
Benzene	9	1	5
Anisole	10	2	15
Benzaldehyde	17	10	130
Phenol	28	18	800

## REFERENCES

- 1 K. K. Unger, *Anal. Chem.*, 55 (1983) 361.
- 2 W. Golkiewicz, C. E. Werkhoven-Goewie, U. A. Th. Brinkman, R. W. Frei, H. Colin and G. Guiochon, *J. Chromatogr. Sci.*, 21 (1983) 27.
- 3 D. Berek and L. Feltl, *Collect. Czech. Chem. Commun.*, 47 (1982) 582.
- 4 N. A. Chuduk, Yu. A. Eltekov and A. V. Kiselev, *J. Colloid Interface Sci.*, 84 (1981) 149.
- 5 H. Manard, L. Noel, F. M. Kimmerle, L. Tonsignant and M. Lambert, *Anal. Chem.*, 56 (1984) 1240.
- 6 J. H. Knox, K. K. Unger and H. Mueller, *J. Liq. Chromatogr.*, 6 (1983) 1.
- 7 St. R. Bakalyar, R. McIlwrick and E. Roggendorf, *J. Chromatogr.*, 142 (1977) 353.
- 8 N. A. Chuduk and Yu. A. Eltekov, *Zh. Fiz. Khim.*, 55 (1981) 1010.
- 9 Yu. A. Eltekov and N. A. Chuduk, *Zh. Fiz. Khim.*, 56 (1982) 425.