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Chromatographic retention parameters and molecular structure

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Abstract - A brief overview of the works by A.V.Kiselev on the relationship between the retention parameters and molecule structure in gas and liquid chromatography is given. New data on the retention regularities of alkylbenzenes in liquid chromatography are presented. It is shown that the electron density distribution in complex molecules may be predicted by the retention parameters in normal phase chromatography. It is also shown that the separation selectivity for isomers in reverse phase chromatography may be improved with the use of polar adsorbents instead of commonly used nonpolar adsorbents.

INTRODUCTION

The retention of substances in chromatography at constant temperature is determined by the nature of sorbent, mobile phase and by the molecule structure. The notion "molecule structure" implies both the composition and the geometry of the molecule. It is common knowledge that the scientific school of Professor A.V.Kiselev did very much to investigate the effects of adsorbent chemical nature and geometrical structure on the retention. The effects of molecule structure on retention in gas and liquid chromatography were also thoroughly investigated. These problems were intensively explored abroad (Ref.1) in the last few years. Many publications are aimed to extablishing quantitative relationship between the molecule structure and chromatographic parameters. The objects of these studies are:
- to explain the retention mechanism and to predict, on its basis, the retention parameters and separation selectivity
- to correlate the revealed retention regularities with the reactivity or biological activity of substances.
This paper presents an overview of previous works by A.V.Kiselev and coworkers as well as some new data concerwing the problem.

GAS CHROMATOGRAPHY

The influence of carrier gas on retention is in most cases negligible in gas chromatography, therefore the retention for an adsorbent at constant temperature is determined just by the molecule structure. The influence of

molecular structure on retention is highly pronounced for graphitized carbon black. The retention regularities for different classes of compounds as well as for different isomers (in particular cis-, tris-, positional isomers, ect) were investigated on graphitized carbon black in the series of studies (Ref.2-& 6). The influence of molecule geometry on retention was systematically studied for organometallic (Ref. 7), perfluorinated and fluorinated (Ref.8 & 12) and deuterated (Ref.13 & 14) compounds. It was shown that the retention on graphitized carbon black is proportional to electronic polarizability of molecules (Ref.15), that the retention on silica gels gives the idea on electronic effects in complex molecules (Ref.16), that the retention parameters provide the information on the properties of liquid crystals (Ref.17 & 19). These problems are generalized in the monographs (Ref.20 & 21).

LIQUID CHROMATOGRAPHY

The retention mechanism in liquid chromatography is more complex, since the retention is always influenced by the mobile phase used. In a generalized case for normal phase chromatography the retention is mainly due to specific adsorbent-eluent interaction, namely for benzene derivatives on silica gel. In reverse phase chromatography the retention is proportional to the degree of molecule hydrophoby, in particular the retention is proportional to van der Waals molecule volumes (Ref.21). The interaction of polar molecules with nonpolar eluent is very strong on hydroxylated silica gel. In some cases the retention may be due hydrogen bonding and donor-acceptor interactions. The retention will be caused to a considerable extent by the distribution of electronic density in molecules (Ref.22 & 24). Fig.1 illustrates the dependence of polymethylbenzene free adsorption energy change on summarized Gammet constants indicating that the retention is mainly due to electronic effects. The figure also presents the data

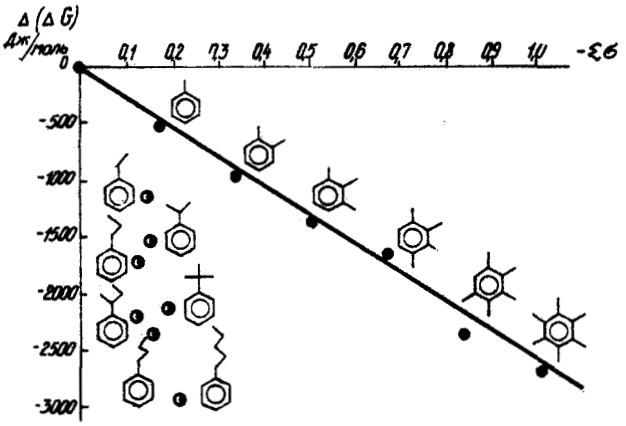

Fig. 1

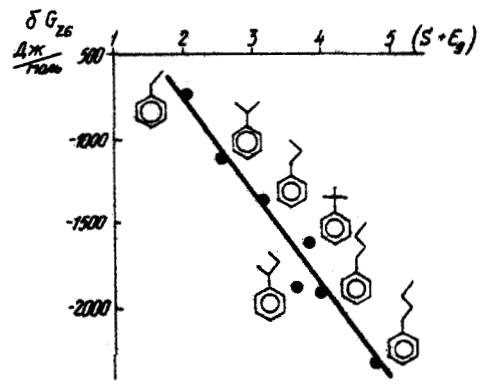

Fig.2

Fig. 1. Dependence of $\Delta(\Delta G)$ on summarized Gammet constants for benzene alkylderivatives. Column: 15 x 0,4 cm, hydroxylated silica gel; eluent - hexane, 3 cm^3/min, 25°C.

Fig.2. Dependence of $\Delta(\Delta G)$ on steric constants for benzene alkylderivatives. Analysis conditions as in fig.1.

for alkylbenzenes. Their retention changes are insignificant since the electron density of benzene ring for these compounds undergoes slight changes. A small difference in alkylbenzene retention is mainly caused by the length of the alkyl chain, which alters the adsorption spatial hindrance on the surface. This is confirmed by fig. 2 showing a good correlation between the change of free adsorption energy and steric constants. The method of electron adsorption spectroscopy of change transfer complexes provides the estimation of π -electron shell condition for the aromatic ring. The correlation between free adsorption energy changes and charge transfer band maximum frequencies in charge transfer complex of polymethylbenzenes with tetracyanethylene in methylenechloride indicates donor-acceptor interaction (fig.3).

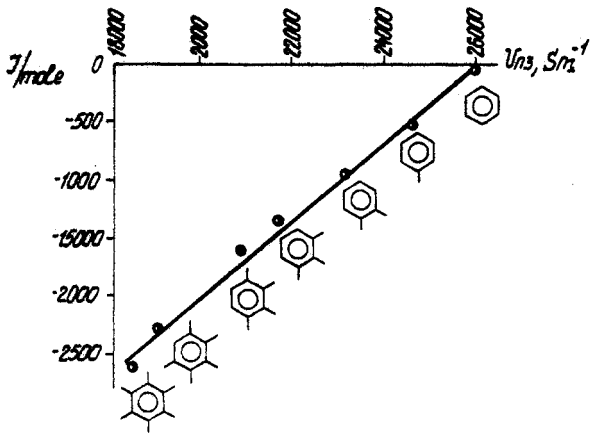

Fig.3

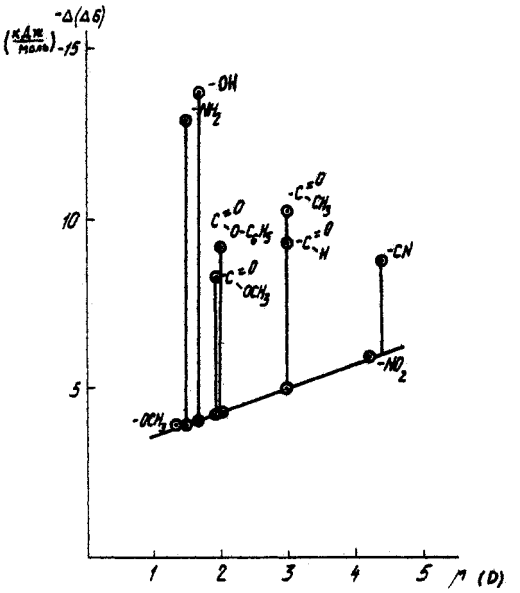

Fig.4

Fig.3. Relationship between Δ (Δ G) and frequencies of charge transfer band maximum in charge transfer complex of alkylbenzenes polymethylbenzenes with tetracyanethylene in methylene chloride.

Fig.4. Dependence of Δ (Δ G) for benzene substituents on dipole moments of adsorbate. Column: 10 x 0,4 cm, hydroxylated silica gel, 5 μm; eluent - hexane, 1 cm^3/min, 23°C.

Fig.4 shows that the retention is strongly influenced by hydrogen bonding. It illustrates the variation of free adsorption energy Δ(Δ G) with the dipole moments of adsorbed substances. A notable deviation of Δ(Δ G) from this plot for polar substances is due to considerable contribution of hydrogen bonding to the retention. The hydrogen bonding contribution may be estimated using the difference between Δ(Δ G) values of experimental points above the line and the points on the line where they should have been located in the absence of strong hydrogen bond contribution. The retention sharply decreases on dehydroxylated silica gel

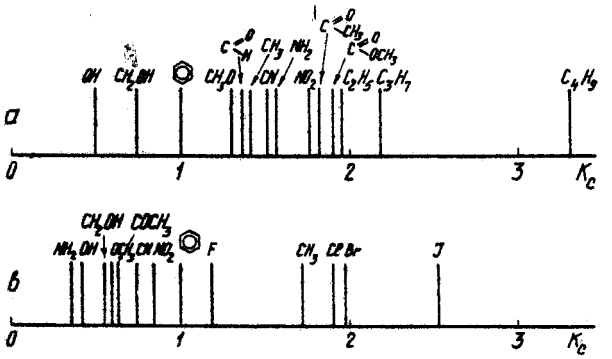

Fig.5. Relationship between K_e and the nature of benzene derivative functional groups:
a) Column: 10 x 0,6 cm, dehydroxylated silica gel (800 °C, 5 h); eluent: isopropanol-water (1:5).
b) Column: 10 x 0,6 cm, silanized silica gel; eluent: isopropanol-water (1:5).

(calcined at 800 °C for several hours) and the elution order changes for some polar substances. Varying the degree of dehydroxylation one may change the retention over a wide range. Dehydroxylated silica gels may find their use in reverse phase chromatography. Fig.5 presents the comparison of retention sequence for different benzene derivatives on hydroxylated and silanized (treated with trimethylchlorosilane) silica gels. Both the values of capacity factors (Kc) and the elution order of polar aromatic derivatives vary considerably for these two columns. The retention in reverse phase chromatography is due to nonspecific substance - adsorbent interaction and specific substance-eluent interaction. The retention and selectivity may be altered in reverse phase chromatography using polar adsorbents i.e. including also specific substance-adsorbent

TABLE 1. Relative retention times of benzene derivatives (versus benzene) on column with silica gel, 5 μm, modified by different functional groups. Column: 10 x 0,4 cm, eluent: water-isopropanol (3:1), 50 °C, 1 cm^3/min.

Compound	KCK + CN	KCK + $C_{12}S$	KCK + $COOCH_3$
Phenol	0.22	0.2	0.29
Aniline	0.16	0.21	0.42
Benzonitrile	0.42	0.31	0.44
Nitrobenzene	0.76	0.48	0.77
Anisole	0.72	0.77	-
Benzene	1	1	1
Toluene	1.47	2.06	1.6
Chlorobenzene	2.26	3.56	2.6
Ehyl benzene	2.3	3.87	2.74

TABLE 2. Capacity factors for halogen-substituted benzenes on silica gel doped with alkylsilane (C_{16}) and alkylthiosilane (C_{12}). Column: 10 x 0,4 cm; eluent: water-isopropanol (3:1), 50 °C, 1 cm^3/ min.

Compound	Substituent	Ke		
		KCK+CN	$KCK+C_{12}S$	$KCK+COOCH_3$
Fluorobenzene		1.18	1.72	1.46
Chlorobenzene		1.91	2.60	1.36
Bromobenzene		1.97	3.7	1.88
Iodobenzene		2.53	4.5	1.78

interaction. Table 1 presents relative retention times of benzene derivatives (versus benzene) on a column with silica gel, modified by different functional groups. The table shows, that both the capacity factor values and the elution order of the same derivatives can be altered using different sorbents. This is also confirmed by the retention data for halogen-substituted benzenes on the silica gels, mentioned above (table 2). Ion-pair chromatography is based on the same principle. The surface polarity is changed by the addition of dissociative substances to the eluent. Separation selectivity for isomers of some strongly polar substances, aromatic acid derivatives in particular, may be greatly enbanced (fig.6). In

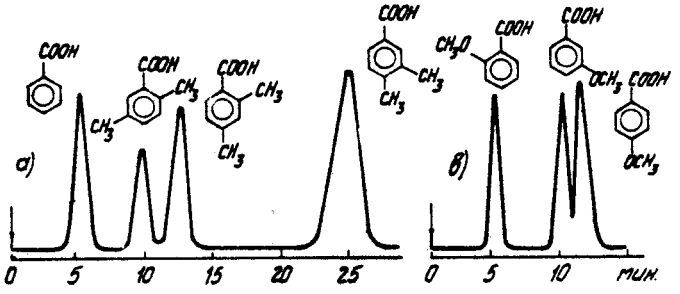

Fig.6. Chromatogram of benzoic acid derivatives. Column: 10 x 0,6 cm, silasorb C_{18}; eluent: isopropanol-water with 0,001 M tetrabutylammonia chloride: a) 20 % of isopropanol, b) 10 % of isopropanol.

this case positional isomers of benzoic acid derivatives are adequately separated. Separation selectivity and retention may be adjusted in this method both with the concentration of modifier (tetrabutylammonia chloride) and with the concentration of isopropanol. In this case the change in free adsorption energy is proportional to dissociation constants of acids.

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