The influence of arrangement of substituents in isomeric chlorobenzenes on their adsorption on graphite

A. K. Buryak

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 335 1778. E-mail: glazunov@lmm.phyche.msk.su

Henry's constants and the heats of adsorption of benzene chloro derivatives on graphitized thermal carbon black were calculated by the semiempirical molecular statistical theory of adsorption. The best agreement between the experimental and calculated data was achieved by introducing corrections for the presence of other chlorine atoms in the *ortho*-positions into the calculation of the atom-atomic potential of the intermolecular interaction of the chlorine atom with the carbon atom of graphite.

Key words: chlorobenzenes, adsorption, *ortho*-effect, semiempirical molecular statistical calculation, heat of adsorption, Henry's constant.

The specific features of the physicochemical properties of compounds related to the presence of substituents in the *ortho*-position of the aromatic, in particular, benzene, ring have been studied for a wide scope of organic compounds.[1—3] The appearance of the *ortho*-effect is commonly explained by overlapping of van der Waals radii of atoms of the *ortho*-substituents, resulting in a change in the polarizability and the geometric structure of the *ortho*-substituents or the whole molecule. In calculations of the polarizability of molecules,[4] dipole moments,[5] and relative retention indices[6] using additive schemes for *ortho*-substituted isomers, a deviation from additivity is observed, and agreement between experiment and calculation is achieved by the introduction of special corrections for the *ortho*-effect. The thermodynamic parameters of adsorption (TPA) on the uniform planar surface of graphitized thermal carbon black (GTCB), which is close in properties to the surface of the basis face of graphite, depend mainly on the geometric structure and polarizability of the molecules.[7] Therefore, the *ortho*-effect is also observed for adsorption on GTCB, which is manifested as a change in TPA, first of all, that in Henry's constants.[8]

The purpose of this work is to study the influence of the *ortho*-substituents in isomeric chlorobenzenes on their TPA on GTCB. For this study, we used experimental TPA and those calculated by the semiempirical molecular statistical method. Comparison of the experimental and calculated data gives the parameters of atom-atomic potentials (AAP) for the intermolecular adsorbate—adsorbent interaction taking into account the influence of the *ortho*-effect on TPA. Application of these AAP for calculations is of great practical significance because TPA can be calculated for a wide scope of chlorine-containing compounds bearing fragments with *ortho*-arranged atoms. First of all, this is related to superecotoxicants (polychlorinated dibenzodioxines, dibenzofurans, and diphenyls), whose experimental studies are very difficult because of their high toxicity.

Experimental

Adsorption of chlorobenzenes on GTCB has been studied in detail[8—12] by GC. Semiempirical molecular statistical calculations were performed as described previously.[7] The AAP parameter used for calculations of the intermolecular interaction of Cl atoms and graphite C atoms was chosen in the Buckingham—Corner form (*cf.* Ref. 8). The initial data necessary for calculations of the AAP parameters were taken from the handbook.[1] The geometric parameters of molecules were obtained[13] by electronography or determined by the combination of the known parameters for other molecules of this group. All isomers were assumed in calculations to have the planar structure. The AAP obtained were refined by the introduction of the correction factor β determined in the comparison of the experimental and calculated data for 1,4-dichlorobenzene (the reference molecule).[9] To take into account possible differences in AAP parameters for Cl atoms in the *ortho*-positions to each other, we introduced additional corrections in calculations of the potential, using 1,2-dichlorobenzene as the reference molecule. To refine AAP for the Cl atom localized between two adjacent Cl atoms, *i.e.*, in the *ortho-ortho*-position, we introduced an additional correction.

The data on atomic refractions[4] for Cl atoms in the aromatic and aliphatic parts of a molecule differ. In this work, for the calculation of AAP parameters, we chose the polarizability values for the Cl atom in aromatic systems.[8—10] The initial data and corrections introduced are presented in Table 1.

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Table 1. Comparison of the original data used for the calculation of parameters of atom-atomic potentials (AAP) for the Cl atom

AAP shape	Variant of calculation	$\alpha \cdot 10^{-30}$ [a]	$\chi \cdot 10^{-36}$ [b]	$r_0{}^c$/nm	Correction β		
		m^3			for parameters	for *ortho*-effect	for *ortho-ortho*-effect
Lennard-Jones	I[d]	2.34	30.7	0.36	—	—	—
Buckingham—Corner	II[e]	2.40	30.7	0.376	0.87	0.86	—
	III[f]	2.245	33.4	0.4	0.95	0.92	0.89

[a] Polarizability. [b] Diamagnetic susceptibility. [c] Equilibrium Cl—C distance (from graphite). [d] See Ref. 10. [e] See Refs. 8 and 9. [f] Data of this work.

Table 2. Experimental[9—12] differential adsorption heats (q) of chlorobenzenes on GTCB

Compound	q/kJ mol^{-1}			
	1[a]	2[b]	3[c]	4[d]
Chlorobenzene	46	44	47.3±0.8	46
1,3-Dichlorobenzene	53	52	46.0±2.1	—
1,2-Dichlorobenzene	54	54	51.9±5.0	—
1,4-Dichlorobenzene	54	53	51.9±3.8	55
1,3,5-Trichlorobenzene	60	60	61.5±2.9	—
1,2,4-Trichlorobenzene	61	64	62.3±2.1	63
1,2,3-Trichlorobenzene	61	—	—	—
1,2,3,5-Tetrachlorobenzene	63	—	—	—
1,2,4,5-Tetrachlorobenzene	66	71	76.6±3.4	—
1,2,3,4-Tetrachlorobenzene	69	—	75.3±1.3	—
Pentachlorobenzene	71	—	92.1±2.9	—

Note. The results were obtained with an accuracy of ±1 kJ mol^{-1}.
[a] See Ref. 10. [b] See Ref. 9. [c] See Ref. 11. [d] See Ref. 12.

Table 3. Changes in increments of Cl atoms to the adsorption heats of chlorobenzenes with an increase in the degree of substitution calculated from the published[9—12] data

Homologs used for determination of increment	Increment/kJ mol^{-1}			
	1[a]	2[b]	3[c]	4[d]
Di—mono	8	9	5	9
Tri—di	7	9	10	8
Tetra—tri	5	9	14	—
Penta—tetra	5	—	17	—

[a] See Ref. 10. [b] See Ref. 9. [c] See Ref. 11. [d] See Ref. 12.

Results and Discussion

The main TPA are differential adsorption heats and Henry's constants. Different experimental[3,7] and calculation methods[7,9,14] are used for the determination of the differential adsorption heats. The differential adsorption heats of chlorobenzenes found by GC [8—12] are presented in Table 2. It is seen that the data obtained by different authors on the adsorption heats of mono-, di-, and trichlorobenzenes coincide satisfactorily within the experimental error except for the value of 46 kJ mol^{-1} for 1,3-dichlorobenzene,[11] which is close to the adsorption heat of chlorobenzene and seems to be incorrect. Differences exceeding the experimental error are observed for the adsorption heats of tetra- and pentachlorobenzenes. These divergences can be due to a higher temperature (473—573 K, unlike 373—473 K for mono-, di-, and trichlorobenzenes) and, correspondingly, to a lower experimental accuracy for these high-boiling compounds. The differences in the physicochemical properties within the groups of isomeric trichlorobenzenes and tetrachlorobenzenes are low, whereas the adsorption heats of tetrachlorobenzenes differ sufficiently strongly.[10] For isomeric tri- and tetramethylbenzenes, the differences in the adsorption heats within each group of isomers do not exceed experimental errors.[15] An increment for each new fragment, in particular, for each Cl atom, can serve as a qualitative criterion for the reliability of experimental values of adsorption heats in the homologous series. These increments are determined as the difference of the values for adjacent homologs, and they are usually unchanged or decrease weakly due to the *ortho*-effect for polymethylbenzenes.[15]

It is seen in Table 3 that the increments obtained from the published data[11] increase anomalously, *i.e.*, the adsorption heats for tetra- and pentachlorobenzenes are overestimated. According to the data of all authors, for di- and trichlorobenzenes, the increment values coincide satisfactorily. Probably, to determine the validity of these values, an additional criterion is needed, in particular, the results of semiempirical molecular statistical calculations performed previously[8—10] and in the present work.

The results of semiempirical molecular statistical calculations (Table 4) performed by different authors using different AAP and initial parameters are close. The adsorption heat values calculated without and with refinement of the AAP parameters are close, within the experimental error (see Table 4, variants I and II). The influence of corrections for the *ortho*-effect is also insignificant; therefore, the adsorption heats can be calculated with sufficient accuracy without labor-consuming refinement of the AAP parameters. According to the data of all authors, the increment per Cl atom is virtually unchanged and amounts to 8—9 kJ mol^{-1}, which corresponds to the atom-atomic approximation on which the calculations are based. Comparison of the experimental (see Table 2) and calculated (see Table 4) values asserts that the most reliable and consistent values of adsorption heats were obtained by the calculation method. It is noteworthy that the differences in the calculated adsorption heats are very insignificant and for tetrachlorobenzenes they do not correspond to those determined experimentally.[10]

The possibility of determining adsorption heats of the molecules for which experimental values cannot be measured is an important advantage of calculations. In particular, hexachlorobenzene is a molecule whose high boiling temperature does not allow reliable TPA to be obtained even by GC. The calculated adsorption heats for hexachlorobenzene are presented in Table 4. It is seen that the introduction of the corrections for the *ortho*-effect affects their values weakly.

Great difficulties appear for calculations of Henry's constants, first of all, because the adsorption on GTCB characterized by this constant depends mainly on the geometric structure and polarizability of molecules, and the calculation based on the atom-atomic approximation cannot take into account the differences in polarizability of the isomers.[7–9] To take into account these differences, we used the corrections to the *ortho*- and *ortho*-*ortho*-arrangement of Cl atoms in molecules (see Table 1).

Table 4. Differential adsorption heats (q) calculated by the semiempirical molecular statistical method

Molecule	q/kJ mol^{-1}				
	I[a]	II[b]	III[c]		
			1[d]	*2*[e]	*3*[f]
Chlorobenzene	41	45	44	44	44
1,3-Dichlorobenzene	50	54	53	53	53
1,2-Dichlorobenzene	51	54	54	53	53
1,4-Dichlorobenzene	50	54	53	53	53
1,3,5-Trichlorobenzene	58	61	61	61	61
1,2,4-Trichlorobenzene	59	62	61	61	61
1,2,3-Trichlorobenzene	60	62	62	62	62
1,2,3,5-Tetrachlorobenzene	68	70	70	70	69
1,2,4,5-Tetrachlorobenzene	68	70	69	69	69
1,2,3,4-Tetrachlorobenzene	70	70	70	70	69
Pentachlorobenzene	77	79	78	78	77
Hexachlorobenzene	—	87	87	87	85

[a] See Ref. 10. [b] See Refs. 8 and 9.

[c] Data of this work.

[d] Without corrections for the *ortho*-effect.

[e] The correction for the *ortho*-effect was introduced.

[f] The correction for the *ortho*-*ortho*-effect was introduced.

The values of Henry's constants obtained[8–12] by GC are presented in Table 5. It is seen that Henry's constants are more sensitive than the adsorption heats to differences in the geometric structure and polarizability of isomeric molecules. This is indicated by the differences in retention times observed by all authors for isomeric di- and trichlorobenzenes, except for the retention value for 1,2,3-trichlorobenzene, which coincides with that obtained[10] for the 1,2,4-isomer. Considerable divergences are observed[10,11] for the retention times of 1,2,4,5- and 1,2,3,4-tetrachlorobenzenes. Only the values obtained in several works[8,9,12] coincide within the experimental error, and the data of other authors differ by 20—30%. It is noteworthy that Henry's constant for 1,3-dichlorobenzene obtained previously[11] is incorrect, because it does not correspond to the order observed by other authors for the elution of dichlorobenzene[8–10] and dimethylbenzene[15] isomers from the chromatographic column.

Since absolute retention times cannot be calculated without introducing corrections into the AAP parameters, reliable experimental data should be chosen for use as reference values.

It is known[7,10,15] that for each chromatographic column with a certain weighed sample and specific adsorbent surface, the most reliable values of Henry's constants can be obtained for average retention values. That is why 1,4- and 1,2-dichlorobenzenes have been used previously[8,9] and in this work as the reference molecules to refine the parameters and introduce corrections for the *ortho*-effects.

The relative differences in the retention times of homologs and isomers (Table 6) are close. If the chlorobenzene molecules studied are arranged in the order of their increasing Henry's constants and the differences in these values for the nearest neighbors are calculated, one can observe that the results obtained by different authors

Table 5. Comparison of experimental[8–12] values of Henry's constants ($\ln K_1$) at 473 K for adsorption of chlorobenzenes on GTCB

Chlorobenzene	$\ln(K_1/\mathrm{cm}^3\ \mathrm{m}^{-2})$			
	I[a]	II[b]	III[c]	IV[d]
Chlorobenzene	−0.30	−0.44	−1.23	−0.58
1,3-Dichlorobenzene	1.37	0.93	0.85	—
1,2-Dichlorobenzene	1.41	1.01	0.60	—
1,4-Dichlorobenzene	1.47	1.06	0.69	0.92
1,3,5-Trichlorobenzene	2.64	2.23	1.97	—
1,2,4-Trichlorobenzene	2.82	2.41	2.16	2.32
1,2,3-Trichlorobenzene	2.82	—	—	—
1,2,3,5-Tetrachlorobenzene	4.26	—	—	—
1,2,4,5-Tetrachlorobenzene	4.42	3.89	3.99	—
1,2,3,4-Tetrachlorobenzene	4.64	—	4.00	—
Pentachlorobenzene	6.20	—	5.51	—
Hexachlorobenzene	—	—	7.07	—

[a] See Ref. 10. [b] See Refs. 8 and 9. [c] See Ref. 11. [d] See Ref. 12.

Table 6. Relative differences in Henry's constant values ($\ln K_1$) for the closest isomers and homologs of chlorobenzenes

Compared molecules	$\ln(K_1/\mathrm{cm}^3\ \mathrm{m}^{-2})$		
	I[a]	II[b]	III[c]
1,3-Dichlorobenzene—chlorobenzene	1.67	1.37	2.08
1,2-Dichlorobenzene—1,3-dichlorobenzene	0.04	0.08	−0.25[d]
1,4-Dichlorobenzene—1,2-dichlorobenzene	0.06	0.05	0.09
1,3,5-Trichlorobenzene—1,4-dichlorobenzene	1.17	1.17	1.28
1,2,4-Trichlorobenzene—1,3,5-trichlorobenzene	0.18	0.18	0.19
1,2,3-Trichlorobenzene—1,2,4-trichlorobenzene	0.00	—	—
1,2,3,5-Tetrachlorobenzene—1,2,3-trichlorobenzene	1.44	—	—
1,2,4,5-Tetrachlorobenzene—1,2,3,5-tetrachlorobenzene	0.16	—	—
1,2,3,4-Tetrachlorobenzene—1,2,4,5-tetrachlorobenzene	0.22	—	0.01
Pentachlorobenzene—1,2,3,4-tetrachlorobenzene	1.56	—	1.51
Hexachlorobenzene—pentachlorobenzene	—	—	1.56

[a] See Ref. 10. [b] See Refs. 8 and 9. [c] See Ref. 11. [d] This value should not be taken into account, since the $\ln K_1$ value for 1,3-dichlorobenzene was determined incorrectly.

Table 7. Comparison of calculated values of Henry's constants ($\ln K_1$) at 473 K for adsorption of chlorobenzenes on GTCB

Molecule	$\ln(K_1/\mathrm{cm}^3\ \mathrm{m}^{-2})$				
	I[a]	II[b]	III[c]		
			1	*2*[d]	*3*[e]
Chlorobenzene	−0.68	−0.47	−0.44	−0.44	−0.44
1,3-Dichlorobenzene	0.68	0.94	0.98	0.98	0.98
1,2-Dichlorobenzene	0.79	1.02	1.15	1.01	1.01
1,4-Dichlorobenzene	0.82	1.05	1.06	1.06	1.06
1,3,5-Trichlorobenzene	1.99	2.26	2.25	2.25	2.25
1,2,4-Trichlorobenzene	2.27	2.50	2.59	2.44	2.44
1,2,3-Trichlorobenzene	2.39	2.62	2.82	2.59	2.52
1,2,3,5-Tetrachlorobenzene	3.82	4.04	4.19	3.95	3.86
1,2,4,5-Tetrachlorobenzene	3.86	4.06	4.23	3.92	3.92
1,2,3,4-Tetrachlorobenzene	4.05	4.25	4.47	4.16	4.03
Pentachlorobenzene	5.7	5.88	6.15	5.76	5.54
Hexachlorobenzene	—	7.74	8.12	7.64	7.21

[a] See Ref. 10. [b] See Refs. 8 and 9. [c] Data of this work.
[d] After introducing the correction for the *ortho*-effect.
[e] After introducing the correction for the *ortho-ortho*-effect.

coincide, first of all, for di- and trichlorobenzenes. This indicates that the relative arrangement of isomers and homologs of di- and trichlorobenzenes have been chosen correctly. When the most reliable experimental data[8,9] are chosen for these molecules (see Table 5), we can refine the AAP parameters (see Experimental).

The absence of reliable experimental data for 1,2,3-tri- and 1,2,3,4-tetrachlorobenzenes does not allow them to be used directly for the determination of corrections for the *ortho-ortho*-effect; however, for this purpose, their relative arrangement on the chromatograph can be used.

The order of elution of isomers from the chromatographic column is the most important criterion that allows one not only to evaluate the reliability of experimental and calculated data but also to introduce corrections into AAP. In particular, as can be seen in Tables 5 and 7, the correction for the *ortho-ortho*-effect makes it possible to reach a correspondence between the experimentally found and calculated order of elution of 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes (see Table 7). For molecules containing no substituents in the *ortho*-positions, it is enough to introduce one correction factor to reach agreement with the experiment. In the case of *ortho*-substituted isomers, a special correction for the *ortho*-effect should be introduced, whose value depends on the parameters of the AAP used. Only in the case of introducing an additional correction for the *ortho-ortho*-effect, can one obtain experimental and calculated values consistent within the experimental error and the correct order of elution of isomers from the chromatographic column.

Calculations performed with these refined parameters and corrections for the *ortho*-effect and *ortho-ortho*-effect (see Table 7) are most reliable. Comparison of the experimental and most reliable calculated values of Henry's constants shows that the *ortho*-arrangement of Cl atoms results in a decrease in the adsorption value, probably, due to a decrease in the total polarizability of the molecule. This decrease in the polarizability and, correspondingly, in the adsorption compensates for the energetically more favorable arrangement of *ortho*-substituted isomers on the graphite surface, which by itself tends to increase the adsorption. As a whole, the *ortho*-effect results in a decrease in the differences between the values of Henry's constants of isomers. This result should be taken into account for prognostication of the possibility of chromatographic separation of isomeric molecules containing substituents in *ortho*-positions.

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