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PREDICTION OF RETENTION DATA OF POLYCHLOROBENZENES AND -NAPHTHALENES ON GRAPHITIZED CARBON BLACK

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SUMMARY

The thermodynamic functions of the adsorption of polychlorobenzenes and -naphthalenes on graphitized carbon black have been determined experimentally by gas chromatography and computed theoretically using the methods of the molecular statistical theory of adsorption. The theoretical model includes the contribution of the large anisotropic tensor of polarizability of graphite. The relevance of introducing the dipole moment-induced dipole moment interaction and of using approximate molecular geometries is discussed. The retention orders predicted by theory agree with the experimental orders in most instances. The differential adsorption energies are quantitatively predicted with good accuracy.

INTRODUCTION

The possibility of the *a priori* calculation of retention data on graphitized carbon black is a well known and developed topic in gas adsorption chromatography. Many useful results have been obtained by employing the methods of the molecular statistical theory of adsorption¹⁻⁶. To date, such an approach has been applied to a limited class of structurally simple compounds (rare gases, simple aliphatic and aromatic hydrocarbons). Recently, the molecular statistical model was considerably improved⁷ by taking into account the important contribution of the anisotropic tensor of polarizability of the atom force centres, which provides for a more realistic model of adsorption⁸⁻¹⁰.

In this paper, the usefulness of this extended computational model is verified by its ability to predict exact gas chromatographic elution orders of two classes of compounds on graphite: polychlorobenzenes and -naphthalenes. The principal purpose of this work was to study the adsorption behaviour of components with one or several chlorine atom(s) substituted on the aromatic ring. The consequence of an

exact knowledge of the molecular geometry on the predicted retention volumes and the other thermodynamic functions of adsorption is also discussed.

Several interesting studies have been performed in order to attain optimal conditions for the chromatographic analysis of chloro- and polychlorobenzene isomers¹¹⁻¹⁹ and of chloronaphthalene isomers²⁰⁻²². However, the aim of the present work was to develop further the possibilities of using the theoretically computed retention orders for identifying unknown compounds or for elucidating the geometrical structures of complex compounds (*i.e.*, contributing to the development of Kiselev's chromatography²³).

The compound classes considered here are the building blocks for more complex compounds (*e.g.*, chlorodioxins, chlorodibenzofurans, polychlorinated biphenyls) whose importance in pollution studies is well known.

Experimental retention parameters (retention volumes, adsorption energy, relative retention) on a classical packed graphite column are presented for most of the available geometrical isomers of polychlorobenzenes and -naphthalenes. For all these compounds, and also for those which were not available, the values of these quantities predicted by the theoretical model are presented, compared with experimental data and discussed. These data are of great importance in identifying the components of mixtures when efficient porous carbon black capillary columns are employed for analytical applications²⁴.

THEORETICAL

In ideal linear gas adsorption chromatography, the retention volume is equal to the second adsorbate surface virial coefficient, B_{AS} . For quasi-rigid molecules (no degrees of freedom of internal rotation except for unhindered rotation of methyl groups around a C-C bond²⁴), the retention volume is predicted from the ratio of the partition functions in the gaseous and the adsorbed phases⁴. When the adsorbed surface is one crystallographic plane:

$$V_A = \int \dots \int [\exp(-\Phi/RT) - 1] dx dy dz \sin\theta d\theta d\varphi d\psi \quad (1)$$

where Φ is the adsorption potential, R the gas constant, T the absolute temperature, x , y and z , are the coordinates of the molecule mass centre and θ , φ and ψ are the Euler orientation angles with respect to the adsorbing crystal surface.

The differential heat of adsorption, q_d , is derived from the change in V_A with temperature:

$$q_d = R d \ln V_A / d(1/T) \quad (2)$$

To predict retention volumes and differential heats of adsorption, it is necessary to calculate the adsorption potential for all distances and orientations of the molecule and, therefore, simplified potential equations with a classical thermodynamic approach will be used.

The adsorption potential is divided into the sum of different contributions: electrostatic, Φ^E ; dispersion, Φ_i^D ; and repulsion potentials, Φ_i^R :

$$\Phi = \Phi^E + \sum_i \Phi_i^D + \sum_i \Phi_i^R \quad (3)$$

where Φ_i^D and Φ_i^R are the dispersion and repulsion contributions to the potential interaction of each adsorbate atom, i , with the surface.

For polar molecules adsorbed on graphite, the electrostatic contribution Φ^E is^{2,5}

$$\Phi^E = -(\alpha_{j1} F_x^2 + \alpha_{j2} F_y^2 + \alpha_{j3} F_z^2) \quad (4)$$

where F_x , F_y and F_z are the components of the electrical field produced by the dipole moment $\vec{\mu}$ of the molecule at a distance r_{ij} ; $F_x = -\partial u/\partial x$, $F_y = -\partial u/\partial y$ and $F_z = -\partial u/\partial z$ along the axes x , y and z of the polarizability tensor of graphite; α_{j1} , α_{j2} , α_{j3} are the main components of this tensor and u is the corresponding potential:

$$u = \vec{r}_{ij} \vec{\mu} / r_{ij}^3 \quad (5)$$

Meyer's anisotropic adsorption model⁸, describing the adsorption of molecules on graphite, has been applied to calculate the dispersion potential:

$$\Phi_i^D = - C_{ij} \sum_j \sum_{k=1}^3 \sum_{l=1}^3 (A_{ij}^{kl})^2 \alpha_{ik} \alpha_{jl} \quad (6)$$

with

$$C_{ij} = \frac{mc^2}{\frac{\bar{\alpha}_i}{\bar{\chi}_i} + \frac{\bar{\alpha}_j}{\bar{\chi}_j}} \quad (7)$$

$$A_{ij}^{kl} = \frac{1}{r_{ij}^3} \left[\bar{K}\bar{L} - \frac{3}{r_{ij}^2} (\bar{K}\vec{r}_{ij}) (\bar{L}\vec{r}_{ij}) \right] \quad (8)$$

The polarizability components of the adsorbate atom, i , are α_{i1} , α_{i2} and α_{i3} and those of the adsorbent atom, j , are α_{j1} , α_{j2} , α_{j3} . The corresponding mean polarizabilities and diamagnetic susceptibilities are $\bar{\alpha}_i$, $\bar{\chi}_i$ and $\bar{\alpha}_j$, $\bar{\chi}_j$; m is the mass of an electron and c the velocity of light; \vec{r}_{ij} is the vectorial distance between the adsorbate and the adsorbent atoms; \bar{K} and \bar{L} are the directions of the unit vectors of the adsorbate and the adsorbent polarizability tensor, respectively.

For adsorption on graphite, it has been shown⁷ that, in the special case where the adsorbate polarizability tensor is isotropic, eqn. 6 reduces to

$$\Phi_i^D = - 3C_{ij} \bar{\alpha}_i \alpha_{j1} (1 + P) \sum_j r_{ij}^{-6} = - D_i \sum_j r_{ij}^{-6} \quad (9)$$

where

$$P = \alpha_{j1}/\alpha_{j3} = \alpha_{j2}/\alpha_{j3} \quad (9a)$$

In this work $P = 0.29$. This is the realistic value assigned to the polarizability tensor of graphite discussed in ref. 7 and derived by Carlos and Cole¹⁰ from the anisotropic polarizability tensor of aromatic compounds.

As for the Lennard-Jones potential, an inverse twelfth power law has been assumed for the repulsive term of the adsorption potential:

$$\Phi_i^R = B_i \sum_j r_{ij}^{-12} \quad (10)$$

The repulsion constant is calculated for each type of atom i , and for each orientation when the adsorbate polarizability tensor is isotropic. Thus, the potential curve ($\Phi_i^D + \Phi_i^R$) is at a minimum for the Van der Waals distance z_0 to the graphite surface; z_0 is equal to the sum of the adsorbate and adsorbent Van der Waals radii, r_w . The adsorption potentials are calculated by direct summation of the contributions of the adsorbent (C) atoms contained in a hemispherical volume of radius 2 nm. The relative error in neglecting the other carbon atoms is 10^{-3} . The C-C distance in the basal plane of graphite is 0.142 nm and the interlayer spacing is 0.335 nm. The parameters that are necessary for calculating the adsorption potential are summarized in Table I. The polarizabilities and diamagnetic susceptibilities for the atom centres are incremental values derived from experimental data. An isotropic polarizability tensor is assumed for H and Cl adsorbate atoms. The dispersion and repulsion constants, D_i and B_i , are given in Table I for when the polarizability tensor of the adsorbate molecule is isotropic, as they do not depend on molecule orientation.

EXPERIMENTAL

The gas chromatograph used was equipped with a flame-ionization detector (Varian, Palo Alto, CA, U.S.A.). The signal was amplified by a current amplifier (Model 417 K; Keithley, Cleveland, OH, U.S.A.).

TABLE I
PARAMETERS OF THE CONSTANTS OF THE ADSORPTION POTENTIAL

Numbers in parentheses are literature references.

Force centre	$\bar{\alpha}_i \times 10^{24}$ ($\text{cm}^3/\text{molecule}$)	$\alpha_{i1}/\alpha_{i3} =$ α_{i2}/α_{i3}	$\chi_i \times 10^{30}$ ($\text{cm}^3/\text{molecule}$)	r_w (nm)	D_i ($J \text{ nm}^6 \text{ mol}^{-1}$)	$(D_i/B_i)^{1/6}$ (nm)
C	1.14	0.29	1.20	0.170	—	—
(graphite)	(26)	(10)	(29)	(32)	—	—
C	1.30	0.39	1.19	0.170	—	—
(aromatic ring)	(27)	(27)	(30)	(32)	—	—
C	1.32	0.43	1.26	0.170	—	—
(naphthalene ring)	(28)	(28)	(30)	(32)	—	—
H	0.42	1	0.33	0.120	0.477	0.297
	(27)		(30)	(32)		
Cl	2.34	1	3.07	0.180	3.908	0.472
	(27)		(31)	(32)		

A splitting system allowed the injection of samples smaller than $0.1 \mu\text{g}$. The carrier gas was helium. The column was placed in an air-stirred oven whose temperature was controlled to within $\pm 0.1^\circ\text{C}$ by a microcomputer, with a proportional and integral corrector program.

The chromatographic column ($50 \text{ cm} \times 2 \text{ mm}$ I.D., stainless steel) was packed with graphitized carbon black (Carbopack C; Supelco, Bellefonte, PA, U.S.A.). The amount of adsorbent was 1.5 g ; its surface area, measured by the BET method, was $10 \text{ m}^2/\text{g}$. The reproducibility of retention volume measurements on one column was about 1% , but the reproducibility of retention volumes from column to column was about $\pm 10\%$.

The samples were commercial products: polychlorobenzenes from Merck (Darmstadt, F.R.G.) and mono- and dichloronaphthalenes from RFR Corp. (Hope, RI, U.S.A.).

RESULTS AND DISCUSSION

Chlorobenzenes

The selectivity of the graphite column towards the compounds of this class and especially towards the different geometrical isomers of chlorobenzenes is shown in Fig. 1 and Tables II and III. The results show that graphitized carbon black is able to separate the 1,2,3,5- and 1,2,4,5-tetrachloro isomers, but not the 1,2,3- and 1,2,4-trichloro isomers. The retention order is different from that observed with liquid stationary phases¹⁴⁻¹⁹ or that obtained on stationary phases modified with Bentone 34¹¹⁻¹³ where the retention order seems to be determined by the dipole moment of

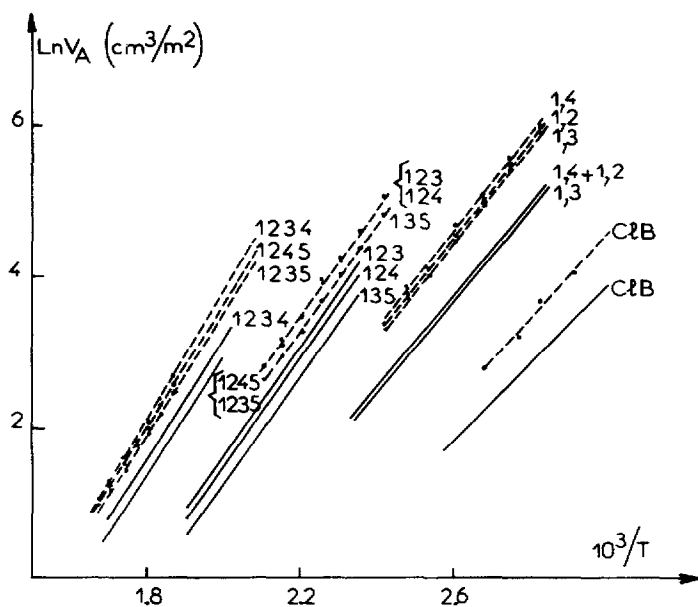


Fig. 1. Change of retention volume with temperature for chlorobenzenes and polychlorobenzenes. Broken lines, experimental on graphitized carbon black; solid lines, theoretical model on graphite (model A).

TABLE II
THERMODYNAMIC FUNCTIONS OF ADSORPTION ON GRAPHITIZED CARBON BLACK
FOR CHLORO- AND POLYCHLOROBENZENE ISOMERS

<i>Compound</i>	μ^* (<i>D</i>)	<i>Model</i>	$\ln V_A$ ($\text{cm}^3 \text{m}^{-2}$)	q_a (kJ mol^{-1})
Chlorobenzene	1.58	A	-0.685	41.4
		E	-0.520	42.3
		Experiment	-0.297	46
1,3-Dichlorobenzene	1.48	A	0.683	49.9
		E	0.807	50.6
		Experiment	1.369	53
1,2-Dichlorobenzene	2.25	A	0.789	50.5
		E	1.095	52.1
		Experiment	1.406	54
1,4-Dichlorobenzene	0	A	0.819	50.0
		E	0.819	50.0
		Experiment	1.467	54
1,3,5-Trichlorobenzene	0	A	1.990	58.0
		E	1.990	58.0
		Experiment	2.643	60
1,2,4-Trichlorobenzene	1.25	A	2.268	58.8
		E	2.371	59.3
		Experiment	2.820	61
1,2,3-Trichlorobenzene	2.44	A	2.387	59.5
		E	2.742	61.2
		Experiment	2.820	61
1,2,3,5-Tetrachlorobenzene	0.97	A	3.823	67.5
		E	3.885	67.8
		Experiment	4.264	63
1,2,4,5-Tetrachlorobenzene	0	A	3.864	67.5
		E	3.864	67.5
		Experiment	4.418	66
1,2,3,4-Tetrachlorobenzene	1.87	A	4.048	70.0
		E	4.262	69.0
		Experiment	4.637	69
Pentachlorobenzene	1.05	A	5.704	76.5
		E	5.778	76.8
		Experiment	6.201	71

* From ref. 33.

the molecule (1,2-dichlorobenzene is then the last eluted of the three dichlorobenzenes).

The results of the molecular statistical calculations are compared with the experimental results in Table II. In relation to the applicability of the theory to predict retention orders, two questions must be answered apart from discussing the areas of agreement and disagreement between the two sets of results. The first question is whether taking the electrostatic contribution into account in the overall adsorption potential on graphitized carbon black is valid. The second question is whether it is necessary to know the exact molecular geometry (bond distances and angles) to carry out the statistical mechanical calculations of retention volumes. In fact, the exact

molecular structure is often unavailable, especially for many of the complex molecules that are to be separated and identified by gas chromatography.

First, the results obtained by using a standard hexagonal geometry (C-C distance = 0.140 nm; C-H distance = 0.108 nm, C-Cl distance = 0.172 nm) are discussed. Two series of calculations have been made with these distances. Model E in Table II takes into account the contribution of the electrostatic interaction between the dipole moment of the adsorbed molecule and its induction field in the graphite crystal. Model A does not take this kind of interaction into account.

All the values of the differential heat of adsorption predicted by the two models are close to the experimental values and the additional dipole contribution to the heat of adsorption is only about $0.5-1 \text{ kJ mol}^{-1}$. These differences are smaller than the experimental error and therefore the two models are similar on this basis. The difference between the measured and predicted heats of adsorption is larger than the error of measurement, however.

Let us now consider the retention volumes. Model A (no dipole-induced dipole contribution) predicts correctly the relative retention order of all the chlorobenzene geometrical isomers, whereas model E (dipole interaction) does not behave as well: 1,2-dichlorobenzene is predicted to be the last dichlorobenzene to be eluted whereas in fact it is the second; the elution order of 1,2,3,5- and 1,2,4,5-tetrachlorobenzene is also reversed. Thus it seems that a further extension of the interaction potential between the adsorbed molecule and the graphite crystal to include the electrostatic dipole moment-induced dipole moment is of minor relevance and of no use in explaining and predicting the relative retention order on graphite, at least for adsorbate molecules such as chlorobenzenes.

For many polychlorobenzene isomers the exact geometric structures were available. All these compounds exhibit minor deviations from the standard hexagonal aromatic structure described above. These differences are about 2° in the bond angles, 0.002 nm in the C-C bond length, 0.008 nm in the C-H bond length and 0.003 nm in the C-Cl bond length. With the exception of *p*-dichlorobenzene, all these isomers are planar³⁴⁻³⁹. Some authors³⁵ claim that the high-temperature triclinic *p*-dichlorobenzene form has a non-planar structure ($2-4^\circ$ in the C-Cl and C-C bond angles). In the crystal structure stable at low temperature *p*-dichlorobenzene is, instead, strictly planar³⁶.

The use of a non-planar structure in statistical calculations obviously results in lower values of the computed thermodynamic quantities, in agreement with the larger approach distance of the adsorbed molecule to the graphite crystal surface. However, no definitive conclusion can be made on the basis of the comparison between experimental and theoretically computed retention volumes. Comparison of the relative retention orders (experimental and theoretical) is more interesting, as the aim of this work is to predict it quantitatively.

The results are presented in Table III, where the relative retention order is given with chlorobenzene as reference. The experimental results are compared with those obtained with models A and E and with model A with calculations carried out with the experimental molecular structure. It can be seen that the use of the exact geometrical structure neither significantly changes the relative retention order nor substantially improves the ability of the molecular statistical theory approach to predict the right retention order on graphite. Further, it can be observed that the

TABLE III
RELATIVE RETENTION RATIO OF POLYCHLOROBENZENE ON VARIOUS STATIONARY PHASES: COMPARISON BETWEEN THEORY AND EXPERIMENT ON GRAPHITE

Compound	Graphite (200°C)		Graphitized carbon black (200°C)		Apiezon L (150°C) (non-polar): experiment (ref. 15)	Polyphenyl silicone (150°C) (moderately polar): experiment (ref. 15)	Silicone phase modified with Bentone 34 (150°C): experiment
	Model E assumed geometrical structure	Model A assumed geometrical structure	Model A experimental geometrical structure*	Experiment			
Chlorobenzene	1.0	1.0		1.0	1.0	1.0	1.0
1,3-Dichlorobenzene	3.9	3.8	1.0 (34)	5.3	2.7	2.4	2.0**
1,2-Dichlorobenzene	5.0	4.4	{ 3.5 (35) 4.9 (36)	5.5	3.2	2.8	3.4**
1,4-Dichlorobenzene	3.8	4.5		5.8	2.7	2.5	1.5**
1,3,5-Trichlorobenzene	12.3	14.5	14.7 (37)	18.9	5.4	5.2	1.9***
1,2,4-Trichlorobenzene	18.0			22.6	6.7	5.6	3.4***
1,2,3-Trichlorobenzene	26.1	21.6	21.7 (38)	22.6	8.6	7.3	9.9***
1,2,3,5-Tetrachlorobenzene	81.9	90.7		95.7	14.8	11.8	
1,2,4,5-Tetrachlorobenzene	80.2	94.2	92.7 (39)	111.6	15.8	11.4	
1,2,3,4-Tetrachlorobenzene	119.3	113.6		138.9	20.3	15.8	
Pentachlorobenzene	543.5	595.3		663.8	39.8	26.7	
Hexachlorobenzene					153.3	74.4	

* Numbers in parentheses are literature references.

** Ref. 12.

*** Ref. 13.

relative retention order of *p*-dichlorobenzene computed on the non-planar structural basis is further from the experimental value than the planar structure. The planar structure is probably more relevant as it permits a stronger interaction in the adsorption process. Further, there is no reason for the molecule to exhibit the same deformation in the gas phase and in the crystalline state.

Chloronaphthalene compounds

In Table IV, the experimental results are presented together with the thermodynamic quantities calculated with model A using the same standard hexagonal geometry as previously and where the contribution of the electrostatic interactions to the adsorption potential is not taken into account.

The predicted elution order generally agrees with the experimental order, except for 1,4- and 1,5-dichloronaphthalene and for 1,2-, 1,8- and 2,3-dichloronaphthalenes. For these last three isomers, the chlorine atoms are located on two consecutive carbon atoms, and the hypothesis of a planar hexagonal geometry is probably unrealistic because of steric hindrance effects. Hence the previous conclusions about the general usefulness of the computation of elution order by the molecular statistical theory of adsorption are confirmed.

Now, let us consider the relative retention orders of some geometrical isomers more closely. For example, for 2- and 1-chloronaphthalene the value predicted by the theory (1.07) is considerably lower than the experimental value (1.27). This failure of the theoretical computation to achieve correct quantitative predictions of relative retentions is not new; it has also been observed in other instances, *e.g.*, in predicting

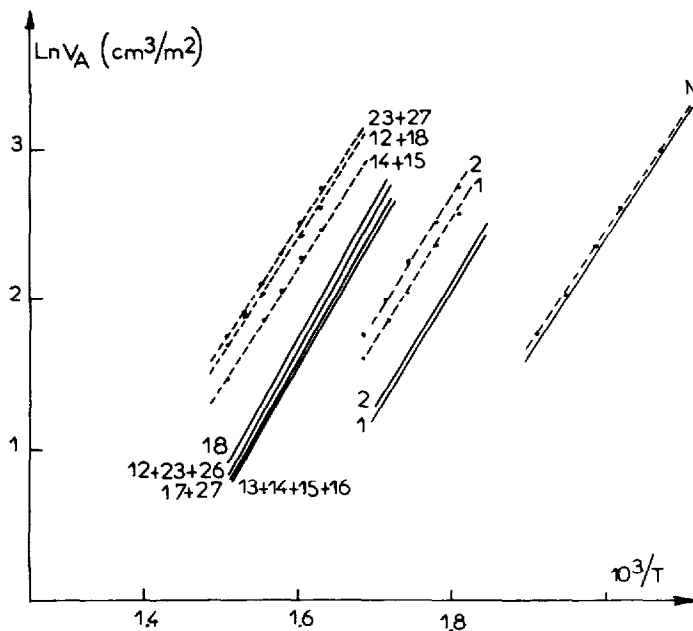


Fig. 2. Change of retention volume with temperature for naphthalene, chloronaphthalenes and dichloronaphthalenes. Broken lines, experimental on graphitized carbon black; solid lines, theoretical model on graphite (model A).

TABLE IV
RETENTION DATA FOR NAPHTHALENE, CHLORO- AND DICHLORONAPHTHALENES ON VARIOUS STATIONARY PHASES: COMPARISON BETWEEN THEORY AND EXPERIMENT ON GRAPHITE

Compound	Theory (model A): graphite (300°C)		Experiment GC, graphitized carbon black (300°C)		Experiment, GC ²⁰ Carbowax 20M		Experiment, GC ²⁰ Bentone 34-OV-101		Experiment, HPLC ^{21,22} , silica gel n- hexane	
	$\ln V_A$ ($\text{cm}^3 \text{m}^{-2}$)	q_d (kJ mol^{-1})	$\ln V_A$ ($\text{cm}^3 \text{m}^{-2}$)	q_d (kJ mol^{-1})	r	r	r	r	r	r
Naphthalene	0.561	62.7	1.00	0.584	1.00	1.00	1.00	1.00	1.00	1.00
1-Chloronaphthalene	1.608	70.4	2.85	2.084	66	4.48	1.15	1.15	0.58	0.58
2-Chloronaphthalene	1.672	70.4	3.04	2.243	66	5.25	1.00	1.00	0.67	0.67
1,4-Dichloronaphthalene	2.847	78.5	9.84	3.432	68	17.25	1.94	1.90	0.40	0.40
1,3-Dichloronaphthalene	2.861	78.8	9.97	—	—	—	1.78	—	0.43	0.43
1,5-Dichloronaphthalene	2.870	78.4	10.06	3.404	68	16.77	1.94	1.71	0.40	0.40
1,6-Dichloronaphthalene	2.877	78.5	10.14	—	—	—	2.16	1.93	0.45	0.45
2,7-Dichloronaphthalene	2.928	78.7	10.67	3.666	68	21.80	2.41	2.26	0.52	0.52
1,7-Dichloronaphthalene	2.933	79.1	10.72	—	—	—	2.16	3.12	0.49	0.49
2,6-Dichloronaphthalene	2.985	78.5	11.29	—	—	—	—	—	0.52	0.52
2,3-Dichloronaphthalene	3.013	79.1	11.61	3.646	66	21.37	2.95	2.82	0.61	0.61
1,2-Dichloronaphthalene	3.043	79.2	11.97	3.574	67	19.99	2.41	3.02	0.54	0.54
1,8-Dichloronaphthalene	3.073	79.2	12.33	3.604	73	20.49	3.97	5.45	0.68	0.68

the relative retentions of isomers such as anthracene and phenanthrene⁷ and 1- and 2-methylnaphthalene²⁴. This is probably due to the fact that the same polarizability increments are attributed to the atom force centres and, therefore, the model does not take into account the difference between the internal electronic structures of the molecules. More realistic polarizability values should be attributed to the force centres, when available from experimental measurements⁷. However, this more advanced topic is not dealt with here.

As in most instances the theoretical computations do predict correctly the elution order, the computed retention data and other thermodynamic quantities are presented in Table IV for other dichloronaphthalene isomers for which no experimental data are available on graphitized carbon black. The reported quantities can be of some value in solving identification problems in the analysis of complex chloronaphthalene mixtures on graphite when other methods are unavailable or fail to give clear responses (*e.g.*, mass spectrometry).

It may be noticed that the predicted retention order of the monochloronaphthalenes on the one hand and of the dichloronaphthalenes on the other is close to that observed in gas chromatography on Carbowax 20M and in liquid chromatography on silica gel with a weak eluting solvent (*n*-hexane). The exceptions are the elution orders of the following pairs: 1,3- and 1,5-dichloronaphthalene, 1,7- and 2,7-dichloronaphthalene and 1,2- and 2,3-dichloronaphthalene.

CONCLUSIONS

The molecular statistical theory of adsorption is able, with only minor exceptions, to predict the retention order of chlorobenzenes and chloronaphthalenes on graphite. The usefulness of this theoretical approach in identification problems in gas chromatography on graphitized carbon black is thus extended to aromatic molecules containing a chlorine atom. The presence of chlorine does not require a further extension of the anisotropic adsorption potential model previously established for aromatic compounds. Nor is the exact knowledge of the molecular structure from X-ray diffraction data (or other methods) critical for computing a correct elution order.

The proposed model may possibly be further improved by a better choice of the polarizability values employed in the calculations. Thus more difficult problems, such as the prediction of the elution order of substance classes of great practical interest, *e.g.*, polychlorodioxins, can be tackled with a high probability of obtaining useful conclusions.

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