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Estimation of the Sorption of Substituted Aromatic Compounds onto Modified Clay

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Recently, the use of modified clays as sorbents for removal of organic compounds from water and soil has been an active research field (Cadena 1989; Steven et al. 1998; Lin 2000). The majority of the research in this area has focused on developing innovative and promising adsorbent materials (Lee et al. 2001) and examining the effects of pH, solvent, and electrolytes on the adsorption of organic compounds onto organo-clays (Stapleton 1994; Nzengung et al. 1996; Nzengung et al. 1997). However, regarding sorption partition coefficients of a set of compounds on modified clay, few studies so far are reported.

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 27 substituted aromatic compounds on modified clay and to produce a predictive model.

MATERIALS AND METHODS

Twenty-seven substituted aromatic compounds were from the Aldrich Chemical Company, USA. Their listed purities were more than 99%. Their molecular names are given in Table 1.

The natural montmorillonite was obtained from Jiangning, Jinagsu province. The cationic surfactant used to modify montmorillonite was 99% cetyltrimethylammonium bromide (CTMAB) obtained from Shanghai Chemical Co. Adsorption of CTMAB onto montmorillonite was conducted in 5 L batch type

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

No.[a]	Chemical name	log K_{OC}
1	2,4-Dichloro-benzenamine	3.72
2	3,4-Dichloronitrobenzene	3.76
3	2,4-Dichlorophenol	3.63
4	4-Chlorobenzaldehyde	3.48
5	3-Chloro-nitrobenzene	3.61
6	3,4-Dichloroaniline	3.62
7	2,4-dinitro-chlorobenzene	3.78
8	Pentachlorophenol	4.13
9	4-Chloro-2-nitro-benzenamine	3.68
10	4-Chloro-2-amino-phenol	3.41
11	4-Chloro-2-nitro-phenol	3.56
12	4-Chloro-benzonitrile	3.41
13	3,4-Dichloro-benzonitrile	3.61
14	2-Chloro-4-fluoroaniline	3.49
15	4-Chloro-iodobenzence	3.77
16	2,6-Dichloro-4-nitrobenzenamine	3.70
17	2-Chloro-5-nitro-benzenamine	3.63
18	4-Chloro-3-nitro-benzenamine	3.53
19	2,3-Dichloroaniline	3.74
20	1-Bromo-2, 3-dichloro-benzene	3.93
21	1-Bromo-2, 6-dichloro-benzene	3.84
22	1,3-Dichloro-2-fluoro-benzene	3.83
23	1,3-Dichloro-4-fluoro-benzene	3.73
24	1,2-Dichloro-3-iodo-benzene	4.00
25	1,2,3-Trichlorobenzene	3.97
26	2-Chloro-4-nitro-benzenamine	3.63
27	2,5-Dichloroaniline	3.76

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

reactor with 4L of 4% CTMAB solution. 500 g of montmorillonite were mixed with the CTMAB solution, and then agitated with a mechanical stirrer at 300 rpm for two hrs under the condition of a 60~70℃ water bath. After agitation, the mixture was vacuum filtered and washed several times with distilled water. The organo-montmorillonite was dried at 50℃ in an electric oven and then activated for two hrs at 105℃. The dry organo-montmorillonite was ground to pass 80-mesh sieve and sampled. The content of organic carbon are 17.3%.

The sorption coefficients for the organo-montmorillonite were determined using the shake-flask method according to the OECD guidelines for 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 an

UV/Vis spectrophotometer against water blank. The concentrations in the organo-montmorillonite were calculated by the difference. Batch equilibrium sorption isotherms were obtained in an organo-montmorillonite /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 organo-montmorillonite. The results of K_{OC} are listed in Table 1.

Molecule structure has been represented by different sets of descriptors: constitutional, geometrical, topological, electrostatic and quantum chemical descriptors (Wu et al. 2001). The octanol/water partition coefficient (log K_{OW}) for every compound, determined by Wu et al. (2001), was added to the pool of descriptors, as it is known to describe the hydrophobic interaction. Their values are listed in Table 2.

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; Vowels and Mantoura 1987; Sabljić et al. 1995). Regression between log K_{OC} and log K_{OW} of tested chemicals yields the following equation:

$$\log K_{OC} = 3.197 + 0.168 \log K_{OW} \qquad (1)$$

$R=0.887$, $R^2 = 0.787$, $n = 27$, $SE = 0.083$, $F = 92.24$

As measured by R, 88.7% of the variation in K_{OC} data is explained by K_{OW}, there is a good correlation between these two properties. In comparison, a poor correlation of K_{OW} to K_{OC} would obtained and estimates using their model will be off by as much as 1.2 log units within 95% confidence (Baker et al. 2000). Fetter's conclusion (1993) is that there may be no universal equation that relates log K_{OC} to log K_{OW} for all classes of compounds. However, although our studied compounds are also nonclass-specific with different polar functional groups such as –X, $-NO_2$, –OH, $-NH_2$, -CN and –CHO, a good correlation was still yielded. Therefore, This result provides indirect evidence regarding the mechanisms of modified montmorillonite adsorption, namely, the partitioning process of substituted aromatics between hydrophobic layer on the surface of modifid montmorillonite and water plays an important role.

Baker et al. (1997) showed that addition of molecular connectivity index could

Table 2. Regression equation descriptors.

No.	K_{OW}	$^{3}\chi_{c}$	π^{*}	α	O
1	2.76	0.760	0.722	76.344	1.253
2	3.29	0.971	0.692	81.696	1.280
3	2.90	0.760	0.688	70.979	1.250
4	2.16	0.493	0.685	69.496	1.263
5	2.49	0.789	0.671	70.127	1.269
6	2.55	0.760	0.724	76.425	1.250
7	2.18	1.205	0.7	86.791	1.301
8	5.04	1.155	0.713	102.464	1.278
9	2.56	0.994	0.757	83.809	1.275
10	1.79	0.760	0.744	71.532	1.248
11	2.48	0.539	0.704	76.386	1.274
12	2.24	0.493	0.75	73.556	1.269
13	2.98	0.676	0.747	83.574	1.278
14	2.04	0.760	0.716	68.153	1.245
15	4.12	0.577	0.676	74.647	1.246
16	2.84	1.164	0.744	93.028	1.294
17	2.23	0.971	0.738	82.037	1.279
18	2.09	0.994	0.74	82.542	1.273
19	2.74	0.664	0.709	74.746	1.242
20	4.64	0.664	0.652	76.728	1.244
21	4.12	0.664	0.649	76.307	1.241
22	3.78	0.664	0.657	67.148	1.245
23	3.45	0.760	0.658	67.380	1.248
24	4.84	0.664	0.667	82.150	1.243
25	4.13	0.664	0.663	74.507	1.243
26	2.14	0.971	0.75	83.322	1.279
27	2.75	0.760	0.717	75.796	1.253

increase the estimation accuracy of $\log K_{OC}$ from $\log K_{OW}$. In our study, a stepwise multiple regression was also performed on the K_{OC} data with $\log K_{OW}$ and all of the available molecular connectivity indices on our chemical data set. This regression was performed to determine whether the correlation in equation 1 could be improved with the addition of a second parameter. The stepwise regression equation is given as follows.

$$\log K_{OC} = 2.960 + 0.174 \log K_{OW} + 0.276\,{}^{3}\chi_{c} \qquad (2)$$

$R=0.940$, $R^2=0.884$, $n=27$, $SE=0.063$, $F=90.55$

As seen from equation 2, square of correlation coefficient improves from 0.787 to 0.884 and SE decreased from 0.083 to 0.063. This further affirmed a molecular connectivity index resulted in a slight improvement of the Equation 1. This additional term, the third order molecular connectivity index, is an indicator of flexibility of a molecule. Their values are listed in Table 2. Although this term does improve the fit of the correlation, calculating ${}^{3}\chi_{c}$ requires that correlation users have the program or the knowledge to calculate molecular connectivity indices. Moreover, the accuracy for estimation of $\log K_{OC}$ would depend on the accuracy for determination of $\log K_{OW}$. Thus, the development of other quantitative structure-property relationship models is of significance.

Quantum chemical descriptors can be easily obtained by computation. There have been some 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 based on PM3 method, as was described in the literature (Wu et al. 2001). The values of three parameters for 27 substituted aromatic compounds in regression equation are listed in Table2. The equation is:

$$\log K_{OC} = 10.129 + 0.022\alpha - 3.504\,\pi^* - 4.48O \qquad (3)$$

$$R=0.929,\ R^2 = 0.863,\ n = 27,\ SE = 0.069,\ F = 48.23$$

Where α is molecular polarizability, π^* is equal to α/ Connolly accessible volume, O is the ovality of a molecule. All other variables were found statistically insignificant. For our studied dataset, the equation 3 gives correlation coefficient square of 0.863 and standard errors of 0.069, respectively. Figure 1 shows excellent fits between the predicted and observed values. Based on this equation, $\log K_{OC}$ of an unknown substituted aromatic compounds having similar structure might be predicted from its $\log K_{OW}$.

T test (see Table 3) reveals the parameters significant. It is clear that molecular size, shape (ovality), and molecular polarizability play a dominant role in the partition properties of compounds. Within the parameters, the contribution of α is great.

Table 3. Model fitting results for $\log K_{OW}$.

Independent variable	coefficient	SE	t-statistics	p
Constant	10.129	1.220	8.302	0.000
π^*	-3.504	0.465	-7.529	0.000
α	0.022	0.002	9.654	0.000
O	-4.480	1.126	-3.979	0.001

Ovality is a volume-related parameter. The parameter is one of the most significant descriptors in our model. It means that the most important factor of the partition is the creation of a cavity in the structure of hydrophobic layer of modified clay as well as solute-solvent dispersion interactions. This parameter,

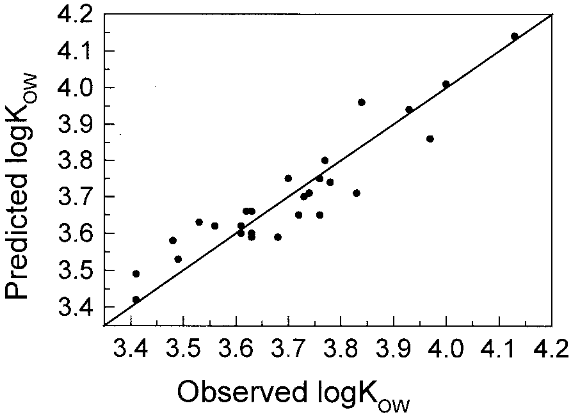

Figure 1. Plot of predicted versus observed log K_{OC} values.

however, cannot fully describe the wide variation of the partition properties. The remaining quantum chemical parameters are the overall descriptors of the interaction among the solvent and solute molecules. The estimation model is well suited to predict compound properties, because it more fully illustrates the partitioning mechanism.

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