POSTER

HPLC STUDY OF ADSORPTION THERMODYNAMICS ON CARBON

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INTRODUCTION

High-perfomance liquid chromatography with the use of sensitive detectors permits investigation of adsorption from solutions in the region of very low concentrations unaccessible by other methods.

The application of mesoporous adsorbents with small particles (3-5 mm) at low viscosity and optimal flow rate of eluent at least in the case of rather small adsorption energy allows one to approach thermodynamic equilibria under the dynamic conditions of a HPLC experiment. In this case it is possible, first, to determine Henry's constant for adsorption from solution, and second, to determine the initial part of the isotherm of adsorption from solution. This isotherm can be calculated from the HPLC data [1].

This paper reports the results of the HPLC study with aromatic compounds of different chemical structure on mesoporous carbon sorbents. The results are used to explain a mechanism of intermolecular interactions of solute molecules with the carbon surface.

EXPERIMENTAL

The study was carried out on a microcolumn liquid chromatograph Milichrom (Scientific Instruments, Russia) with a UV detector (cell volume 1.5 μl). Carbon Sorbents were packing in a stainless steel column of 40 mm length and 1.5 mm i.d. As a mobile phases pure n - heptane, tetrahydrofuran (THF), acetonitrile (ACN) and mixtures of ACN and water were used in this work. The flow rate was 100 ml/min. The column temperature was 293 K. The mobile phase volume was calculated as a half-sum of retention volumes of n-octane and n-hexane when n-heptane was used as an eluent. The mobile phase volume was assumed to be constant for every mobile phase. The relative retention coefficient -capacity factor K' was evaluated as

$$K' = (V_R - V_0)/ V_0 \qquad (1)$$

where V_R and V_0 are the retention volumes of the test compound and the mobile phase, respectively.

Carbon Sorbent CLD (specific surface area $A=340 m^2/g$, predominant pore diameter d=17nm, particles size d_p = 10 μm) was from Polymer Institute (Bratislava, Slovakia). Carbon Sorbent PGC 101 (A = 150 m^2/g, d =25 nm, d_p = 10μm) was from Shandon (Runcorn, UK) [2].

As test compounds we used benzene, toluene, ethylbenzene, o- and p-xylene, pseudocumene, p-diethylbenzene, biphenyl,naphtalene,durene, fluorene, anthracene and as a nitrogen- and oxygen-containing organic compounds we used acetophenone, anilin, anisole, benzaldehyde, benzoic acid, methylbenzoate and also chlorbenzene and fluobenzene.

RESULTS AND DISCUSSION

Table 1 contains the capacity factor values for alkylbenzenes , polynuclear hydrocarbons and oxygen-containing aromatic compounds on Carbon Sorbent CLD. The Table demonstrates an influence of an eluent nature on an relative retention coefficient and hence the change of adsorption Gibbs energy. The flat molecules of THF interact with the carbon surface more strongly than the rod - like molecules of n-heptane or small polar molecules of ACN and therefore they decrease markedly the capacity factor of test compounds. The intermolecular interaction of oxygen-containing test compounds with the ACN or THF molecules led to a decrease in the capacity factor values.

Figure 1 and Figure 2 show the effect of mobile phase composition on the retention of aromatic compounds on Carbon Sorbent CLD. Increase in concentration of organic modifier usually gives a decrease in the retention for aromatic compound molecules. However, the dependences have a complex character. It is important to notice that the linear dependences of log K' versus log c were not observed in practice. This fact indicates the essential contribution of intermolecular interactions in

bulk phase of chromatographic system. Chromatographic study of aromatic compounds behavior on modified silicagel surface from ACN-water solution has led to similar results [3]. Anisole and benzaldehyde molecules are adsorbed on Carbon Sorbent CLD more strongly than benzene and phenol molecules. This indicates that this carbon sample contains a small number of specific active centres on its surface.

Table 2 gives a comparison of the relative retention coefficients K'/K'_0 for aromatic compounds on some sorbents. The value K'_0 relates to benzene retention on the particular sorbent. It should be noted that the K'/K'_0 ratios for the appropriate aromatic compounds are closed for both test samples of Carbon Sorbents (CLD and PGC 101). The chromatographic properties of modified silicagel-Lichrosorb RP[3] are different from the properties of CLD and PGC 101. It is important to note that benzoic acid molecules are adsorbed very weakly from a mixed ACN-water (2 : 3) solution on both modified silicagel and Carbon Sorbent. Maximum adsorption values are: on modified silicagel for benzene , on Carbon Sorbent CLD for benzaldehyde and on Carbon Sorbent PGC 101 for methylbenzoate. The difference in the chromatographic properties of these sorbents is due to their surface chemistry.

CONCLUSION

The adsorption properties of Carbon Sorbents have been studied with the use of the appropriate test substances and mobile phases by the HPLC method. The HPLC method offers a possibility for investigation of adsorption from solutions and especially in the range of very dilute solutions and very low surface coverages which were unaccessible earlier.

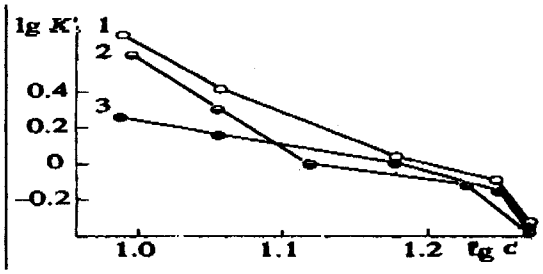

Figure 1 Plot of log K' vs. log C for o-xylene(1), toluene(2) and benzene(3) on CLD. C(mol/l) is the concentration ACN in water solution.Temperature 293K.

Table 1 - Capacity Factor Values for Test Compounds on CLD. Column 40 x 1.5 i.d. mm. Flow rate 100µl/min. Temperature 293 K.

Compound	THF	n-Heptane	ACN
Benzene	0.09	0.56	0.46
Toluene	0.12	0.60	0.53
o-Xylene	0.19	0.29	0.48
Pseudocumene	0.20	0.49	0.69
Durene	0.24	0.35	0.45
Naphthalene	0.34	1.20	0.82
Biphenyl	0.23	4.34	1.76
Fluorene	0.69	6.14	5.62
Anthracene	2.76	10.00	7.75
Anisole	0.20	1.54	0.69
Benzaldehyde	0.46	7.39	1.42
Phenol	0.10	10.20	1.20
Acetophenone	0.31	6.05	0.57

Table 2 - The Values of K'/K'_0 for the Test Compounds on Different Sorbents. Mobile phase: ACN - WATER (2:3 v/v). Temperature 293 K.

Compound	PGC 101	CLD	Silica RP [3]
Benzene	1 (0.85)	1 (1.48)	1 (4.7)
Benzaldehyde	1.92	2.22	0.47
Anisole	1.85	1.93	0.91
Phenol	0.73	0.69	0.83
Benzoic acid	0.58	0.43	0.064

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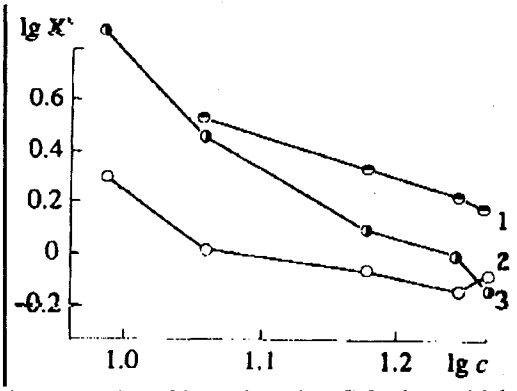

Figure 2- Plot of log K' vs. log C for benzaldehyde(1), anisole(2) and phenol(3). Conditions in Figure 1.