JOURNAL OF THE TENNESSEE ACADEMY OF SCIENCE 69(1):1-6 JANUARY 1994

CALCULATIONS OF HENRY'S LAW CONSTANTS FOR ADSORPTION OF AROMATIC HYDROCARBONS ON A GRAPHITIC CARBON SURFACE

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ABSTRACT--Correlations were developed and used to calculate energetic and structural parameters which, in turn, were used to calculate Henry's law constants for the adsorption of a series of aromatic hydrocarbons on a graphitic carbon surface. The adsorption energetic parameter was correlated with a ratio involving the critical temperature divided by the square root of the critical pressure of the adsorbate molecule. The structural parameter was correlated with the cross-sectional molecular area obtained from available molecular modeling software, CAChe. Calculations of Henry's law constants per unit surface area were compared to available experimental values for 17 aromatic hydrocarbons divided into groups of mono-substituted benzene and methyl-substituted benzene. This approach could be used to predict the extent adsorption in the Henry's law region using only adsorbate molecular properties where correlations have been established for a series of molecules of similar structure.

Earlier research applied the virial coefficient theory (Steele and Halsey, 1954; Pierotti and Thomas, 1971) to model the adsorption of gas molecules on solid surfaces (Zhang and Rybolt, 1992). Additional research developed methods of calculating energy parameters that affect the virial coefficients (Rybolt et al., 1992). If the energy parameters and the structural parameters which affect virial coefficients could be calculated from properties of the adsorbate molecule and adsorbent surface, it should be possible to predict the extent of gas adsorption. Gas adsorption could then be predicted as a function of pressure, temperature, and adsorbate molecular parameters even without direct adsorption experiments.

The general purpose of the present study is to determine the extent to which known gas adsorption data can be calculated with virial values determined from energetic and structural correlations based on molecular parameters. The specific objective of this research is to develop a means of predicting virial values, $V_{A,1}$ (retention volumes per unit surface area), based on independent molecular and structural parameters that do not depend on adsorption data. These independent molecular parameters are correlated with properties of adsorption data.

Virial coefficients at specific temperatures may be determined experimentally by plotting the number of moles adsorbed versus pressure. A linear relationship is observed when temperature is held constant, and the virial coefficient is proportional to the slope of this line. Virial coefficients may also be determined from gas chromatographic data where retention times are proportional to gas-solid interaction.

The adsorption data used in this study were obtained by Kalashnikova et al. (1979) for a series of polycyclic hydrocarbons on a graphitized thermal carbon black. Chromatographic measurements of retention volumes at zero sample size (Henry's law constants) were obtained and expressed as $V_{A,1}$ values (Kalashnikova et al., 1979). Two sets of data were considered in attempting to find structural and energetic parameter correlations with adsorption data. One set consisted of mono-substituted alkyl aromatic hydrocarbon adsorbates and the other set consisted of methyl-substituted aromatic hydrocarbon adsorbates.

THEORY

In the Henry's law region of low coverage, the moles of gas adsorbed per gram of solid adsorbent, n_{ad}, is given by

$$n_{ad} = B_{2s}(P/RT) \quad (1)$$

where B_{2s} is the second gas-solid virial coefficient, P is the pressure, R is the gas constant, and T is the temperature. The B_{2s} can be expressed as a configurational integral, which for a flat surface is given as

$$B_{2s} = A_s z^* \int [\exp(-u_{1s}(y)/kT) - 1]\, dy \quad (2)$$

where k is the Boltzmann constant, y is a reduced variable ($y = z/z^*$), z is the internuclei adsorbate-adsorbent separation, z^* is the equilibrium adsorbate-adsorbent distance, and u_{1s} is the gas-solid interaction potential (Steele, 1967). If equation (1) is divided by the surface area A_s and the natural logarithm of both sides taken, the equation is expressed as

$$\ln(B_{2s}/A_s) = \ln(z^*) + \ln \int [\exp(-u_{1s}(y)/kT) - 1]\, dy. \quad (3)$$

It frequently has been observed that plots of $\ln B_{2s}$ versus 1/T over a broad temperature range give linear plats (Pierotti and Thomas, 1971). In these plots, the slope is proportional to E* (expressed in units of K), the gas-solid interaction energy divided by the Boltzmann constant, which suggest that equation (3) could be approximated by

$$\ln(B_{2s}/A_s) = \ln(z^*) + E^*(1/T). \quad (4)$$

The slope of equation (4) is related to gas-solid interaction energy (E*), and the intercept should be related to the size of the adsorbate molecule.

A series of available Henry's law, virial values for aromatic and substituted aromatic hydrocarbons determined from gas chromatographic work over various temperatures (Kalashnikova et al., 1979)

were used to examine the utility of this correlation. In the work of Kalashnikova et al. (1979), plots of ln $V_{A,l}$ versus 1/T yielded linear relations expressed as

$$\ln V_{A,l} = A + B/T \quad (5)$$

where A is the intercept (not surface area, A_s) and B is the slope of this line. They reported A and B values for equation (5) found for a series of polycyclic hydrocarbons on a graphitized thermal black adsorbent. By comparing equations (4) and (5), it is seen that it should be possible to relate their B-value to interaction energy and their A-value to the adsorbate size. In the following work, we discuss our efforts to predict A- and B-values and compare our calculated values with experimental data from Kalashnikova et al. (1979).

Analyses and Results

To ultimately predict $V_{A,l}$-values using equation (5), correlations must be determined from experimental values for the intercepts (A) and the slopes (B) for various adsorbate molecules. We consider two groups of molecules which we will refer to as mono-substituted and methyl-substituted aromatic adsorbates. It was not possible to group these two sets together and achieve satisfactory correlations to predict values of A, B, and $V_{A,l}$. However, we have included benzene and toluene in both of these groups to compare correlations determined for these sets of molecules. The mono-substituted aromatic hydrocarbons included benzene, toluene (methylbenzene), ethylbenzene, n-propylbenzene, isopropylbenzene, n-butylbenzene, n-amylbenzene (n-pentylbenzene), and n-hexylbenzene. The experimental temperature ranges, A-values, and B-values for these molecules are given in Table 1. Table 1 also gives experimental temperature ranges, A-values, and B-values for the methyl-substituted adsorbates which included benzene, toluene, m-xylene, o-xylene, p-xylene, 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, and 1,2,3,4-tetramethylbenzene.

The intercept (A) is related to the size of the adsorbate. Values of A were plotted versus molecular parameters (van der Waals molecular area and cross-sectional molecular area) to determine a correlation for the intercept and are presented in Table 2. Plots of the logarithm of these molecular areas provided only marginally better fits than the molecular areas plotted directly versus A-values from Kalashnikova et al. (1979). Therefore, molecular areas were used directly as shown in Fig. 1. Values for van der Waals molecular area were obtained directly from the program PCModel (Serena Software) which uses a MMX force field (Taylor et al., 1992) to find the minimum energy conformation of a molecule. Values for the cross-sectional molecular area were determined indirectly from the program CAChe (CAChe Scientific) which uses a MM2 force field (Allinger, 1977) to find the minimum energy conformation of a molecule.

A cross-sectional area relative to benzene was obtained for each of the adsorbates using CAChe. The adsorption area per molecule for benzene, 44.5 Å^2 (McClellan and Harnsberger, 1967) was used to calculate the cross-sectional molecular areas for the molecules. The relative cross-sectional areas were obtained by cutting and weighing printouts of two-dimensional molecular projections of van der Waals radii. Three printouts of each molecule were prepared, and the results averaged. The relative values were converted to absolute values using benzene as a reference.

TABLE 1. Experimental (Exp; from Kalashnikova et al., 1979) and calculated (Cal) values of A and B for mono-substituted and methyl-substituted benzene adsorbates.

Adsorbate	Temperature Range (K)	A		B	
		Exp	Cal	Exp (K)	Cal (K)
Mono-substituted					
Benzene	332-418	-11.35	-11.36	4474	4478
Toluene	373-473	-11.45	-11.70	5160	5117
Ethylbenzene	398-483	-11.94	-12.02	5636	5671
n-Propylbenzene	398-483	-12.93	-12.35	6452	6205
Isopropylbenzene	398-483	-11.97	-12.13	5786	6129
n-Butylbenzene	408-505	-12.87	-12.64	6862	6741
n-Amylbenzene	433-549	-12.97	-12.98	7336	7296
n-Hexylbenzene	448-572	-13.07	-13.33	7806	7874
Methyl-substituted					
Benzene	332-418	-11.35	-11.40	4474	4505
Toluene	373-473	-11.45	-12.02	5160	5430
m-Xylene	398-483	-12.79	-12.53	6337	6307
o-Xylene	398-483	-12.69	-12.55	6336	6260
p-Xylene	398-483	-12.69	-12.56	6336	6325
1,3,5-Trimethylbenzene	423-513	-13.44	-13.14	7196	7092
1,2,4-Trimethylbenzene	423-513	-13.42	-13.17	7278	7108
1,2,3-Trimethylbenzene	423-513	-13.40	-13.15	7307	7022
1,2,3,5-Tetramethylbenzene	453-558	-13.53	-13.72	7938	8091
1,2,4,5-Tetramethylbenzene	453-558	-13.47	-13.74	7922	7900
1,2,3,4-Tetramethylbenzene	453-558	-13.49	-13.74	8000	8244

TABLE 2. Molecular parameters used in correlations involving A and B.

Molecule	T_b (K)	T_c (K)	P_c (bar)	Molecular area (Å²)	
				Van der Waals[1]	Cross-sectional[2]
Benzene	353.244	562.16	48.98	105	44.5
Toluene	383.780	591.80	41.06	123	51.1
Ethylbenzene	409.352	617.20	36.06	139	57.6
n-Propylbenzene	432.392	638.32	32.00	160	64.1
Isopropylbenzene	425.561	631.10	32.09	166	59.6
n-Butylbenzene	456.420	660.53	28.87	180	69.7
n-Amylbenzene	478.610	678.8	25.9	200	76.6
n-Hexylbenzene	499.250	696.3	23.3	224	83.4
m-Xylene	412.270	617.05	35.36	147	56.5
o-Xylene	417.579	560.33	37.34	145	56.7
p-Xylene	411.509	616.23	35.11	141	56.9
1,3,5-Trimethylbenzene	437.893	637.35	31.27	165	63.1
1,2,4-Trimethylbenzene	442.528	649.17	32.32	160	63.4
1,2,3-Trimethylbenzene	449.267	664.47	64.54	158	63.2
1,2,3,5-Tetramethylbenzene	471.150	679.0	28.6	185	69.2
1,2,4,5-Tetramethylbenzene	469.950	675.0	29.4	182	69.4
1,2,3,4-Tetramethylbenzene	478.190	689.7	28.6	180	69.5

[1]Obtained from PCModel program.
[2]Obtained from CAChe program.

Table 3 contains the slopes, intercepts, and correlation coefficients (R) obtained for the mono-substituted and methyl-substituted adsorbates from the experimental values for A versus cross-sectional molecular areas from CAChe and van der Waals molecular areas from PCModel. The values of A versus cross-sectional molecular areas yielded the better correlation and are shown in Fig. 1. Figure 1 shows plots of A-values versus cross-sectional molecular area for the mono-substituted and methyl-substituted benzene derivatives.

The slopes (B-values) from equation (5) are related to gas-solid interaction energy. Several molecular parameters were plotted against B to find a suitable correlation for the slope. Values of the boiling point (T_b), the critical temperature (T_c), and the critical pressure (P_c) are given in Table 2 (Marsh, 1985). The relationship between energy and a ratio of critical constants T_c and P_c ($T_c/P_c^{0.5}$) has been previously established (Berezin, 1983). The slopes, intercepts, and correlation coefficient (R) for plots of B-values versus ($T_c/P_c^{0.5}$), T_c, and T_b are given in Table 3.

All three correlations were similar with ($T_c/P_c^{0.5}$) and T_c having the better correlation coefficients of approximately $R = 0.99$ for both mono-substituted and methyl-substituted aromatic hydrocarbons. The correlation based on B versus the critical constants relation of $T_c/P_c^{0.5}$ was used to predict values of B for the adsorbates. Although each of the correlations for the parameters explored yielded adequate R-values, the critical constant relation established by Berezin (1983) will be used because it has proven to be a useful method for predicting virial values. The correlation of B versus $T_c/P_c^{0.5}$ for the methyl-substituted and mono-substituted benzene adsorbates is shown in Fig. 2.

CONCLUSIONS

The experimental and predicted values of ln $V_{A,l}$ over specified temperature ranges for the mono-substituted and methyl-substituted benzene adsorbates are presented in Table 4. The values of ln $V_{A,l}$ at the high and low extreme of temperature for each of the adsorbates are determined from experimental values of Kalashnikova et al. (1979) and from the predicted values of A and B given in Table 1 using equation (5). The values shown in these two tables closely match, and a graphical representation is presented in Fig. 3 for 1,2,3,4-tetramethylbenzene,

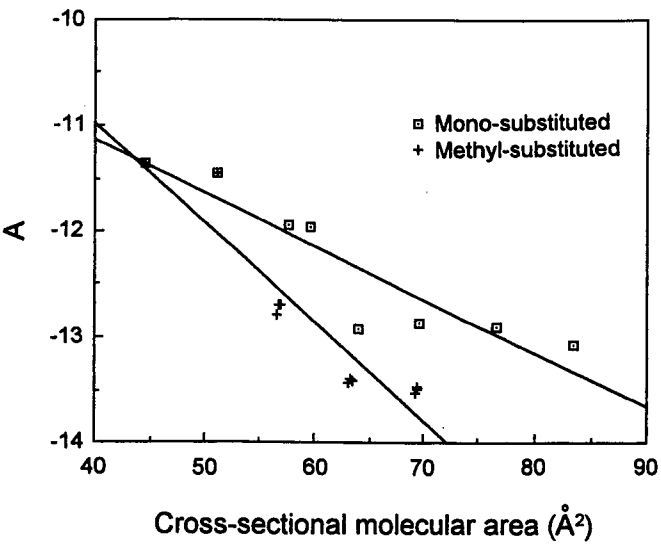

FIG. 1. Values of A versus cross-sectional molecular area for mono-substituted and methyl-substituted benzene adsorbates.

TABLE 3. Correlations of experimental A- and B-values with molecular parameters for the mono-substituted and methyl-substituted adsorbates.

Y-value	X-value	Adsorbate	Intercept	Slope (K)	*R*
A	Cross-sectional molecular area	Mono-substituted	-9.110	-0.0506	0.918
		Methyl-substituted	-7.231	-0.0937	0.935
A	Van der Waals molecular area	Mono-substituted	-9.730	-0.0159	0.884
		Methyl-substituted	-8.259	-0.3008	0.934
B	$T_c/(P_c)^{0.5}$	Mono-substituted	211.2	53.12	0.989
		Methyl-substituted	-1670.0	76.88	0.989
B	T_c	Mono-substituted	-9774	25.16	0.991
		Methyl-substituted	-11620	28.28	0.979
B	T_b	Mono-substituted	-3771	23.17	0.992
		Methyl-substituted	-5966	29.60	0.993

n-amylbenzene, 1,3,5-trimethylbenzene, and ethylbenzene from left to right, respectively.

As a result of the agreement between the experimental and predicted values of $V_{A,1}$ shown in Table 4, we conclude that it is possible to calculate approximate virial values from energetic and structural parameters. This process has been treated in an empirical manner and led to the following equation for mono-substituted alkylbenzene adsorbates

$$\ln V_{A,1} = [-9.11 - 0.0506(a)] + [211.2 + 53.12(T_c/(P_c)^{0.5})]/T \quad (6)$$

and the following equation for methyl-substituted benzene adsorbates

$$\ln V_{A,1} = [-7.23 - 0.0937(a)] + [-1670 + 76.88(T_c/P_c^{0.5})]/T \quad (7)$$

where a (Å^2) is the cross-sectional molecular area obtained from CAChe molecular modeling and $T_c/(P_c)^{0.5}$ (K/bar$^{0.5}$) values are obtained from available thermodynamic data. Equations (6) and (7) are obtained by substituting values from Table 3 into equation (5).

To use this approach to predict Henry's law adsorption, it is necessary to develop relations for the energetic parameter and structural parameter for a series of structurally similar adsorbate molecules that may be of interest. However, once these relations are established it should be possible to predict Henry's law constants and, hence, the extent of adsorption for other molecules which fit within the same series. With a low surface area solid such as a graphite, it is necessary to divide adsorbate molecules into similar structural groups such as was done in the current work. However, our preliminary results for a similar process for a microporous carbon adsorbent suggest that a variety of different types of adsorbates can be grouped together in one correlation used to determine the energetic parameter.

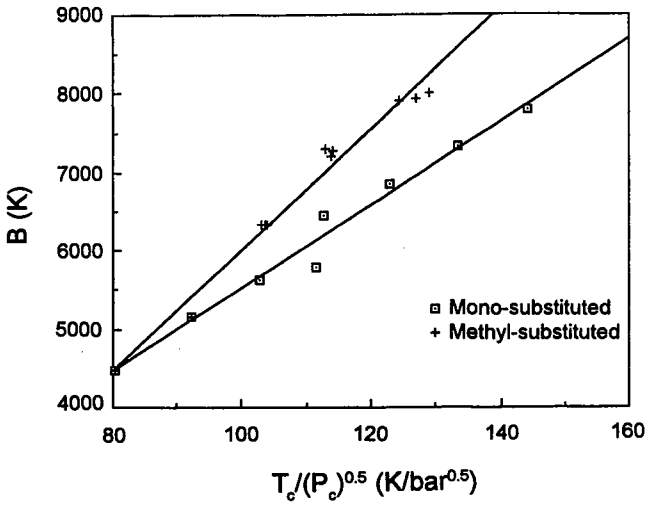

FIG. 2. Values of B versus critical constants ratio for mono-substituted and methyl-substituted benzene adsorbates.

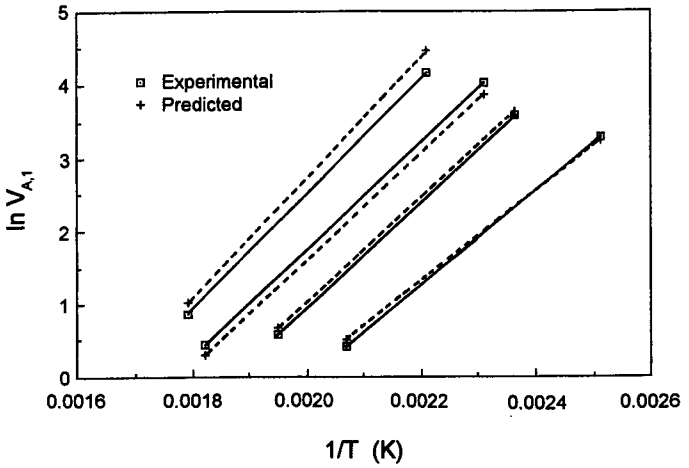

FIG. 3. Experimental (from Kalashnikova et al., 1979) and calculated ln $V_{A,1}$ versus 1/T for selected substituted benzene adsorbates (from left to right): 1,2,3,4-tetramethylbenzene; n-amylbenzene; 1,3,5-trimethylbenzene; ethylbenzene.

TABLE 4. Comparison of experimental (from Kalashnikova et al., 1979) and calculated values of ln $V_{A,1}$ for mono-substituted and methyl-substituted benzene adsorbates.

Adsorbate	Temperature (K)	ln $V_{A,1}$	
		Experimental	Predicted
Mono-substituted			
Benzene	332	2.13	2.13
	418	-0.65	-0.65
Toluene	373	2.38	2.02
	473	-0.54	-0.88
Ethylbenzene	398	2.22	2.23
	483	-0.27	-0.28
n-Propylbenzene	398	3.28	3.24
	483	0.43	0.50
Isopropylbenzene	398	2.57	3.27
	483	0.01	0.56
n-Butylbenzene	408	3.95	3.89
	505	0.72	0.71
n-Amylbenzene	433	4.03	3.87
	549	0.45	0.31
n-Hexylbenzene	448	4.35	4.25
	572	0.58	0.44
Methyl-substituted			
Benzene	332	2.13	2.17
	418	-0.65	-0.62
Toluene	373	2.38	2.53
	473	-0.54	-0.54
m-Xylene	398	3.13	3.32
	483	0.33	0.53
o-Xylene	398	3.23	3.18
	483	0.43	0.41
p-Xylene	398	3.23	3.33
	483	0.43	0.54
1,3,5-Trimethylbenzene	423	3.58	3.62
	513	0.59	0.68
1,2,4-Trimethylbenzene	423	3.79	3.63
	513	0.77	0.69
1,2,3-Trimethylbenzene	423	3.87	3.45
	513	0.84	0.53
1,2,3,5-Tetramethylbenzene	453	3.99	4.14
	558	0.70	0.78
1,2,4,5-Tetramethylbenzene	453	4.02	3.70
	558	0.73	0.42
1,2,3,4-Tetramethylbenzene	453	4.17	4.46
	558	0.85	1.03

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