The method of introducing correction factors into parameters of atom-atom potentials of intermolecular interaction used for calculation of thermodynamic characteristics of adsorption

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Different methods of introducing correction factors into parameters of atom-atom potentials of intermolecular interaction used for calculation of thermodynamic characteristics of adsorption by the semiempirical molecular statistical theory were compared. A method of isostructural fragments based on the application of the atom-atom potential corrected for the molecular fragment was suggested for introducing the correction factors. The advantages of this method were demonstrated for chlorobenzenes, chlorodioxines, and chlorobiphenyls.

Key words: atom-atom potentials; method of isostructural fragments; chlorinated derivatives of benzene, dibenzodioxine, and biphenyl; semiempirical molecular statistical calculations; adsorption Henry's constants.

Calculations of the thermodynamic characteristics of adsorption (TCA) by molecular statistics are reported for inert gases on alkali metal halides,[1] inert gases, and the simplest polar molecules as well as for hydrocarbons on silicalite[2] and the zeolites of different types.[3,4] The development of calculations with molecular statistics has been especially advanced for the system graphitized thermal carbon black (GTCB)—hydrocarbons and their derivatives.[5–8] An interest in this adsorbent stems from the uniform planar surface of GTCB with the geometry and chemical properties studied in more detail. The sensitivity of adsorption on the surface of GTCB to the structure of molecules is the source of the ability of this sorbent to separate geometric isomers[9–11] and the reason for the development and improvement of calculations with molecular statistics. By combining molecular statistical calculations and GC-MS data individual isomers can be, as a rule, unambiguously identified in their mixtures.[12,13]

The semiempirical molecular statistical theory of adsorption[5] is based on the atom-atom approach for the potential function of the adsorbate—adsorbent intermolecular interaction.

$$\Phi = \sum_{A}\sum_{C(GTCB)}\varphi_{A...C(GTCB)} \qquad (1)$$

As can be seen in Eq. (1), the potential function Φ is presented as the sum of atom-atom potentials (AAP) of the intermolecular interaction of each atom (A) of the adsorbate molecule with each carbon atom (C) of the GTCB adsorbent. The AAP for the interaction of the adsorbate atom with the adsorbent atom was chosen in the Buckingam—Corner form, where r is a distance between the molecule and the surface, q is a constant (parameter of repulsion forces) equal to 35.7, and C_i are dispersion attraction constants.

$$\varphi_{A...C(GTCB)} = -C_1r^{-6} - C_2r^{-8} + B\exp(-qr) \qquad (2)$$

Henry's constant (K_1) is calculated assuming free motion along a mathematically uniform surface (the model of dimeric ideal gas) and harmonic vibration perpendicular to the surface.

$$K_1 = \frac{1}{4\pi}\iint\left(\frac{2\pi kT}{\Phi''_z}\right)^{0.5}\exp\left(-\frac{\Phi_0}{kT}\right)\sin\theta d\theta d\psi \qquad (3)$$

In this equation, Φ_0 is the value of the potential energy of interaction of the molecule with the surface at the potential minimum, and Φ_z'' is the second derivative of Φ with respect to z, where z is the distance from the surface. The Euler angles ψ and θ define the position of the molecule on the surface. Other TCA are calculated from K_1 and its derivatives. In the framework of this approach, the parameters of the atom-atom potential functions of the adsorbate—adsorbent intermolecular interaction (C_1, C_2, B) are determined by the approximate quantum-chemical formulas derived from the properties of the adsorbate and adsorbent. Thus obtained AAP for the interaction of adsorbate atoms with carbon atoms of graphite are refined by comparison of the theoretically calculated and experimentally determined

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K_1 values. The experimental K_1 values are found in a study of the adsorption of reference molecules. The initial and refined AAP differ by the correction value only. To the present time, the AAP φ^* for hydrogen, carbon in different valent states, and main subgroups of Group VI and VII elements have been determined.[5,7,14—17] Meanwhile, as the experimental material is accumulated and the range of compounds studied increases, the number of molecules increases whose TCA cannot be predicted with satisfactory accuracy. This is especially pronounced for the identification of isomers in their mixtures. The calculation predicts the order of elution of the isomers from a column with GTCB that does not coincide with the experimentally observed sequence. This is due to the difference between the AAP parameters for the atoms in the molecule under study and those adjusted by using reference molecules. The difference in the AAP parameters is usually due to a change in the nearest environment of the atom or its valent state, which usually appears as a change in its polarizability. Therefore, for reliable identification of individual isomers in their mixtures and calculation of reliable TCA values, it is necessary to determine reliable values of the AAP parameters.

The purpose of this work is to consider possible methods of introducing correction factors into the AAP parameters and to choose a method which would result in corrected AAP that reliably predict TCA of substances of different classes adsorbed on GTCB.

Comparison of the methods of introduction of correction factors into AAP parameters

Several methods of introduction of correction factors into the AAP parameters are now available.

In the framework of the semiempirical molecular statistical theory,[5,7] the AAP parameters are determined by the approximate quantum-chemical formulas. Polarizabilities, diamagnetic susceptibilities, and van der Waals radii or equilibrium distances for adsorbate and adsorbent atoms are used. It is assumed that the obtained AAP correctly predict TCA for all molecules of this class containing the corresponding atoms. In this way, the AAP parameters for adsorption of alkanes, alkenes, alkynes, and aromatic hydrocarbons on GTCB were determined and refined, whereas methane, ethane, ethylene, acetylene, and benzene, respectively, were used as the reference molecules. Therefore, the method developed by the authors of the semiempirical molecular statistical theory of adsorption[5] can be recognized as the first of refining AAP parameters. The method involves calculation of the individual AAP using the reference molecules. Three AAP were obtained for the carbon atom with sp^3-, sp^2-, and sp^1-hybridizations differing by only the value of the correction factor β equal to 1.00, 1.07, and 1.27, respectively.

$$\varphi_{\text{A...C(GTCB)}} = \beta\varphi^*_{\text{A...C(GTCB)}} \tag{4}$$

Two AAP for the oxygen atom in ethers and ketones were determined by the same method. They differ by a β factor equal[14] to 0.72 and 0.92, respectively. The AAP for sulfur, selenium, fluorine, chlorine, and bromine were determined,[15,16] for which the correction factors β were 0.87, 0.89, 0.85, 0.95, and 0.76, respectively. In fact, this approach is close to the methods used for the calculations of polarizabilities, diamagnetic susceptibilities, and dipole moments of molecules by the additive schemes.[18,19] The AAP thus determined led to prediction of TCA for several hydrocarbons and their derivatives which agree well with the experimental values.[5,7,14—17] However, it is impossible to use this method and correctly predict TCA for a large number of molecules. Differences are observed not only for molecules with strained structures, bulky substituents, several heteroatoms encountered in unusual combinations, but also for sufficiently simple molecules: *ortho*-halobenzenes,[20] perhydroanthracenes and perhydrophenanthrenes,[21] and heterocyclic nitrogen-containing compounds.[8]

The described method of introduction of correction factors comprises the following disadvantages. The method assumes the refinement of AAP by changing the nearest environment of each atom rather than the valency state. Carbon, oxygen, and nitrogen atoms should have especially many AAP. In addition, this method ignores changes in AAP due to the mutual effect of covalently unbound atoms.

A method of calculation is known[22] in which the influence of the geometric parameters of a molecule on the hybridization of the carbon atom and, hence, on the AAP parameters is taken into account. By using this method the author could obtain calculated values for several molecules with strained structure, derivatives of cyclopropane and some bicyclic compounds, that were in good agreement with the experimental data. The prediction of the experimentally confirmed order of elution of C_8H_{12} isomers, dicyclobutadiene and bicyclo(3.3.0)oct-1,5-ene, from a column with GTCB is an important example of the efficiency of the method proposed. At the same time, this method can be used only for molecules with known geometry. In addition, to determine the correction factor, we need at least two boundary potentials corresponding to other values of the geometric parameters. Finally, this method does not allow one to refine a change in the AAP parameters that is not related to a change in the geometry of the molecules.

The method that assumes the variation of the AAP parameters to obtain agreement between the experimental and calculated values for two groups of molecules is of interest. This variation is performed to minimize the misfit between the experimental and calculated data for all molecules of the group under consideration and can be accomplished, for example, by the regularization method.[23] One parameter can also be varied, for example, by changing the equilibrium distance between the carbon atom of graphite and the bromine atom.[20] The calculated values for bromobenzene obtained in this way are in good agreement with the experimental results.[20]

However, this method also allows one to match experimental results with calculated data only for a specified group of molecules. The extension of this group usually results in discrepancies between experiment and calculation. For example, AAP refined by varying the equilibrium distance of the carbon atom of graphite—halogen[20] make it possible to adjust the experimental and calculated values only for molecules of halobenzenes containing no *ortho*-atoms of halogen. For *ortho*-substituted molecules, the calculations performed with these AAP do not allow the experimental data to be described with satisfactory accuracy, which can be achieved only by the introduction of additional correction factors into the *ortho*-effects.

It is known[24] that the mutual effect of atoms can change their polarizability. In the calculations of TCA, this change can be taken into account both by the introduction of additional correction factors into AAP[14,20] and using the refined polarizability values. The latter is especially efficient for the calculation of TCA of perhalogenated compounds, first of all, Freons, for which isostructural fragments can hardly be chosen or which are too numerous. The heats of adsorption of these compounds[25] are satisfactorily described within an experimental error without introducing any correction factors; however, correction factors for AAP are necessary for the prediction of Henry's constants. The method of refinement of AAP by using refined initial data, first of all, polarizabilities and diamagnetic susceptibilities, for the calculation of the C_1 and C_2 parameters (formula (2)) is of certain interest. The reason is that extensive experimental material has been accumulated to date and detailed additive schemes of calculation of polarizabilities in molecules of various classes, especially for perhalogenated compounds, have been developed.[24]

This approach is restricted by the fact that the use of polarizabilities calculated by the additive schemes can result, due to their low accuracy,[24,25] in an increased error in the calculations of TCA. Another disadvantage is the necessity to measure polarizabilities for unstudied molecular fragments experimentally.

The mutual effect of atoms, in particular, in *ortho*-arrangement,[26] alters the AAP parameters. Varying these parameters, the calculated values for an *ortho*-substituted molecule for which experimental TCA are known can be adjusted to the experimental results. These refined AAP can further be used for calculations of TCA of other molecules with *ortho*-arranged atoms. The applicability of this approach (introduction of correction factors into the *ortho*-effect) has been shown[20,26] for halobenzenes. In fact, this method of refinement of AAP is similar to the method of reference molecules, but covers a more narrow group of molecules. In several cases, to achieve agreement between the experiment and calculation, it is necessary to introduce additional correction factors, for example, for the *ortho-ortho*-effect.[26]

The method of isostructural fragments (IF) is based on using AAP refined for a molecule or its fragment. The IF is chosen by comparing the geometric structure of the IF with that of the group of molecules under study. The comparison is based on electron diffraction data, regularities governing changes in bond angles and bond lengths in groups of related molecules, or quantum-chemical calculations. A molecule or its fragment entering into molecules of the class under study is usually chosen as the IF. For example, this is cyclopropane for derivatives of cyclopropane and 1,2-dichlorobenzene for *ortho*-substituted chlorobenzenes and naphthalenes.

In fact, the method of isostructural fragments serves to overcome the restrictions of the atom-atom approximation and to take into account the mutual effect of atoms and groups of atoms, including changes in the polarizabilities and geometric parameters of the interacting fragments.

The performed comparison of the proven and potential methods of introduction of correction factors into the AAP parameters suggests that the following methodical procedures are especially promising: introduction of correction factors into the initial data for the calculation of the AAP parameters, first of all, to the polarizability; introduction of correction factors for the *ortho*-effect; and the IF method.

The use of the geometric structure of molecules in the calculation of their TCA is an important advantage of the semiempirical molecular statistical theory of adsorption. At the same time, this imposes additional restriction, because the reliable parameters of the molecular structure were determined for a limited range of substances and are usually unavailable for the majority of isomers.

Variation of the geometric parameters of molecules performed, in particular, for the prediction of retention of perhydroanthracenes and perhydrophenanthrenes is an alternative to the refinement of AAP.[21] Using this variation, we succeeded in obtaining the order of elution of isomers from a column with GTCB that coincided with the sequence observed in the experiment. Let us try to compare the results of the calculations performed for the variation of the geometry of the molecules or the application of various methods of refinement of AAP.

Experimental

For the comparative estimation of different methods of introduction of correction factors into AAP, we calculated K_1 by AAP refined by different methods and compared the results obtained for several chlorobenzenes with different extents of substitution. Even for molecules containing no fragments with strained structure or *ortho*-arranged atoms, agreement between the experiment and calculation of the K_1

values can be obtained only by the introduction of a correction factor into AAP using reference molecules.[26] Accordingly, all corrections for the AAP parameters were introduced to a value of the refined potential which was 5% lower than the initial value. This implies that the value of the β correction factor for the chlorine atom determined by the reference molecule is 0.95. The series of chlorobenzenes was chosen as model adsorbates, because in this row the order of elution of homologs and isomers from a column with GTCB is an important criterion for the reliability of calculations. Moreover, an ample body of experimental and calculated TCA obtained by different methods is available for these molecules.[15,26]

The results of the calculations performed with AAP refined from experimental data ($\ln K_1$) for the reference molecule of 1,4-dichlorobenzene were taken from the literature[15,26] or obtained in the present work; they are presented in Table 1.

The correction factors for the polarizability were applied to the experimental polarizability value determined for the chlorine atoms in 1,2-dichlorobenzene.[18] In the calculations of $\ln K_1$, these refined AAP were applied only for the *ortho*-arranged chlorine atom (see Table 1).

In the calculations of $\ln K_1$ performed by introducing correction factors for the *ortho*-effect, we applied the previously determined[17,26] AAP parameters and correction factors for them that considered the influence of the *ortho*- and *ortho-ortho*-effects. The corresponding results are presented in Table 1.

In the calculations performed by the IF method, the AAP parameters were refined on the basis of the experimental $\ln K_1$ or using the differences in retention (the differences in $\ln K_1$) for neighboring isomers for which the experimentally observed order of elution from a column with GTCB remained unchanged. 1,2-Di-, 1,2,3-, and 1,2,4-trichlorobenzenes were chosen as such molecules. The values of the correction factor for the AAP obtained by these molecules are 0.92 and 0.91 for the fragments containing two or three *ortho*-arranged chlorine atoms, respectively. The results of these calculations are also presented in Table 1.

Table 1. Comparison of Henry's constants ($\ln K_1$) at 473 K for adsorption of chlorobenzenes on GTCB calculated by AAP and refined by different methods (*1*—*5*) with experimental data[15]

Position of substituents	$\ln(K_1/\text{cm}^3\ \text{m}^{-2})$					
	Experiment[15]	Calculation*				
		1	*2*	*3*	*4*	*5*
Chlorobenzene	−0.44	−0.44	−0.44	−0.44	−0.44	−0.44
1, 3	0.93	0.98	0.98	0.98	0.98	0.98
1, 2	1.01	1.15	1.10	1.01	1.01	1.08
1, 4	1.06	1.06	1.06	1.06	1.06	1.06
1, 3, 5	2.23	2.25	2.25	2.25	2.25	2.25
1, 2, 4	2.41	2.59	2.54	2.44	2.44	2.50
1, 2, 3**	2.42	2.82	2.74	2.52	2.52	2.60
1, 2, 3, 5**	3.86	4.19	4.11	3.86	3.88	3.40
1, 2, 4, 5	3.89	4.23	4.12	3.92	3.92	4.02
1, 2, 3, 4**	4.24	4.47	4.37	4.03	4.06	3.58

* Methods of calculation: *1*, by reference molecules; *2*, introduction of correction factors into polarizability; *3*, introduction of correction factors into *ortho*-effects; *4*, IF method; and *5*, variation of geometry.

** Reliable experimental values of Henry's constants are lacking for these isomers; however, the observed order of elution of the isomers from the column packed with GTCB can serve as an important criterion in the evaluation of the reliability of calculations.

For comparison with the methods of introduction of correction factors into AAP, we calculated $\ln K_1$ by varying the geometry of the molecules. Agreement between the experiment and calculation was achieved under the assumption that the *ortho*-arrangement of the chlorine atoms resulted in the deviation of the carbon—chlorine bond from the plane of the benzene ring. The values of the angles of deviation of the carbon—chlorine bonds from the benzene ring plane for chlorobenzenes were taken from the literature.[15] For other isomers, we assumed that the angle values can be transferred; and for the calculation of $\ln K_1$ of 1,2,3-trichlorobenzene, an angle value equal to 7° was used (as in 1,2,4-trichlorobenzene), and 12° was used for 1,2,3,4- and 1,2,3,5-tetrachlorobenzenes (as in the 1,2,4,5-substituted isomer) (see Table 1).

The procedure of the molecular statistical calculations has been described previously.[5,15] The geometric parameters of the molecules have been determined by electron diffraction[13] or obtained by combination of the known parameters of other molecules of this group. The AAP parameters for the interaction of the oxygen atoms with the carbon atom of graphite were taken from the literature.[14] The experimental data for chloronaphthalenes used for the determination of the correction factors by the IF method have been published previously.[27] The results of the calculations for chlorodioxines and chlorobiphenyls are presented in Tables 2 and 3, respectively.

The GC-MS study was performed on a JMS D-300 mass spectrometer coupled with an HP-5890 chromatograph. Mass spectra were recorded under the following operating conditions: temperature of an ion source 150 °C, energy of ionizing electrons 70 eV, mass interval 40—400 amu, scan rate of 2 s per scan. The chromatographic study was carried out on a micropacked column 50 cm × 1 mm with graphitized thermal carbon black (GTCB) Sterling MT with a specific surface of 7.6 $\text{m}^2\ \text{g}^{-1}$ and a grain size of 0.16—0.18 mm. To monitor the separation efficiency, we used a capillary column 30 m × 0.53 mm with a DB-5 (5% methylphenylsiloxane) low-polarity phase. The carrier gas was helium with a flow rate for the packed column of 15—25 $\text{mL}\ \text{min}^{-1}$ and that for the capillary column of 2 $\text{mL}\ \text{min}^{-1}$. The chromatograph was connected with the mass spectrometer by a jet separator with a temperature of 200—250 °C. For the work with the capillary column, a sample was introduced with a flow ratio of 1 : 20. In the case of micropacked columns, a sample was introduced into the initial region of the column, which was placed directly in the injector of the chromatograph. The chromatographic separation was optimized by varying the initial temperature from 100 to 200 °C for the capillary column and from 150 to 250 °C for the micropacked column, and the temperature-programmed heating rates were varied from 0.5 to 15 $\text{deg}\ \text{min}^{-1}$. The chromatograms detected under conditions that provided the optimum chromatographic separation for the mixture under study are presented in Fig. 1, *a* for the capillary column and in Fig. 1, *b* for the micropacked column.

Results and Discussion

In this work, the suggested IF method was tested for the calculations of TCA of chlorobenzenes. 1,2-Di- and 1,2,3-trichlorobenzenes were chosen as IF. Based on the experimental data for these molecules (Henry's constants and the differences in the values for the closest isomers), we obtained the values of the correction factors for the AAP of the interaction of the chlorine atom with the carbon atom of graphite. The

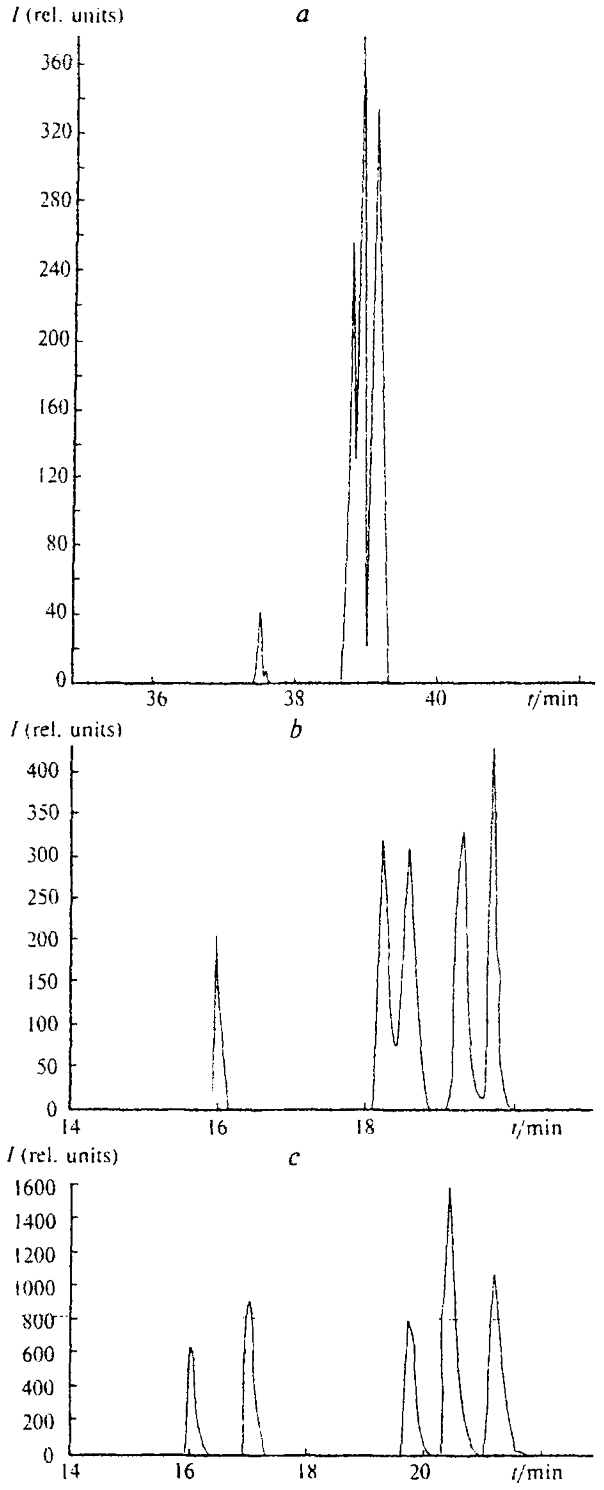

Fig. 1. GC-MS of di- and trichlorobiphenyls obtained from chromatograms by total ion current for the separation of a mixture of chlorobiphenyls on capillary (*a*) and micropacked (*b*, *c*) columns by characteristic ions with m/z = 256 (*a*, *b*) and 226 (*c*).

results of the calculations performed by different methods are compared in Table 1. It can be seen that the introduction of the correction factors on the basis of different methods does not always provide the best agreement between the experiment and calculations. For example, using the method of reference molecules and variation of the geometry, we observed deviation from the order of elution of the isomers from the column with GTCB and considerable (to 0.3 in the $\ln K_1$ values) discrepancies between the experimental and calculated values for some isomers. The introduction of correction factors into the polarizability also does not lead to reasonable agreement between the experiment and calculation. The best fit between the experimetal data and the results of calculation is achieved by the IF method and the method based on introduction of the correction factors for the *ortho*-effects. At the same time, the IF method seems to be more versatile and reliable, because it avoids an uncertainty related to the geometric structure of molecules.

The calculation of $\ln K_1$ of chlorinated dioxines is an important example for the application of AAP refined by the IF method. The IF based on 1,2-di- and 1,2,3-trichlorobenzenes were used in the calculations of TCA of chlorinated dioxines. It is seen from the fragments in Fig. 2 marked by dotted lines that their application is warranted. The applicability is further confirmed by the similar values of the bond angles and bond lengths known from the electron diffraction data and quantum-chemical calculations.[28] The results obtained for all tetrachloro-substituted isomers are presented in Table 2 along with the results of the calculations performed with the AAP obtained by the traditional method.[15] It is seen in Table 1 that the $\ln K_1$ values for the *ortho*-substituted isomers decreased substantially, as in the case of 1,2,3,4-, 1,2,7,8-, and 2,3,7,8-tetrachlorodioxines. This decrease should change the general order of elution of the isomers from the column with GTCB, implying that the *ortho*-substituted isomers should be eluted earlier than other chlorodioxines. This should be taken into account for the identification of individual isomers and preparative isolation.

Chlorinated biphenyls are also interesting and practically significant objects. From the viewpoint of molecular statistical calculations, polychlorinated biphenyls are more complex molecules than chlorobenzenes and chlorodioxines, and more isostructural fragments should be used for the calculation of their TCA, because biphenyl derivatives are capable of internal rotation about the bond connecting the benzene rings. The internal rotation decreases the interaction between the atoms in the *ortho*-position to the bond connecting the benzene rings, but does not change the interaction of the *ortho*-substituents with the carbon atoms of the benzene rings in positions 1 and 1". This interaction is virtually identical to the interaction of the carbon atoms in position 8 of the naphthalene ring with the chlorine atom in position 1, as for example, in 1-chloro-

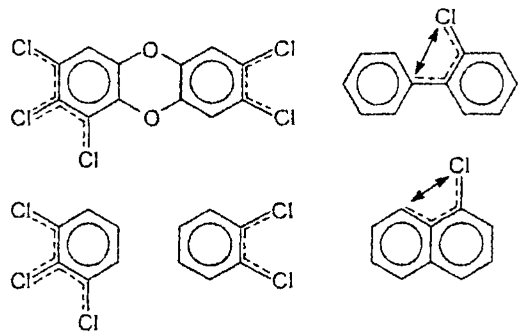

Fig. 2. Molecules used as IF for the refinement of AAP parameters in calculations of Henry's constants of chlorodioxines and chlorobiphenyls (the coinciding IF of the molecules are marked by the dotted line).

naphthalene. It is seen in Fig. 2 that the *ortho*- and *ortho*-*ortho*-arrangements of the chlorine atoms can be described by IF derived from 1,2-di- and 1,2,3-trichlorobenzenes, and the interaction between the chlorine atom and the adjacent ring described by IF derived from 1-chloronaphthalene. The change in the AAP parameters for the chlorine atom in the *ortho*-position to the carbon atom of the adjacent benzene ring does not allow one to unambiguously determine the values of these correction factors, because the angles of internal rotation of these molecules are unknown. This uncertainty impedes the calculations of TCA of chlorobiphenyls and prediction of the order of elution of the isomers from the column with GTCB by conventional calculations. In this case, the IF method is the only one that serves to introduce correction factors into AAP, calculate TCA, and refine the geometric parameters of the molecules. Using the AAP refined by the IF method and the experimental data[10] on the previously described procedures,[7,8,11,12] we determined the angles of internal rotation. The angles were 60°, 65°, and 53° for 2,4,6-, 2,6,2-tri-, and 2-chlorobiphenyls, respectively. Using these values and assuming that the angle of internal rotation is the same in other trichlorobiphenyls containing two chlorine atoms in the *ortho*-position to the bond connecting the benzene rings, the calculations for other isomers can be performed. The angle of internal rotation of 38° was accepted[12,13] for the molecules containing no chlorine atoms in the *ortho*-position.

Table 2. Henry's constants ($\ln K_1$) for isomeric tetrachlorodioxines at 500 K calculated by reference molecules (*1*) and IF method (*2*)

Position of substituents	$\ln(K_1/\text{cm}^3\ \text{m}^{-2})$		Position of substituents	$\ln(K_1/\text{cm}^3\ \text{m}^{-2})$	
	1	*2*		*1*	*2*
1, 3, 6, 8	12.20	12.20	1, 2, 3, 7	12.43	12.13*
1, 3, 6, 9	12.26	12.26	1, 2, 6, 7	12.49	12.19
1, 4, 7, 8	12.26	12.11	1, 2, 4, 9	12.53	12.37
1, 3, 7, 9	12.28	12.28	1, 2, 4, 6	12.53	12.38
1, 3, 7, 8	12.30	12.15	1, 2, 3, 6	12.53	12.24*
1, 2, 4, 8	12.33	12.17	1, 2, 3, 8	12.63	12.33*
1, 4, 6, 9	12.33	12.33	1, 2, 7, 9	12.64	12.49
1, 2, 6, 8	12.33	12.18	1, 2, 7, 8	12.66	12.36
1, 2, 4, 7	12.34	12.19	1, 2, 3, 4	12.80	12.36*
1, 2, 6, 9	12.40	12.25	1, 2, 3, 9	12.82	12.52*
2, 3, 7, 8	12.41	12.11	1, 2, 8, 9	13.03	12.72

* For molecules of the isomers marked by asterisks, additional calculations were performed by the introduction of correction factors into the *ortho*-*ortho*-effect, but, since the differences between the $\ln K_1$ values and the data obtained by the IF method do not exceed 0.01, these values are not presented in Table 1 in a special column.

The advantages of the calculations based on using the AAP refined by the IF method can be demonstrated in identification of microadmixtures formed in the catalytic dimerization of chlorobenzene.[12] The formation of trichlorobiphenyls can easily be confirmed based on the mass spectrometric data; however, it is impossible to identify individual isomers because their mass spectra are identical. The mass chromatograms obtained by the molecular ions of tri- and dichlorobiphenyls with m/z 256 and 226, respectively, are presented in Fig. 2. It is seen that the trichlorobiphenyls under study are eluted from the column with GTCB between two groups of dichlorobiphenyls. All dichlorobiphenyls formed were identified,[12] and their Henry's constants can be used as reference values for the identification of individual isomers of trichlorobiphenyls. The results of the calculations of the retention values (Henry's constants) of *ortho*-substituted trichlorobiphenyls are presented in Table 3 and compared with the data for dichlorobiphenyls. It is seen that 2,4,6-, 2,6,4′-, and 2,3,6-trichlorobiphenyls are eluted before 3,3′-dichlorobiphenyl. The retention of 2,3,2′-trichlorobiphenyl is close to that of 2,3′-dichlorobiphenyl, and the retentions of 2,5,4′-trichlorobiphenyl and 3,3′-dichlorobiphenyl are the same. Note that the efficiency of separation of the isomers of the compounds under study achieved on the micropacked column with GTCB is higher than that on the capillary column with the low polarity stationary liquid phase. This result is explained by a high sensitivity of GTCB toward the differences in the molecular structure. Taking into account the high difference in the retention values (Henry's constants, see Table 3), we may be positive that, in this case, complete separation of the mixture was achieved and each chromatographic peak corresponded to a single isomer.

It is noteworthy that no geometric parameter of the molecules was varied in the calculations of Henry's constants and identification of the isomers under study. For the calculations, we used the angles of internal rotation determined by the comparison of the experimental and calculated values of other isomers containing the same number of chlorine atoms in the *ortho*-positions as the molecules under study. With this assumption good agreement between the experiment and calculation can be achieved for molecules of different classes, for example, for methylbiphenyls, terphenyls, and fluorobiphenyls.[8,13]

Table 3. Calculated Henry's constants ($\ln K_1$) for tri- and dichlorobiphenyls at 500 K and the values of internal rotation angles (α) used for calculations

Position of substituents	Conformation*	α/deg	$\ln(K_1/\text{cm}^3\ \text{m}^{-2})$
2, 6, 2′	—	65	2.88
2, 3′	*syn*	53	3.34
	anti	127	2.91
2, 3, 2′	*syn*	60	3.38
	anti	120	2.97
2, 5, 2′	*syn*	60	3.15
	anti	120	3.48
2, 6, 3′	—	60	3.62
2, 4, 2′	*syn*	60	3.70
	anti	120	3.30
2, 4′	—	53	3.94
2, 4, 6	—	60	4.15
2, 6, 4′	—	60	4.32
2, 3, 6	—	60	4.57
3, 3′	*syn*	38	4.85
	anti	142	4.50
2, 5, 4′	—	53	4.87

* Two conformers differing in the internal rotation angles can exist for nonsymmetrical molecules, for example, 2,3,2′-trichlorobiphenyl. Since the geometric structure of the molecules in the adsorbed state is unknown, the calculations were performed for two possible conformations, *syn* and *anti*.

The potential area of application of the IF method for the refinement of the AAP parameters extends the examples presented above. In this context it seems especially promising to use this method to calculate the thermodynamic characteristics of adsorption of isomeric molecules containing different heteroatoms and fragments with a strained structure.

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