ADSORPTION OF SUBSTITUTED AROMATIC COMPOUNDS BY POWDERED ACTIVATED CARBON: A MECHANISTIC APPROACH TO QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS

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Introduction

Because of their widespread prevalence in ground and surface waters, aromatic compounds pose a significant risk to public health. Of the current biological, chemical, and physical methods for remediation of these contaminants, activated carbon has been chosen as the primary method of treatment by many drinking water facilities. However, questions remain concerning the economic feasibility of activated carbon use, and determining suitable carbons for specific contaminants often requires extensive experimentation, time, and cost. Previous work in developing predictors of carbon performance, or quantitative structure-activity relationships (QSARs), has fallen short of providing accurate models for carbon adsorption. While the literature reports the ability of a few powdered activated carbons (PACs) to remove benzene from contaminated water, knowledge concerning the performance of the broad group of commercially available PACs in removing benzene or substituted benzene compounds is not widely available.

Quantitative structure-activity relationships (QSARs) have basis in the knowledge that molecular variations caused by a change in substituent effect a change in activity. QSARs have been used in a variety of applications, including for prediction of toxicities of chemicals, enhancement of drug design, assessment of enzyme inhibition, design of 'greener' chemical processes, and prediction and description of biodegradation processes and mechanisms [1, 2]. Use of QSARs to predict adsorptive behavior of carbons is a relatively new endeavor, however. Previous studies have reported the use of topological molecular connectivity indices [3] that encode for molecular size, surface area, degree of branching, molecular volume, topology of unsaturation and heteroatoms, etc. to predict the extent of carbon adsorption of a wide variety of compounds. For example, Brasquet et al. [4] showed that adsorbability for fibrous activated carbon in the presence of 14 aromatic compounds increased with increasing molecular size and decreased with increasing number of heteroatoms and degree of insaturation. Despite a high R^2 value of 0.9241, no other statistic (e.g., F-ratio, Q^2, etc.) was presented to reflect the robustness of the resulting correlation. It is important to note that R^2 values alone do not reflect robust correlations with predictive ability. Also,

use of the topological methods such as the molecular connectivity indices has been criticized because of the inability to interpret the physicochemical sense of the regression equation [5].

This study attempts to address the questions provoked by the previous work by using descriptors that describe not only hydrophobicity differences in the adsorbates but also differences in the electronic and steric nature of the substituents. The method used in this study was the 'traditional' method of QSAR development [1, 6]. In this traditional approach, experimental and/or calculated parameters are used individually to derive correlations that allow the practitioner to observe the effects of electronics, sterics, or hydrophobicity on the measured activity [6, 7, 8]. By using all three types of substituent descriptors as independent variables, a correlation can be obtained that provides not only robust predictive ability but also a better understanding of the mechanism of adsorption. The ultimate goal of this modeling research is to build the training set of substituted benzenes to enable construction of robust predictive correlations.

Table 1 lists a set of selected independent variables used in this correlation analysis. For a thorough explanation of each descriptor, please refer to Hansch and Leo [6] and Lindner et al. [2]. Field electronic effects of substituent on adsorption were assessed in terms of Hammett's constant σ_{Ind} and F, and resonance electronic effects were assessed in terms of R [8]. Steric effects were measured in terms of MR, the molar refractivity of the substituent, Taft's constant, E_s, and compound molar refractivity [8]. Other properties that were assessed for their influence on adsorption included molecular weight (MW), the aqueous solubility, S_{aq} (parts/100 parts of water) and log C^s_w (moles/L), boiling and melting points, density, and heat of enthalpy [9, 10, 11]. The dependent variables tested were Freundlich constants, K_f and 1/n, measured for the Calgon F400 activated carbon. Linear, quadratic, cubic, and power correlations between the dependent variables and independent variables were constructed using the SPSS software with 95% confidence limits.
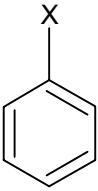
Experimental

Adsorption isotherms were developed by adding a known concentration of contaminant (100-μg/L) to distilled deionized (DDI) water at a pH of 5±1. The desired amount of Calgon F400 powdered carbon was weighed and dried overnight at 105ºC. After cooling the carbon in a dessicator, a carbon stock slurry (10,000-mg/L) was prepared by combining the carbon and DDI water by mixing on a stir plate. The slurry was stored in a dessicator at room temperature and mixed on a stir plate before each application. Isotherms were created for each target contaminant using concentrations of carbon varying from 1-ppm up to 75-ppm. For each run, the desired amount of stock solution was added to the 100-mL syringe, yielding a final volume of 100-mL. The syringe was then mixed end over end on a rotator for 2 hours. After mixing, the samples were filtered into VOC vials using 25-mm Fisherbrand 0.45-µm nylon syringe filters. Samples were sealed with Teflon septa caps and stored at 4°C until analysis. All samples were analyzed with a Saturn 2100T GC/MS using a Supelco VOCOL™ Fused Silica capillary column with a Supelco SPME 75-µm CAROXEN™ PDMS fiber, utilizing an oven

temperature program that holds at 40°C for 2 minutes and then climbs to 210°C at a rate of 8°C/min.

In order to assess trends in the nature of the benzene substituent on adsorption by the Calgon F400, a regression analysis was performed using SPSS 12.0 software (SPSS., Inc., Chicago, IL, USA). As shown in Table 1 below, the substituents initially tested were hydrogen (-H), chloro- (-Cl), isopropyl- (-HC(CH$_3$)$_2$), nitro- (-NO$_2$), hydroxyl- (-OH), and n-butyl (-CH$_2$(CH$_2$)$_2$CH$_3$) groups. These represent a broad range of electronic, sterics, and hydrophobicity character to provide an effective range for a first-basis view of substituent effects on adsorption behavior.

Criteria for "robust" QSAR applied in this study were the following: 1.) only correlations with adjusted R^2 greater than 0.7 were considered and 2.) F-ratio (calculated) > $F_{\alpha, n, n-k-1}$ (where α is the confidence imposed on the correlation, which was no more than 0.1 for this study, k is the degrees of freedom for the regression, n is the number of compounds tested, and n-k-1 is the degrees of freedom for the residual). Since n=6 in this initial analysis, only correlations with one descriptor were deemed suitable for the final set of acceptable models. Even then, caution was taken in making predictions based on these results. Only trends shown by these correlations that will guide future testing of additional adsorbates were possible given the very small number of compounds tested.

Table 1: Selected Descriptors of Substituent or Compound Electronics, Sterics, and Hydrophobicity [8, 9, 10].

Substituent, X	Electronics Descriptors			Sterics Descriptors		Hydrophobicity Descriptors		Physical Properties	
	σ_{Ind}	F	R	MR	Taft Es	Log K_{ow}		MW (g/mole)	Log C^s_w (mole/L)
-H	0.00	0.00	0.00	0.10	0.00	2.17	0.00	78.1	-1.65
-Cl	0.47	0.42	-0.19	0.60	-0.97	2.78	0.39	112.6	-2.39
-HC(CH$_3$)$_2$	0.01	0.04	-0.19	1.50	-1.71	3.66	1.22	120.2	-3.33
-NO$_2$	0.64	0.65	0.13	0.74	-2.52	1.85	-0.85	123.1	-1.79
-OH	0.29	0.33	-0.70	0.28	-0.55	1.44	-1.12	94.1	-0.005
-CH$_2$(CH$_2$)$_2$CH$_3$	-0.04	-0.01	-0.15	1.96	-.163	4.38	2.13	134.2	-3.95

Results and Discussion

The Freundlich constants derived from the batch isotherms are shown in Table 2.

Table 2: Experimentally derived Freundlich constants for benzene and selected mono-substituted benzenes

Compound	Molecular weight g/mol	log k	log 1/n
Benzene	78.1	4.51	0.48
Chlorobenzene	112.6	5.34	0.42
Isopropylbenzene	120.2	5.48	0.44
Nitrobenzene	123.1	5.05	0.53
n-butylbenzene	134.2	4.59	0.65
Phenol	94.1	3.71	0.76

Nine correlations with log K_f and log (1/n), respectively, meeting the quality constraints described previously were obtained, and these are provided in Tables 3 and 4. With the exception of correlation 2 with enthalpy (H) as a descriptor, only descriptors relating to aqueous solubility and octanol-water partition coefficient showed significant influence on adsorption by the Calgon F400 activated carbon. Correlation 2 implies that as the heat of enthalpy of the compound increases, the adsorption by Calgon F400 decreases. The coefficient of H is very small (-4.278×10^{-5}), thus leaving in question the validity of this correlation [1].

Table 3: Results of QSAR Analysis with log K as the Dependent Variable[a, b]

Correlation Log K_f =	R^2	Adjusted R^2	Standard Error	F-Ratio
1.) $-0.016S_{aq} + 0.698$	0.703	0.629	0.038	9.492
2.) -4.278×10^{-5} H + 0.697	0.702	0.627	0.038	9.424
3.) $-0.021 \log C_w^2 -0.114 \log C_w + 0.561$	0.839	0.731	0.032	7.804
4.) $0.016 \log C_w^3 + 0.076 \log C_w^2 + 0.019 \log C_w + 0.569$	0.966	0.914	0.018	18.836
5.) $-0.052 \log K_{ow}^2 + 0.328 \log K_{ow} + 0.221$	0.772	0.621	0.028	5.103

[a] S_{aq} = aqueous solubility (parts/100 parts water), H = heat of enthalpy (mole/kg•bar), C_w = aqueous solubility (moles/L), K_{ow} = octanol-water partition coefficient
[b] Six compounds in the training set (Benzene, Chlorobenzene, Isopropylbenzene, Nitrobenzene, Phenol, and N-Butylbenzene)

Correlations 1, 3, and 4 in Table 3 provide relationships between log K_f and the aqueous solubility of adsorbate. The linear correlation 1 indicates that an increase in aqueous solubility (with units of parts per 100 parts) results in a decrease in log K_f observed with the Calgon F400 carbon. More insight into the effects of adsorbate aqueous solubility on adsorption and improved R^2 values were obtained using log C_w^s (moles/L) as a descriptor. Correlations 3 and 4 show quadratic and cubic relationships with log C_w^s and log K_f, respectively, and these relationships are plotted in Figure 1. The cubic fit resulted in the most robust correlation with an adjusted R^2 of 0.914,

standard error of 0.018, and F-ratio of 18.836. Of the compounds tested, increasing aqueous solubility yielded increasing log K_f values up to isopropylbenzene (log C^s_w = -3.33 moles/L); however, n-butylbenzene showed significantly decreased log K_f in comparison to isopropylbenzene. The relationship of aqueous solubility of adsorbate with adsorption has been previously studied, and the Lundelius rule, stating that adsorption increases with decreasing solubility of the solute in the solvent, was established as a semiquantitative guideline for predictive purposes [12]. As is shown in Figure 1, the Lundelius rule is predicted to be followed up to a log C^s_w of approximately -3 moles/L; however, this rule fails beyond this point. These results suggest an "optimum" aqueous solubility in this series of compounds, beyond which adsorption activity decreases.

Table 4: Results of QSAR Analysis Using Linear Regression and log (1/n) as the Dependent Variable[a, b]

Correlation Log (1/n) =	R^2	Adjusted R^2	Standard Error	F-Ratio
6.) $0.109 \log K_{ow}^2 - 0.652 \log K_{ow} + 0.580$	0.974	0.957	0.021	57.066
7.) $-0.003 \log K_{ow}^3 + 0.127 \log K_{ow}^2 - 0.701 \log K_{ow} + 0.620$	0.974	0.936	0.025	25.598
8.) $0.044 \log C_w^2 + 0.205 \log C_w - 0.108$	0.815	0.692	0.056	6.630
9.) $-0.028 \log C_w^3 - 0.121 \log C_w^2 - 0.021 \log C_w - 0.122$	0.959	0.896	0.032	15.430

[a] K_{ow} = octanol-water partition coefficient, C_w = aqueous solubility (moles/L)
[b] Six compounds in the training set (Benzene, Chlorobenzene, Isopropylbenzene, Nitrobenzene, Phenol, and N-Butylbenzene)

A similar trend was observed between log K_f and log K_{ow}, as shown in correlation 5 and Figure 2A. As log K_{ow} increases up to approximately 3, adsorption also increases; however, above this value, the quadratic correlation predicts a decrease in adsorption. A more robust quadratic fit was obtained with log (1/n) and log K_{ow}, as shown in correlation 6 (Table 4) and Figure 2B. The quadratic fit showed slightly better statistics than the cubic fit shown in correlation 7 in Table 4, and correlation 6 had the highest adjusted R^2 and F-ratio values (0.957 and 57.066, respectively) of all obtained in this study. Figure 2B shows that this correlation predicts that as log K_{ow} increases to approximately 3, log (1/n) decreases. Above a log K_{ow} value of 3, adsorption decreases rapidly.
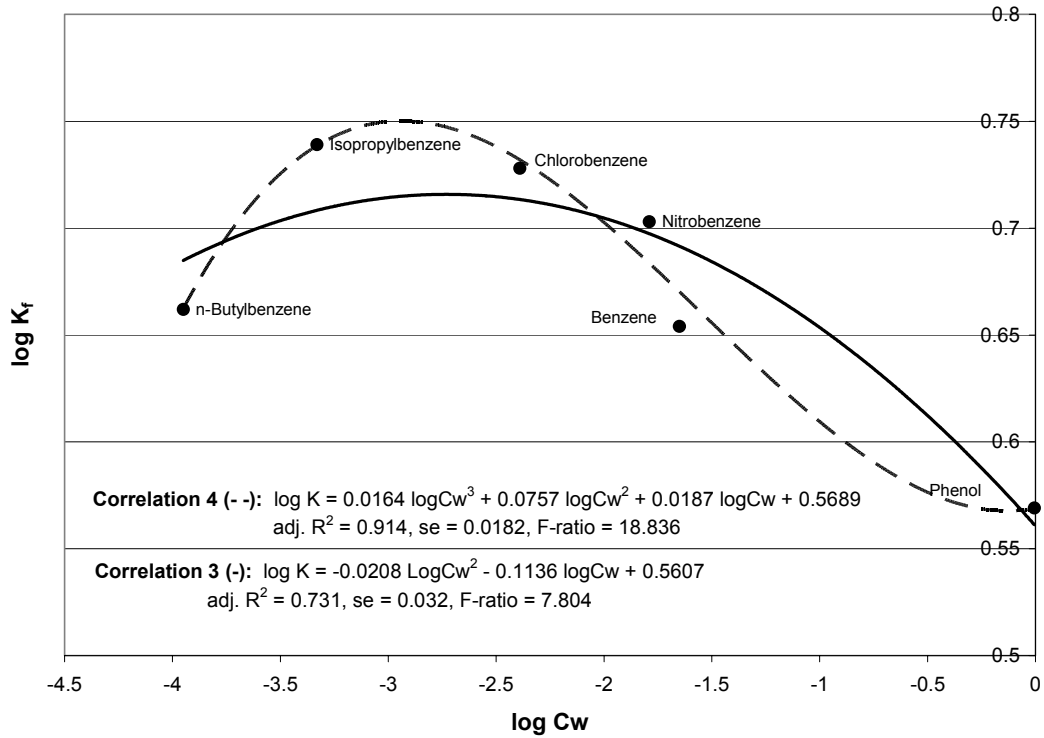
Figure 1: Dependence of Log K_f with log C_w Correlated by Quadratic (solid line) and Cubic (dashed line) Fits. The solid circles are the observed Log K_f values.
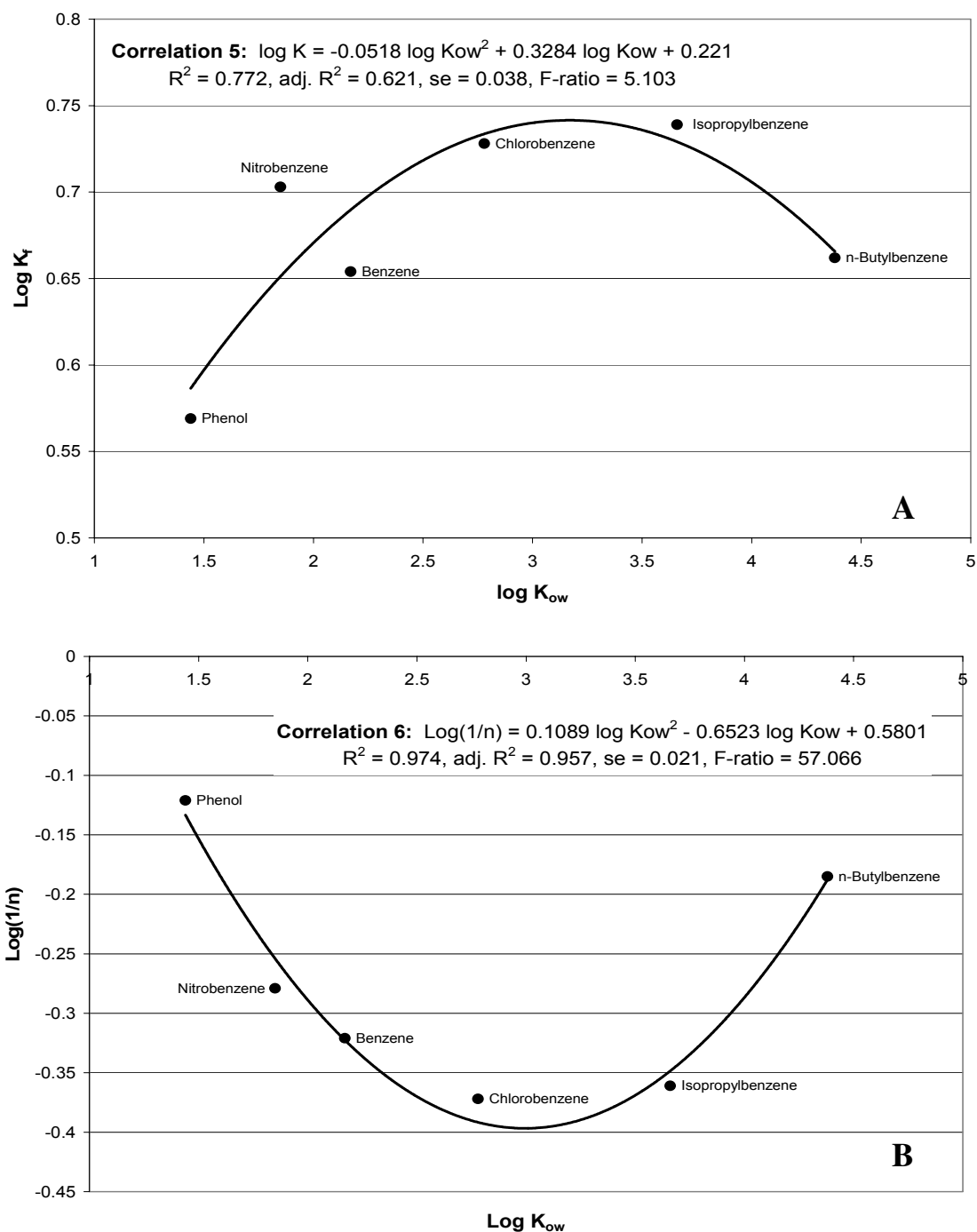
Figure 2: Quadratic Correlations between log K_{ow} and log K_f (A) and log (1/n) (B). The training set contained 6 substituted benzenes, and their empirical values are designated by the solid circles.

Finally, correlations 8 and 9 showing the quadratic and cubic fits (respectively) between log (1/n) and log C^s_w yield similar trends observed with log K_f. As the solubility of the solute decreases in water, log (1/n) also decreases up to an "optimum" concentration beyond which log (1/n) increases. Whether this trend is strictly caused by solubility

effects is not known. There is a strong negative correlation between Log K_{ow} and Log C^s_w and the molar refractivity of the substituents (MR) in this study with R^2 values of 0.815 and 0.743, respectively, meaning that as solute bulkiness increases, aqueous solubility decreases. While no valid linear correlation was obtained with MR, this well-studied trend [13] does suggest, however, that solute size may also play a very important role in the adsorptive behavior of the Calgon F400.

Conclusions

Current studies focus on increasing the training set of substituted compounds to allow construction of correlations for prediction of adsorption by the Calgon F400 carbon. Other substituents that are being tested include -F, -Br, -I, -NH$_2$, -CHO, thus providing an even greater range of substituent character. In addition to examining the effects of substituents, Langmuir isotherm data will be incorporated into the QSAR with the aspiration of highlighting the differences between the Langmuir and Freundlich models. Future studies will incorporate the testing of various carbons so that multilinear regression analysis can be performed using carbon characteristics (e.g., pore size, surface area, concentration of active sites, etc.) as independent variables. Modeling system behavior using one carbon type/multiple compounds and multiple carbon types/one compound will not only elucidate the mechanism of adsorption but will also increase our ability to more effectively select the appropriate carbon for the removal of any given substituted benzene.

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