Retention times and heats of adsorption of aromatic compounds on carbon adsorbents

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SUMMARY

A high-performance liquid chromatographic method was applied to the determination of the adsorption isotherms and heats of benzene, toluene, ethylbenzene, *o*-xylene, pseudocumene, *p*-diethylbenzene and anisole from *n*-heptane on carbon adsorbents. The retention times of these compounds were determined at 20, 40 and 60°C. Comparison of the results of chromatographic and static investigations allowed the character of the dynamic process to be established. The heats of adsorption of aromatic compounds on carbon and silica adsorbents were compared. The mechanism of the adsorption interaction is discussed.

INTRODUCTION

Of the various carbon adsorbents, graphitized thermal carbon black has been used with success in gas chromatography. Fundamental work carried out by Kiselev and co-workers[1–3] stimulated the development of a new method for the determination of molecular structure, the so-called chromatoscopy[2]. However, carbon adsorbents have not yet been applied in liquid chromatography.

Knox and Unger[4] and Unger[5] showed that microparticles of carbon adsorbents obtained by carbonization of polymeric materials possessed great selectivity and high capacity, and could be applied in the liquid chromatography of molecules and macromolecules.

This paper reports some results of a study of the structure and surface properties of two carbon adsorbents, Carboraffin[6] and active carbon AU-40[7], by HPLC and static methods. The main aim was to establish the possibility of applying HPLC for the determination of the thermodynamic characteristics of adsorption on carbon adsorbents.

EXPERIMENTAL

Adsorbates

Benzene, toluene, *o*-xylene, ethylbenzene, *p*-diethylbenzene, pseudocumene and anisole (V. O. Khimreaktiv, U.S.S.R.) were used as adsorbates. They were purified by

fractional distillation *in vacuo* or by recrystallization and their purity was controlled chromatographically.

Solvent
        n-Heptane (V. O. Khimreaktiv) was used as the solvent and the eluent. It was distilled, dried and kept under NaA zeolite.

Adsorbents
        Active carbon AU-40 had the following structural parameters[7]: total micropore volume, $W_0 = 0.32$ cm^3 g^{-1}; half-width of micropores, $x_0 = 0.6$ nm; characteristic adsorption energy, $E_0 = 18.6$ kJ mol^{-1}; and specific surface area, $S = 500$ m^2 g^{-1}. Carboraffin was kindly provided by Dr. O. Kadlec (Institute of Physical Chemistry and Electrochemistry, Prague, Czechoslovakia), and had the following structural parameters[6]: $W_0 = 0.95$ cm^3 g^{-1}, $x_0 = 2.2$ nm, $E_0 = 8.9$ kJ mol^{-1} and $S = 940$ m^2 g^{-1}.

Apparatus
        The investigations were conducted on a Tsvet-304 chromatograph with a UV detector ($\lambda = 254$ nm), cell volume 7 μl. An LDC (Riviera Beach, FL, U.S.A.) differential refractometer, cell volume 5 μl, was also used. The chromatographic column was 10 cm × 0.3 cm I.D., partical size of adsorbent 10 ± 2 μm and flow-rate 1 ml min^{-1}. In static experiments the equilibrium concentrations were determined from the difference in the heights of the chromatographic peaks on a high-performance analytical column.

RESULTS AND DISCUSSION

Calculation of adsorption isotherm.
        The excess adsorption value in static experiments was calculated from the equation

$$\Gamma_1^{(v)} = n\Delta x_1/mS \tag{1}$$

where n is the total number of moles of solution, Δx is the difference in concentrations before and after adsorption, m is the adsorbent mass and S is the specific surface area of the adsorbent.
        The adsorption value of component 1 under conditions of equilibrium chromatography can be determined from the equation

$$\Gamma_1^{(\delta)} = 1/A \int_0^{c_1} V_R dc_1 \tag{2}$$

where V_R is the retention volume, A is the total surface area of the adsorbent in the column and c_1 is the concentration of component 1 in the mobile phase.
        The procedure for calculating the adsorption isotherms for the aromatic compound–*n*-heptane system from the liquid adsorption chromatographic data was
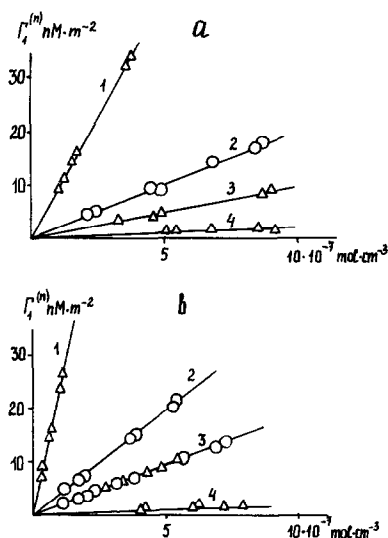
Fig. 1. Isotherms for the adsorption of (a) toluene and (b) anisole from solutions in n-heptane on active carbon AU-40 (1, 2), silica [$S = 80 \, m^2 \, g^{-1}$ (ref. 8)] (3) and graphitized carbon black [$S = 85 \, m^2 \, g^{-1}$ (ref. 9)] (4) at 20°C. $\triangle$, Static measurements; $\bigcirc$, chromatographic measurements.

described in detail elsewhere[8]. Fig. 1 shows thus calculated isotherms for the adsorption of (a) toluene and (b) anisole from solutions in n-heptane with active carbon AU-40 (1 and 2) and silica (3). Fig. 1 also shows for comparison the isotherms for the adsorption of toluene and anisole from solutions in n-heptane on the surface of graphitized carbon black, obtained by the static method (4). From Fig. 1, it can be seen that for toluene and anisole in the adsorption on AU-40 active carbon the static adsorption isotherm lies much higher than the adsorption isotherm calculated from the liquid adsorption chromatographic data. This non-coincidence of the adsorption isotherms obtained by different methods, as shown previously[9], is indicative of the non-equilibration of the conditions under which the chromatographic experiment was conducted. The sharp difference between the adsorption of toluene and anisole on active carbon and on graphitized black indicates a difference in the structure of these adsorbents with a similar nature of their surface, *i.e.*, the presence of micropores in the active carbon. Micropores in the active carbon increase the adsorption potential, and so the adsorption isotherms of toluene and anisole, obtained by the static method on active carbon, lie higher than those obtained on non-porous graphitized carbon black[10]. It seems that not all the pores in the microporous active carbon take part in the chromatographic process, as the mass exchange in narrow micropores is strongly impeded and, as a result, the static and the chromatographic toluene and anisole adsorption isotherms do not coincide. With macroporous silica one observes complete coincidence of anisole adsorption isotherms obtained by the static and the chromatographic methods, which indicates equilibration of the chromatographic process in this instance.

Adsorption equilibrium constant

Previously an expression was proposed[8] for the adsorption equilibrium constant in the following form:

$$K_1 = \Gamma_1^{(v)}\gamma_{a,1}/c_1\gamma_{v,1} = \exp[(\mu_{a,1}^0 - \mu_{v,1}^0)/RT] \tag{3}$$

where $\gamma_{a,1}$ and $\gamma_{v,1}$ are the activity coefficients of component 1 in the surface and the bulk solution, respectively, and $\mu_{a,1}^0$ and $\mu_{v,1}^0$ are the standard chemical potentials of component 1 in the surface and the bulk solution, respectively. For $c_1 \to 0$, $\gamma_{v,1} \to 1$ and $\Gamma_1 \to 0$, $\gamma_{a,1} \to 1$,

$$K_1 = \lim_{c_1 \to 0} \Gamma_1/c_1 = K_H \tag{4}$$

where K_H is Henry's constant. An infinitely dilute solution was chosen as the standard state.

From the theory of equilibrium chromatography, it follows that

$$K_H = V_{A,1} \tag{5}$$

where $V_{A,1}$ is the absolute retention volume of component 1.

To establish the reliability of the chromatographic data and equilibration, the $V_{A,1}$ values obtained from the chromatograms were compared with the K_H values calculated from static adsorption isotherms using eqn. 4 (Table I).

From Table I, it can be seen that with macroporous silica the K_H and $V_{A,1}$ values for toluene and anisole coincide, which indicates that the chromatographic process is taking place under equilibrium conditions. With the mesoporous carbon adsorbent carboraffin, the K_H and $V_{A,1}$ differ *ca.* 1.5-fold and with the microporous active carbon 5-fold. This indicates that not all the surface of microporous adsorbents takes part in the chromatographic process, but only the available surface, which can be estimated from the expression $SV_{A,1}/K_H = S_g$.

Calculation of ΔH^0, ΔF^0 and ΔS^0

Fig. 2 shows the log $V_{R,1}$ *vs.* $1/T$ dependence for the various aromatics on

TABLE I

K_H AND $V_{A,1}$ VALUES OF TOLUENE AND ANISOLE ON SILICA AND CARBON ADSORBENTS

Component 2 = *n*-heptane.

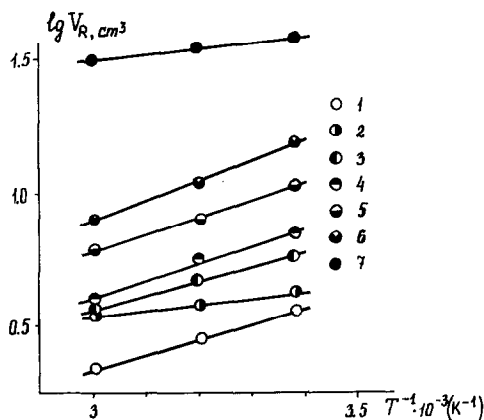| Component 1	Silica		Carboraffin		Active carbon	
	K_H $(mm^3\ m^{-2})$	$V_{A,1}$ $(mm^3\ m^{-2})$	K_H $(mm^3\ m^{-2})$	$V_{A,1}$ $(mm^3\ m^{-2})$	K_H $(mm^3\ m^{-2})$	$V_{A,1}$ $(mm^3\ m^{-2})$
Toluene	7.0	7.0	2.0	1.5	110	22
Anisole	15	15	20	14.5	240	40

Fig. 2. Log V_R vs. $1/T$ for (1) p-diethylbenzene, (2) ethylbenzene, (3) benzene, (4) toluene, (5) o-xylene, (6) pseudocumene and (7) anisole on carboraffin.

carboraffin. The enthalpies of adsorption of these compounds on carboraffin were calculated from the slopes of the curves according to the equation

$$\Delta(\Delta H) = -RT^2 \cdot \frac{\mathrm{d}\ln V_R/T}{\mathrm{d}T} \tag{6}$$

The total enthalpy of the adsorption of aromatic compounds was found taking into account the net heat of adsorption of n-heptane according to the equation

$$-\Delta H^0 = \Delta(\Delta H) + \beta\Delta H_{C_7H_{16}} \tag{7}$$

where β is the displacement coefficient, equal to the ratio of the areas of molecules of aromatic compounds to that of n-heptane.

Fig. 3 shows the dependences of the enthalpies of adsorption of aromatic compounds on the molar volume $\bar{V}_0$ of these molecules. Linear dependences of $-\Delta H^0$ on $\bar{V}_0$ for adsorption on carboraffin are observed for two series of compounds: benzene, toluene, o-xylene and pseudocumene, and anisole, ethylbenzene and p-diethylbenzene.
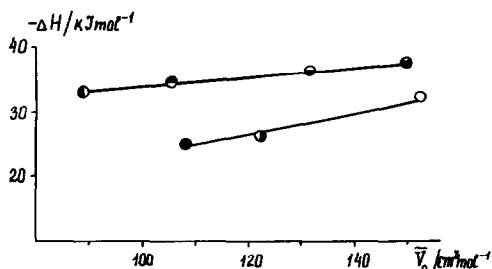

Fig. 3. $-\Delta H^0$ vs. $\bar{V}_0$ for aromatic compounds (numbers as in Fig. 2) on carboraffin.

TABLE II

VALUES OF ΔF^0, ΔH^0 AND ΔS^0 FOR THE ADSORPTION OF AROMATIC COMPOUNDS ON CARBORAFFIN AND HYDROXYLATED SILICA

Substance	Carboraffin			Silica		
	$-\Delta F^0$ (kJ mol^{-1})	$-\Delta H^0$ (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	$-\Delta F^0$ (kJ mol^{-1})	$-\Delta H^0$ (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
Benzene	2.7	33	−100	5.5	24	−60
Anisole	14	25	− 37	8.0	28	−65

Free-energy variations in the adsorption of aromatic compounds were calculated from the equation

$$-\Delta F^0 = 2.3\, RT \log K_H \tag{8}$$

Entropy variations in the adsorption of aromatic compounds on silica and carboraffin were calculated from the equation

$$F^0 = H^0 - T\Delta S^0 \tag{9}$$

An infinitely dilute solution was taken as the standard state in the calculations. Results are given in Table II.

It can be seen from Table II that for the adsorption of benzene from solutions in n-heptane on carboraffin the benzene molecule loses more degrees of freedom than the anisole molecule. Owing to their great affinity, the flat benzene molecules are attached closely to the graphite-like surface of the carbon sorbent, which leads to a loss of mobility of the molecules along the surface and to a decrease in the entropy of adsorption. In contrast to benzene, the methyl group of anisole molecules hinders close contact with the graphite ring on the carbon surface and hence increases the mobility of adsorbed anisole molecules.

The interpretation of two linear dependences in the plots (Fig. 3) of $-\Delta H$ vs. $\bar{V}_0$ involves not only the entropy factor but also the *para*-effect. The interactions of solvent molecules with molecules such as anisole, ethylbenzene and p-diethylbenzene are stronger than those with shorter and more compact molecules such as benzene, toluene, o-xylene and pseudocumene.

The mechanism of adsorption interactions in the carbon sorbent–solvent–aromatic compound systems should become clearer with further systematic HPLC investigations. Other factors (*e.g.*, microporosity, impurities on the carbon surface, diffusion effects) may contribute to the total retention values and the thermodynamic characteristics of adsorption interactions.

REFERENCES

1 A. V. Kiselev and D. P. Poshkus, *Adv. Colloid Sci.*, 9 (1978) 1.
2 A. V. Kiselev and D. P. Poshkus, *Faraday Symp. Chem. Soc.*, 15 (1980) 15.
3 A. V. Kiselev, D. P. Poshkus and Ya. I. Yashin, *Molecular Fundamentals of Adsorption Chromatography*, Khimiya, Moscow, 1986, p. 65.

4 J. H. Knox and K. K. Unger, *J. Liq. Chromatogr.*, 6, Suppl. 1 (1983) 1.
5 K. K. Unger, *Anal. Chem.*, 55 (1983) 361.
6 M. M. Dubinin, O. Kadlec and N. S. Polyakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 4 (1987) 719.
7 M. M. Dubinin, *Dokl. Akad. Nauk SSSR*, 275 (1984) 1442.
8 N. A. Chuduk, A. V. Kiselev and Yu. A. Eltekov, *J. Colloid Interface Sci.*, 84 (1981) 149.
9 N. A. Eltekova and Yu. A. Eltekov, *Zh. Fiz. Khim.*, 60 (1986) 2272.
10 N. A. Eltekova, *J. Chromatogr.*, 364 (1986) 425.