

SPECIFIC INTERACTIONS IN GAS CHROMATOGRAPHY ON ACID ION EXCHANGERS

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The sorption of some hydrocarbons and halogenated hydrocarbons was investigated by measuring the retention volumes on the styrene-divinylbenzene copolymer and the same type of copolymer containing both the $-\text{SO}_3\text{H}$ functional groups and the composite of the $-\text{SO}_3\text{H}$ and $-\text{SO}_3\text{K}$ groups. The effect of adsorbent surface area, of sorbate dipole moment and π -electron structure and the effect of temperature upon the strength and type of interaction was established. The retention volumes were proved to depend on the magnitude of both the nonspecific and specific interactions.

In the investigations into the sorption properties of acid ion exchangers which were described previously¹⁻³ it was found that some of these sorbents can be considered as stationary phases for gas-solid chromatography. Ion exchangers have been utilized for many years in other chromatographic systems. However, their use as sorbents in gas-solid chromatography is not widespread because the chromatographic peaks obtained are asymmetrical due to the nonlinear adsorption isotherm for solutes⁴. The asymmetry can be eliminated to a certain degree⁵ by a partial deactivation of the sorbent surface with some non-volatile liquid such as *e.g.* squalane or diethylene glycol succinate.

The investigation of the sorption mechanism by gas-solid chromatography is of great interest because the type of adsorption interactions can be assumed from the comparison of the changes in retention quantities of different adsorbates on the various types of these sorbents. According to Kiselev⁶ interactions may be divided into nonspecific and specific types. The compounds showing nonspecific interactions are represented by paraffinic hydrocarbons in which each bond is a σ -bond only and it is formed by dispersion forces. On the other hand in specific interactions π -bonds may be effective due to the presence of a region of high electron density. The existence of specific interactions anticipates a substrate to interact with the definite centres of the sorbate. Kiselev also noted that the usual conception of polar and nonpolar sorbates fails to explain the nature of physical adsorption. Other authors⁷ have found that a polarity and also polarizability of a molecule affect its adsorption which becomes evident with larger retention volumes of olefinic hydrocarbons on polar adsorbents^{8,9}.

In the present work we have studied the sorption interactions between selected hydrocarbons and halogenated hydrocarbons on the one hand and on the other hand, styrene-divinylbenzene copolymer both nonsubstituted and containing the sulfonic functional group which was in the further step partially neutralised by the potas-

sium ion. Attention was focused in particular on the effect of the π -electron structure and on the effect of the dipole moment upon the magnitude of the interaction forces.

EXPERIMENTAL

Material and Apparatus

n-Pentane, n-hexane, n-heptane, n-octane, cyclohexane, benzene and toluene (all reagent grade products) were supplied by Lachema, Brno. 1-Hexene, *o*-xylene, *m*-xylene, *p*-xylene, cyclohexene, methylcyclohexane, ethylbenzene, mesitylene, cumene, chlorobenzene, bromobenzene and *o*-chlorotoluene (all indicated as pure) were products of Fluka A.G., Buchs, Switzerland.

Macroreticular styrene-divinylbenzene copolymer S (specific surface area $102 \text{ m}^2/\text{g}$) and sulfonated copolymer containing $-\text{SO}_3\text{H}$ functional groups S—S (specific surface area $53 \text{ m}^2/\text{g}$, content of $-\text{SO}_3\text{H}$ groups 2.4 mval/g) prepared from S were commercial products of the Research Institute for Synthetic Resins and Lacquers, Pardubice. By partial neutralization of the sulfonic groups with potassium hydroxide the following ion exchangers were prepared from S—S by Jeřábek¹⁰: S—S₅₅ (specific surface area $56 \text{ m}^2/\text{g}$, content of $-\text{SO}_3\text{H}$ groups 1.31 mval/g , ion exchange $\text{K}^+ - \text{H}^+$ 45%) and S—S₀ (specific surface area $63 \text{ m}^2/\text{g}$, content of $-\text{SO}_3\text{H}$ groups 0 mval/g , ion exchange $\text{K}^+ - \text{H}^+$ 100%). Some additional properties of the ion exchangers in question were described elsewhere¹. The fraction of the particle size of $0.250 - 0.315 \text{ mm}$ was chosen in all the cases. The packing weights of the column were 1.91, 2.45, 2.46 and 2.55 g respectively for copolymers S,S—S, S—S₅₅ and S—S₀.

The gas chromatographic measurements were carried out with an apparatus constructed in the Development Department of the Czechoslovak Academy of Sciences, Prague. It was equipped with a katharometer (Zimmermann, Leipzig, G.D.R.) and a stainless-steel column of $34 \times 0.4 \text{ cm}$ I.D. Hydrogen was employed as the carrier gas. The samples were introduced with a $10\text{-}\mu\text{l}$ Hamilton microsyringe.

Procedure

Since the position of the retention peak maximum of some compounds was somewhat changed depending on the sample volume, their values extrapolated to the infinite dilution were used for the calculation of the specific retention volumes V_g . The calculation was carried out according to the equation¹¹

$$V_g = \frac{(V_R - V_d) \cdot f \cdot 273.15}{w \cdot T}$$

where V_R is the retention volume, calculated as a product of the retention time t_R and the carrier gas flow rate F , V_d is the dead volume of the system (*i.e.* the retention volume of a non-adsorbed compound), f is the correction factor on a column pressure drop, w is the amount of the stationary phase (in grams) in the column and T is the column temperature. The retention data of the investigated compounds were expressed relative to n-heptane as the standard. The results are summarised in Table I.

RESULTS AND DISCUSSION

The Effect of the Surface Area

As it is evident from Table I the specific surface area of the styrene-divinylbenzene copolymer is diminished approximately to one half by the sulfonation reaction, however, it remains almost unchanged by subsequent exchange of the sulfonic group proton with potassium ion and it is practically comparable for S—S and S—S₅₅. The retention behaviour of such compounds where nonspecific interactions are supposed to play a predominant role essentially corresponds to this fact. The saturated hydrocarbons the retention volumes of which are significantly lowered on the modified sorbents compared with those obtained on the nonsubstituted resin can serve as a typical example. The lowering in question is of course more significant than the specific surface area decrease. For instance, with the ion exchangers S and

TABLE I
Relative Retentions of Selected Compounds on Some Resins at 125°C (relative to n-heptane)

Compound	B.p., °C	<i>r</i> _{1,2}			
		S	S—S	S—S ₅₅	S—S ₀
n-Pentane	36	0.27	0.19	—	—
n-Hexane	69	0.45	0.79	0.42	0.45
1-Hexene	63.5	0.48	2.17	0.57	0.72
n-Heptane	98.4	1.00	1.00	1.00	1.00
n-Octane	125	2.16	3.22	2.24	3.04
Cyclohexane	81	0.80	0.69	0.43	0.46
Cyclohexene	83	0.95	2.54	0.68	0.80
Methylcyclohexane	100.4	1.56	1.51	0.92	0.99
Benzene	80	1.06	2.05	0.98	1.16
Toluene	110.6	2.36	4.04	2.66	4.06
<i>o</i> -Xylene	144	5.86	7.24	4.90	8.62
<i>m</i> -Xylene	139	5.17	6.64	5.03	9.86
<i>p</i> -Xylene	188	4.28	6.89	6.32	8.12
Ethylbenzene	132	4.07	5.70	4.30	7.25
Mesitylene	164.7	—	—	10.19	13.92
Cumene	152	—	9.52	7.66	10.87
Chlorobenzene	132	—	6.45	3.81	4.05
Bromobenzene	155	—	—	6.05	8.45
<i>o</i> -Chlorotoluene	179.5	—	—	6.29	7.01
<i>V</i> _g (n-heptane), ml		30.34	6.09	5.6	7.08

S—S₅₅ it possesses 5 : 1 and 10 : 1 respectively. However, with the compounds the sorption of which is supposed to be significantly affected also by the specific interactions the retention volume ratio should be changed and substantially increased particularly on S—S. The behaviour of unsaturated and aromatic hydrocarbons is consistent with this conception. Although the surface area of the sorbent apparently plays the most important role for the retention of all the substances measured, the effect of the specific interactions is strongly expressed for some of them.

The Effect of the Dipole Moment

The results of separation of closely boiling compounds differing in degrees of polarity are summarised in Table II. If dipole-dipole interaction between the sorbate and adsorbent is the main contribution to the retention of polar compounds, then the more polar compound within the groups should be eluted last. Therefore, ethylbenzene is eluted before chlorobenzene and cumene is eluted before bromobenzene on the ion exchanger S—S. On the contrary, it is conceivable that the retention volumes of the individual compounds within the group are only slightly different on the resin S. Similar behaviour was also observed on the ion exchangers S—S₅₅ and S—S₀. The exchange of proton by potassium ion formed from the sorption point of view a qualitatively different surface where no specific interactions were observed. It is worth noting that the retention volumes order obtained on these sorbents is reversed both to their boiling points and to their dipole moments.

TABLE II
Effect of Dipole Moment upon Retention Volumes of Compounds of Similar Boiling Point at 135°C

Compound	B.p., °C	Dipole moment <i>D</i>	<i>r</i> _{1,2}			
			S	S—S	S—S ₅₅	S—S ₀
Ethylbenzene	132	0.6	4.79	4.35	3.63	5.77
Chlorobenzene	136	1.7	4.45	5.88	2.90	4.01
Cumene	152	0.8	7.43	7.84	5.74	10.1
Bromobenzene	155	1.7	8.09	9.88	4.34	6.17
<i>V</i> _g (n-heptane), ml			16.87	4.93	4.1	5.0

The Effect of π -Electron Structure

The relation between π -electron structure of the investigated compounds and their retention volumes was studied by several closely boiling aliphatic and cyclic six-carbon hydrocarbons. The results are listed in Table I. These hydrocarbons were chosen on the assumption that their similarity in the boiling point suggested the similarity in the nonspecific adsorption degree. The data in Table I indicate that retention on S—S, S—S₅₅ and S—S₀ is essentially dependent on π -electron character of the sorbate. Therefore, n-hexane is eluted before 1-hexene on all the three sorbents mentioned above although their boiling points are reversed. The regularity can be observed also with the groups cyclohexane–cyclohexene and methylcyclohexane–toluene. The comparison of the retention characteristics for n-hexane–cyclohexane shows that also a geometrical factor of the molecule plays a certain role. The linear molecule is retarded longer than the cyclic one even though the former has a 12°C lower boiling point. Considering that practically no microporous structure was found with the ion exchangers S—S, S—S₅₅ and S—S₀ as it was published elsewhere¹ a stronger sorption of n-hexane cannot be accounted for by its easier penetration into small pores. The difference between the sorption of n-hexane and cyclohexane can be ascribed mainly to the presence of a geometrical factor. On the contrary, the retention data measured on the resin S indicate that nonspecific interactions are the sorption determining force and that the separation takes place according to the boiling points of the analysed compounds.

The Effect of Column Temperature

The effect of temperature upon retention volumes of some hydrocarbons was studied on sorbents with different capability of forming specific interactions (S, S—S). The

TABLE III
Effect of Temperature upon Relative Retentions of Some Hydrocarbons

Temperature °C	Compound	$r_{1,2}$ (compound/ pentane)		Temperature °C	Compound	$r_{1,2}$ (compound/ pentane)	
		S	S—S			S	S—S
98	1-Hexene	1.11 ^a	2.14 ^a	124	1-Hexene	1.05 ^a	2.7 ^a
	Cyclohexane	4.47	2.1		Cyclohexane	2.98	2.46
	Cyclohexene	4.80	7.76		Cyclohexene	3.54	9.04
	Benzene	—	6.25		Benzene	3.89	7.3

^a Relative to n-hexane.

results of the measurements are summarised in Table III and expressed by relative retentions which serve as a resolution factor. Lower column temperatures provide better resolution on the resin S where no specific interactions were found. This is in agreement with the general notion valid in gas chromatography. In contrast, this regularity opposes the results obtained on the ion exchanger S—S which is capable of bringing about a specific sorption. The phenomenon observed is consistent with the notion concerning the sorption of organic compounds again and can be interpreted in such a way that the specific interaction is in fact chemisorption which takes place with certain activation energy and consequently possesses steeper temperature dependence.

CONCLUSIONS

Gas–solid chromatography provides convenient means for the investigation of sorption phenomena and sorbate–sorbent interactions. The data proved that sorption on ion exchangers consists of nonspecific and specific contributions. The specific sorption is a composite of several effects such as *e.g.* the degree of sorbate polarity, π -electron structure, geometrical arrangement of the molecule *etc.* Since the retention peaks of the compounds measured showed mostly a symmetrical or slightly asymmetrical shape, the ion exchanger S—S can be employed in gas–solid chromatography for the analytical separation of mixtures containing saturated and unsaturated hydrocarbons with similar boiling points.

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