Bull. Environ. Contam. Toxicol. (2001) 66:777–783

DOI: 10.1007/s00128-001-0076-0

Bulletin of Environmental Contamination and Toxicology

Estimation of the Sorption of Substituted Aromatic Compounds on the Sediment of the Yangtse River

C.-D. Wu, D.-B. Wei, X.-H. Liu, L.-S. Wang

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, People's Republic of China

Received: 19 December 2000/Accepted: 12 April 2001

The Yangtse River, the largest river in China, originates in the remotely western part of China and flows through eight provinces before disgorging its waters into the Yellow Sea. Human activities in the Yangtse basin may produce contaminants finally to flow into the river (Jiang et al. 2000). On the other hand, many regions along the Yangtse River have been using the river water as drinking water resource. So it is of interest to investigate sorption behavior of the aqueous contaminants on the sediment of the Yangtse River.

Substituted aromatics have been used extensively in the chemical industry. They are a class of dangerous toxic compounds and have been released into the environment. Their environmental behavior and ecological effects should be anticipated. The measured or accurately estimated soil sorption coefficients (K_{OC}) of chemicals are critical importance for their environmental risk assessment (Mihelcic et al. 1993). However, for substituted aromatic compounds, especially polyhalogenated aromatics, some of their K_{OC} values are rarely available. The purpose of this work was to study the sorption behavior of nonclass-specific sets of 28 substituted aromatic compounds in the Yangtse River sediment and to produce a predictive model.

MATERIALS AND METHODS

28 substituted aromatic compounds were from the Aldrich Chemical Company, USA. Their purities were more than 99%. Their molecular names are given in Table 1. The sediment of the Yangtse River was air dried, ground to pass an 80-mesh sieve and sampled. The contents of its sand, silt, clay and organic carbon are 37.1%, 49.3%, 13.6% and 1.28%, respectively, and the pH is 7.44.

The sorption coefficients for the sediment and the octanol/water partition were determined using the shake-flask method according to the OECD guidelines for

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Correspondence to: C.-D. Wu

Table 1. The chemicals and their logarithm of observed K_{OW} and K_{OC}

No.[a]	Chemical name	$\log K_{OW}$	$\log K_{OC}$
1	2,4-Dichloro-benzenamine	2.76	2.44
2	3,4-Dichloronitrobenzene	3.29	2.62
3	2,4-Dichlorophenol	2.90	2.59
4	4-Chlorobenzaldehyde	2.16	2.32
5	3-Chloro-nitrobenzene	2.49	2.53
6	3,4-Dichloroaniline	2.55	2.32
7	2,4-dinitro-chlorobenzene	2.18	2.70
8	Pentachlorophenol	5.04	3.16
9	4-Chloro-2-nitro-benzenamine	2.56	2.30
10	4-Chloro-2-amino-phenol	1.79	1.86
11	4-Chloro-2-nitro-phenol	2.48	2.14
12	2-Chlorobenzamide	0.64	2.48
13	4-Chloro-benzonitrile	2.24	1.94
14	3,4-Dichloro-benzonitrile	2.98	2.05
15	2-Chloro-4-fluoroaniline	2.04	2.15
16	4-Chloro-iodobenzence	4.12	2.87
17	2,6-Dichloro-4-nitrobenzenamine	2.84	2.65
18	2-Chloro-5-nitro-benzenamine	2.23	2.43
19	4-Chloro-3-nitro-benzenamine	2.09	2.29
20	2,3-Dichloroaniline	2.74	2.54
21	1-Bromo-2,3-dichloro-benzene	4.64	3.02
22	1-Bromo-2,6-dichloro-benzene	4.12	2.94
23	1,3-Dichloro-2-fluoro-benzene	3.78	2.88
24	1,3-Dichloro-4-fluoro-benzene	3.45	2.81
25	1,2-Dichloro-3-iodo-benzene	4.84	3.22
26	1,2,3-Trichlorobenzene	4.13	2.87
27	2-Chloro-4-nitro-benzenamine	2.14	2.36
28	2,5-Dichloroaniline	2.75	2.49

[a] the number assigned in this table are used to identify the corresponding structures in subsequent table.

testing of chemicals (OECD 1987). The experiments were conducted in triplicate at 25±0.5℃. The equilibrium concentration of chemicals in the aqueous phase was measured by a UV/Vis spectrophotometer against water blank. The concentrations in the sediment and in the n-octanol phase were calculated by the difference. Batch equilibrium sorption isotherms were obtained in a sediment/water using Freundlich model and there are 7~9 points in each isotherm. K_{OC} were calculated as a function of the organic carbon content of the sediment. The results of K_{OW} and K_{OC} are listed in Table 1.

The molecular connectivity indices (MCIs) according to Kier and Hall (1976) were calculated by a computer program CONNECT designed by our laboratory. The $\Delta\chi$, non-dispersive force factor, can be computed for each type of index, as described by Bahnick and Doucette (1988). All of the 42 calculated MCIs were stored as variables in the data file. Quantum chemical descriptors were calculated with MOPAC 97 or derived from the MOPAC-results, and geometrical (3D) descriptors were based on MOPAC-optimised geometries. The AM1 model was used; atomic charges were calculated as electrostatic potential (ESP)-charges and as simple net atomic charges. Table 2 shows a complete list of descriptors with their short descriptors except MCIs.

Table 2. Descriptors used in the study

Parameter	Description
MW	molecular weight
MR	molecular refraction calculated by Toolkit Software (1999)
E_{HOMO}	energy of the highest occupied molecular orbit
E_{LUMO}	energy of the lowest unoccupied molecular orbital
DIFF	E_{HOMO} - E_{LUMO}
HARD	hardness according to Person 1989, $(-E_{HOMO} + E_{LUMO})/2$
EN	electronegativity according to Person 1989, $(-E_{HOMO} - E_{LUMO})/2$
IP	ionization potential
HOF	final heat of formation
TE	total energy
CCR	core-core repulsion
A_{ac}	Connolly accessible area
V_{mc}	molecular van der Waals volume
Ov	ovality
Q_{max}	maximum positive atomic charge
Q_{min}	maximum negative atomic charge
qH^+	maximum positive charge on hydrogen atom
Q_{AB}	maximum atomic charge (absolute)
Q_{TOT}	absolute sum of atomic charges of a solute molecule
B_{MAX}	maximum charge difference between connected atoms
α	molecular polarizabilities
π^*	polarizability index = poarizability / V_{mc}
μ	dipole moment
V^+	potential of the positive atomic charges (Schüürmann, 1990)
V^-	potential of the negative atomic charges (Schüürmann, 1990)
V^{TOT}	potential of the total atomic charges(Schüürmann, 1990)

The statistical analysis was performed using SPSS 8.0 for Windows (SPSS Inc. 1997). The quantitative structure-activity relationships were obtained using the stepwise procedure with a confidence limit of 95%. Correlations between the descriptors were checked and highly correlated parameters were eliminated.

RESULTS AND DISCUSSION

Many correlations that estimate K_{OC} from K_{OW} have been reported (Chiou et al. 1983; Sabljić et al. 1995; Vowels and Mantoura 1987). However, most of these correlations are class specific. For a data set in Table 1, simply linear regression of the values of log K_{OC} against the log K_{OW} resulted in

$$\log K_{OC} = 1.735 + 0.273 \log K_{OW} \qquad (1)$$
$$(\text{Adjusted } r^2 = 0.611,\ n = 28,\ SE = 0.219,\ F = 43.42)$$

As seen, r^2_{adj} is only 0.611, there is a poor relation between log K_{OC} and log K_{OW}. This result is agreement with Fetter's conclusion (1993), namely, there may be no universal equation that relates log K_{OC} to log K_{OW} for all classes of compounds. Therefore, for our studied compounds containing polar functional groups such as $-X$, $-NO_2$, $-OH$, $-NH_2$, $-CN$ and $-CHO$, that hydrophobic bonding controls sorption may not be true and there must be other mechanisms of substituted aromatics sorption on the sediment except partition, such as physical adsorption and chemosorption.

We also investigated whether using more complicated descriptors of MCIs would result in a more statistically reliable estimated value of K_{OC}. A stepwise multiple regression was performed on the K_{OC} data with all of the available molecular connectivity indices. The stepwise regression equation is given as follows.

$$\log K_{OC} = 1.210 + 0.569\, {}^2\chi^v - 1.385\, \Delta^5\chi^v \qquad (2)$$
$$(\text{Adjusted } r^2 = 0.689,\ n = 28,\ SE = 0.196,\ F = 30.82)$$

Where ${}^2\chi^v$ and $\Delta^5\chi^v$ represent the second order valence and non-dispersive force factor, respectively. Their values are listed in Table 3. For Model 2, the r^2 is as bad as the correlation with only log K_{OW}. That is, only 68.9% of the variability in K_{OC} data is accounted for. Other researchers have found that molecular connectivity does not correlate well with K_{OC} for nonclass-specific sets of chemicals (Bahnick and Doucette 1988; Gerstl 1990). However, correlations with molecular connectivity appear work well for very specific chemical classes with different indices (Hong 1997; Sabljić and Protić 1982). For example, a correlation for only the 11 aniline compounds in our study's data set resulted in a r^2_{adj} of 0.92 when using ${}^0\chi^v$ and $\Delta^6\chi_c^v$.

There have been many papers concerning the utility of quantum chemical descriptors for describing adsorption coefficients (Martin 1997; Reddy and Locke 1994). Their advantages are obvious. They are not restricted to compounds with similar structure and describe clearly defined molecular properties. A stepwise multiple regression of log K_{OC} against all the quantum chemical descriptors in Table 2 resulted in Equation 3. The values of four parameters for 28 substituted

Table 3. Descriptors in the regression equations

No.	$^2\chi^v$	$\Delta^5\chi^v$	MW	π^*	V^-	EN
1	2.508	0.112	162.02	0.696	1.529	4.332
2	2.668	0.085	192.00	0.685	0.925	5.957
3	2.438	0.147	163.00	0.666	1.202	4.709
4	2.105	0.116	140.57	0.689	0.853	5.321
5	2.173	0.092	157.56	0.695	0.951	5.825
6	2.486	0.110	162.02	0.697	1.118	4.364
7	2.556	0.121	202.55	0.728	1.564	6.604
8	3.804	0.113	266.34	0.637	0.945	5.276
9	2.396	0.201	172.57	0.761	1.867	5.053
10	2.139	0.185	143.57	0.741	1.255	4.169
11	2.402	0.240	173.56	0.725	1.036	5.613
12	2.271	0.183	155.58	0.687	1.113	5.028
13	2.054	0.053	137.57	0.730	0.823	5.319
14	2.553	0.079	172.01	0.705	0.615	5.450
15	2.080	0.060	145.56	0.720	1.138	4.386
16	3.097	0.000	238.46	0.628	0.359	4.962
17	2.848	0.209	207.02	0.741	1.940	5.229
18	2.324	0.158	172.57	0.754	1.854	5.260
19	2.331	0.226	172.57	0.751	1.774	5.064
20	2.427	0.038	162.02	0.688	1.074	4.395
21	3.172	0.000	225.90	0.615	0.517	5.123
22	3.140	0.000	225.90	0.615	0.518	5.139
23	2.348	0.000	164.99	0.639	0.919	5.154
24	2.400	0.000	164.99	0.640	0.916	5.058
25	3.462	0.000	272.90	0.610	0.505	5.111
26	2.726	0.000	181.45	0.622	0.505	5.073
27	2.369	0.152	172.57	0.769	1.773	5.126
28	2.508	0.038	162.02	0.693	1.182	4.426

aromatic compounds in regression equation are also listed in Table 3.

$$\log K_{OC} = 6.778 + 2.971\times10^{-3}\,MW - 8.739\,\pi^* + 0.550\,V^- + 0.127\,EN \qquad (3)$$

$$(\text{Adjusted } r^2 = 0.949,\ n = 28,\ SE = 0.079,\ F = 127.7,\ p = 0.000)$$

The p and F values in Equation 3 show that the correlation is significant. This equation has large r^2 and low SE, This indicate the observed log K_{OC} is very close to the predicted log K_{OC}. So this model can be used to predict the property of chemicals with a similar molecular structure. Furthermore, a strength of the quantum chemical descriptor approach is that the terms of the equation 3 can be given a physical interpretation. It is seen from the correlation Equation 3 that the molecular weight (MW) is a volume-related parameter, A larger molecular volume is unfavorable for partitioning to the aqueous phase where strong hydrogen bonds have to be broken to create cavity for the solute molecule. The π^* is defined as the depolarity/ polarizability, a large value of π^* is favorable for partitioning into the aqueous phase, which is a strong polar solvent. The V^-, potential of negative atomic charges, has been demonstrated to be particularly well-suited for studying intermolecular interactions, e.g., hydrogen bonding tendencies, solute/solvent (or solute/solute) and recognition interactions (Murry et al. 1993). The electronegativity (EN) is called absolute electronegativity, the difference of which drives the electron transfer. Therefore, the values of EN are shown to be in good agreement with the known chemical behaviors, such as nucleophilic-electrophilic properties and rates of reaction (Pearson 1989). All positive signs of the coefficients for V^- and EN in Equation 3 indicate that, in case of two solutes having the same WM and π^*, the larger the V^- and EN, the bigger K_{OC} will be. With regard to the meaning of V^- and EN, respectively, it is deduced that a hydrogen bonding and electron transfer process may exist between the studied compounds and the components of the sediment. Otherwise, the positive sign of V^- and EN in Equation 3 can not be explained well. Consequently, it is concluded that sorption mechanism for the studied compounds include a hydrogen bonding and electron transfer process except hydrophobic bonding. The organic and inorganic sediment components were mainly responsible for adsorption properties.

Acknowledgments. This study was financially supported by the National Nature Science Foundation of China (No. 29837180).

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