Equilibrium Isotherms of Volatile Alkanes, Alkenes, and Ketones on Activated Carbon

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The sorption of volatile organic compounds (VOCs) on activated carbon was measured. Equilibrium isotherms at 298 K were obtained for *n*-hexane, cyclohexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, cyclohexane, 1-hexene, acetone, 2-butanone, and 2-pentanone. The effect of temperature on *n*-hexane sorption was studied by varying the temperature from (288 to 318) K. Data in this study were collected using a gravimetric apparatus. Some data were replicated with a volumetric apparatus for comparison using an error analysis. For the gravimetric data, it was found that the Langmuir equation (mean deviation 0.020 to 0.025) and the Freundlich equation (mean deviation 0.005 to 0.010) gave good fits of the sorption. Nonpolar or weakly polar sorbates, the sorbates with small steric profiles, or low molecular weight sorbates were more readily adsorbed on the microporous activated carbon. Polar sorbates were more readily adsorbed at high pressure, and low temperature improved the adsorption.

Introduction

Pollution caused by volatile organic compounds or VOCs is a major concern for the furnishing, building material, and chemical industries. VOCs may be carcinogenic or toxic to humans and animals, and it has been suggested that their concentration levels should be reduced. Early studies have shown that indoor concentrations of a number of organic chemicals found in household products can even exceed their outdoor concentrations.[1] Numerous studies have been conducted to treat or identify organic chemical pollutants indoors and outdoors. To the best of our knowledge, few studies have been reported on the adsorption of C_6 alkanes on activated carbon. Since significant levels may be emitted in gasoline depots, petrochemical facilities and chemical plants, the sorption of linear, cyclic, and branched C_6 alkanes is studied here. For comparison and analysis, several ketones and one alkene are included in the study.

Nondestructive methods to remove VOC include adsorption, absorption, condensation, and membrane separation. There is no chemical reaction in such methods, and the VOC can be desorbed from the sorbent. On the other hand, destructive methods like oxidation, photocatalysis, and biofiltration convert VOCs into smaller molecular weight species. The major advantage of using adsorption is that the VOCs can be recovered for appropriate disposal, and the sorbent may be reused.[2]

The amount of VOC uptake on a porous sorbent is determined by the internal surface area, which is much larger than the external surface area for most porous materials. Activated carbons have very large BET surface areas [(500 to 1500) $m^2 \cdot g^{-1}$], and the dominant structures are micropores which are on the scale of nanometers. Activated carbon was selected for this study mainly based on these two features.

To design an adsorption apparatus, equilibrium isotherm data are required. Isotherm data are usually obtained from equilibrium sorption experiments.[3,4] For example, the amount of sorbent for an adsorber unit is determined from equilibrium data, and the selection of an effective sorbent is also dependent on the equilibrium isotherm. In this study, equilibrium isotherm data were obtained by two methods—a gravimetric method in which the VOC uptake was measured with a microbalance and a volumetric method which used an ideal gas equation together with pressure, volume, and temperature ($P-V-T$) data.

Many isotherm models have been proposed to describe sorption behavior. The Langmuir and Freundlich isotherm models are often used for gas adsorption analyses. The Langmuir model is usually applied to sorbents with a homogeneous surface, and the Freundlich model is used to describe sorbents with a nonhomogeneous surface. In this study, the VOC sorption data for activated carbon were fitted using both models. The system pressure and temperature and the molecular characteristics of the activated carbon sorbent and VOC sorbates were factors to be considered.

Experimental System

Sorbent. A commercial activated carbon from coal (China Activated Carbon Industries Co.) was selected as the sorbent in this study. The specific surface area of activated carbon is typically higher than silica gel and zeolite. The surface properties were measured with a BET sorptometer (Micromeritics ASAP 2000). The sorbent was degassed at (473 ± 1) K under vacuum before the nitrogen adsorption measurements were carried out at (77 ± 1) K. The specific surface area, total pore volume, and mean pore diameter were calculated by the BET method.[5] The micropore (< 2 nm) and mesopore (2 nm < pore < 50 nm) volumes were estimated from the cumulative pore volume distribution from nitrogen desorption. The calculated values are shown in Table 1.

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Table 1. Properties of Activated Carbon Measured by BET Sorptometer with Nitrogen

sorbent	S_{BET} ($\mathrm{m^2 \cdot g^{-1}}$)	V_{micro} ($\mathrm{m^3 \cdot kg^{-1}}$)	V_{meso} ($\mathrm{m^3 \cdot kg^{-1}}$)	V_{total} ($\mathrm{m^3 \cdot kg^{-1}}$)	mean pore diameter (nm)
activated carbon	919	$0.24 \cdot 10^{-3}$ (53 %)	$0.09 \cdot 10^{-3}$ (20 %)	$0.45 \cdot 10^{-3}$	1.43

Chemicals. *N*-Hexane (99 %), cyclohexane (99 %), 2-butanone (99.5 %), and 2-pentanone (99.5 %) were purchased from Tedia Co.; 2-methylpentane (97 %), 3-methylpentane (97 %), and 2,2-dimethylbutane (99 %) from Lancaster Synthesis Co.; acetone (99.5 %) from Leda Chemical; and 1-hexene (97 %) from Acros Organics. The chemicals were all reagent-grade. The properties of the alkanes, ketones, cyclohexane, and 1-hexene are listed in Table 2.

Apparatus and Procedure. The gravimetric apparatus has been described in previous work.[6,7] The mass change during adsorption was measured by an electronic microbalance (Cahn C-33, uncertainty ± 0.1 μg). The pressure of this system was controlled from $1.333 \cdot 10^2$ Pa to $14.532 \cdot 10^3$ Pa and measured with a pressure gauge (Cole Parmer U-68700, uncertainty ± 0.1333 Pa).

The adsorption isotherms were plotted from the uptake and relative pressure P/P^0, where P is the operating pressure and P^0 is the saturation vapor pressure of the liquid solvent at the system temperature.

The static volumetric apparatus is shown in Figure 1. Both the gravimetric and volumetric methods have been used in the open literature to determine the equilibrium uptake of gases. There has been a recent trend to use microanalysis with a microbalance.[6−10] Previous studies by one of the authors[6,7] to measure the uptake of aromatic and acetate compounds have used the gravimetric method. Although the volumetric method is an indirect measurement of the adsorbed mass from $P-V-T$ data and requires attention to make leak tests, it may be simpler and less expensive to use.[11]

For the volumetric method, the amount of adsorption or uptake (mg of sorbate/g of sorbent) is calculated with the ideal gas equation of state from the pressure, volume, and temperature at the beginning and end of each experimental run. In Figure 1, the total volume of the system ($V_1 + V_3$) was determined to be 68.24 cm^3. A pressure gauge (Cole Parmer U-68700) was used to measure pressure. The working temperature of the constant temperature bath (Deng Yng, ± 0.05 °C) can be regulated from −20 °C (253 K) to 100 °C (373 K).

The volumetric method for measuring adsorption capacity of VOCs on activated carbon is described below:

(1) After regeneration in a vacuum dryer (373 K, 24 h), ∼ (50 ± 0.1) mg of activated carbon was weighed and placed in the adsorbent site (see Figure 1).

(2) The liquid VOC was put into the glass bottle. Degassing was repeated at least three times (thawing then freezing).

(3) VOC vapor was brought into the known volume V_1, and the initial pressure was measured. The system temperature was maintained at 288 K, 298 K, 308 K, or 318 K with a constant-temperature bath.

(4) The valve was opened to allow the activated carbon in V_3 to contact the VOC vapor. After equilibrium, the pressure of the adsorption system was recorded.

(5) VOC vapor was brought into the adsorption system again to change the pressure.

(6) After equilibrium, the pressure of the adsorption system was recorded again.

Table 2. Properties of VOCs

adsorbate	*n*-hexane	cyclohexane	1-hexene	2-methylpentane	3-methylpentane	2,2-dimethylbutane	acetone	2-butanone	2-pentanone
supplier	Tedia Company	Tedia Company	Acros Organics	Lancaster Synthesis	Lancaster Synthesis	Lancaster Synthesis	Leda Chemcial	Tedia Company	Tedia Company
purity (%)	99	99.5	97	98	97	99	99.5	99.5	99.47
molecular formula	C_6H_{14}	C_6H_{12}	C_6H_{12}	C_6H_{14}	C_6H_{14}	C_6H_{14}	C_3H_6O	C_4H_8O	$C_5H_{10}O$
molecular weight ($\mathrm{g \cdot mol^{-1}}$)	86.18	84.16	84.16	86.18	86.18	86.18	58.08	72.11	86.13
boiling point (°C)	68.8	80.8	63.5	60.3	63.3	49.8	56.3	79.7	102.4
dipole moment (D)	0	0.3	0.4	0.1	—	—	2.9	3.3	2.5
kinetic diameter[a] (Å)	6.26	5.78	6.11	6.19	6.14	6.10	5.37	5.70	5.92
critical diameter[b] (Å)	4.5	6.9	—	5.4	5.4	6.3	—	—	—
critical temperature (K)	507.4	553.4	504.0	497.5	504.4	488.7	508.1	535.6	564.0
critical pressure (atm)	29.3	40.2	31.3	29.7	30.8	30.4	46.4	41.0	38.4
vapor pressure at ($\mathrm{Pa \cdot 10^{-4}}$)									
15 °C	1.28	8.13	1.59	1.83	1.71	2.91	1.96	0.75	0.27
25 °C	2.01	1.31	2.47	2.80	2.55	4.43	3.05	1.23	0.47
35 °C	3.05	2.01	3.71	4.17	3.94	6.19	4.63	1.92	0.77
45 °C	4.49	3.01	5.39	6.04	5.53	8.93	6.79	2.93	1.24

[a] Kinetic diameter is the intermolecular distance of closest approach for two molecules represented as spheres.[22] [b] Critical diameter is the diameter of a cylinder which can circumscribe the molecule in its most favorable equilibrium conformation.[22]

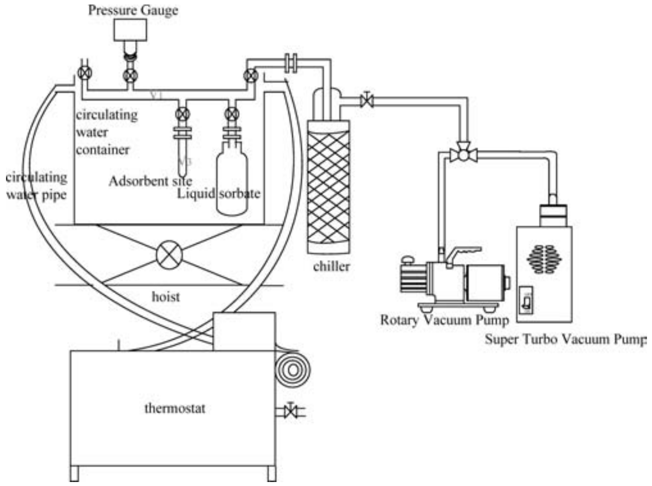

Figure 1. Volumetric adsorption apparatus.

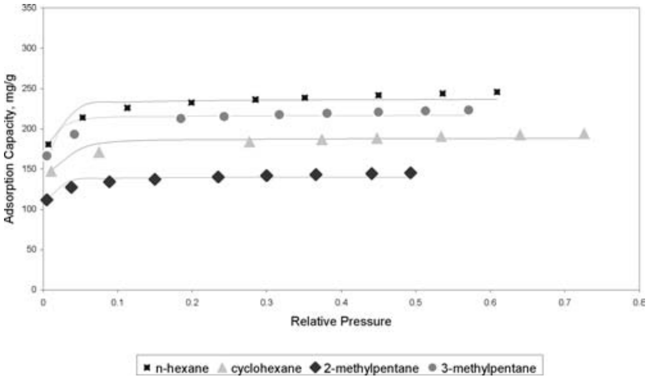

Figure 2. Experimental and predicted adsorption isotherms for C_6 alkanes on activated carbon, at 298 K, using the gravimetric method. Solid line, Langmuir model.

Table 4. Boiling Point of C_6 Alkanes

sorbate	boiling point (°C)
cyclohexane	80.7
n-hexane	68.8
3-methylpentane	63.3
2-methylpentane	60.3
2,2 -dimethylbutane	49.7

(7) Steps 5 and 6 were repeated until the saturation pressure was attained.

Equilibrium uptake was calculated by the ideal gas equation. The isotherms were plotted in the same manner as for the gravimetric method.

Results and Discussion

Adsorption Capacity with Gravimetric Apparatus. Data in the next two sections were obtained with the gravimetric apparatus. This gravimetric apparatus has been tested by comparison of the experimental data obtained from this apparatus with literature data in a previous study.[6]

The adsorption capacities of *n*-hexane, cyclohexane, 2-methylpentane, and 3-methylpentane on activated carbon at 298 K are listed in Table 3. The adsorption capacity for each VOC versus relative pressure P/P^0 was plotted as the isotherm shown in Figure 2. Activated carbon for removal of organic vapors is nonpolar,[12−15] and C_6 alkanes are nonpolar. In addition, the mean pore diameter of the activated carbon was only ∼2 times larger than the molecular size of the adsorbing species, which restricted further sorption of secondary layers. This gave a type I isotherm profile[16] (see also IUPAC classification).

Table 2 shows that the kinetic diameter and critical diameter of C_6 alkanes are comparable to the 1.4 nm mean pore diameter of the activated carbon, and therefore the adsorption capacity was significantly affected by the VOC molecular size and structure. The alkane *n*-hexane is a straight chain molecule, and it encounters the least geometric hindrance. Its adsorption capacity was higher than cyclohexane or the C_6 alkanes with a side chain, as shown in Figure 2. In addition to the geometric hindrance, the boiling point of C_6 alkanes must be considered. A lower boiling point means the attractive force between molecules is weaker (Table 4). In other words, this may allow the VOC molecules to return to the gas phase more readily, and the adsorption capacity is decreased. The order of the boiling point for C_6 alkanes is *n*-hexane > 3-methylpentane > 2-methylpentane, and Figure 2 shows that the adsorption capacity for 2-methylpentane on activated carbon was lower than the other two. It appears that the geometric hindrance for cyclohexane is significant, and its isotherm curve was lower than *n*-hexane and 3-methylpentane.

Adsorption Isotherm Model. To provide useful information for adsorber design, equilibrium data are usually correlated by an adsorption isotherm model. For the low to moderate pressure in this work, the Langmuir[17] and Freundlich[18] isotherm models were used to fit the equilibrium adsorption data.

$$\text{Langmuir equation:} \quad q = \frac{q_0 bP}{1 + bP} \tag{1}$$

or

$$\frac{1}{q} = \frac{1}{q_0 b}\frac{1}{P} + \frac{1}{q_0} \tag{2}$$

$$\text{Freundlich equation:} \quad q = KP^n \tag{3}$$

or

Table 3. Experimental Data for Adsorption on Activated Carbon, at 298 K, Using the Gravimetric Method

n-hexane		cyclohexane		2-methylpentane		3-methylpentane	
P/P^0	q^a (mg·g^{-1})	P/P^0	q^a (mg·g^{-1})	P/P^0	q^a (mg·g^{-1})	P/P^0	q^a (mg·g^{-1})
0.007	180.742	0.011	147.726	0.005	111.930	0.005	166.578
0.053	214.025	0.075	171.235	0.038	127.535	0.042	193.320
0.113	226.068	0.277	184.073	0.089	134.242	0.185	212.755
0.199	232.647	0.374	187.004	0.150	137.344	0.243	215.230
0.285	236.522	0.448	188.712	0.235	140.248	0.317	217.627
0.351	238.843	0.534	190.759	0.300	141.811	0.381	219.359
0.450	241.775	0.640	192.818	0.366	143.140	0.450	220.896
0.536	244.044	0.726	194.453	0.441	144.469	0.513	222.290
0.609	245.789	−	−	0.493	145.355	0.571	223.319

[a] Uncertainty ± 0.002 %.

$$\log q = n \log P + \log K \tag{4}$$

where q is the adsorption capacity (mg sorbate/g sorbent); q_0 is the saturated adsorption capacity (mg of sorbate/g of sorbent); b is the Langmuir equilibrium constant (Pa^{-1}); K is the Freundlich constant; P is the pressure (Pa); and n is the Freundlich exponent. Using the linear form of the Langmuir equation (eq 2), $1/q$ vs $1/P$ was plotted. The values of q_0 and b from a linear regression are shown in Table 5. Similarly, the Freundlich equation was linearized (eq 4) and plotted as $\log q$ vs $\log P$. From the slope and intercept of the linear regression line, the values of n and K were calculated and are shown in Table 6. Figure 2 shows the experimental adsorption capacities and the regressed curves for the Langmuir equation. Figure 3 shows the same plots for the Freundlich equation.

The saturated adsorption capacity q_0 which was obtained for n-hexane using the Langmuir model (Table 5) was 237.53 $\mathrm{mg \cdot g^{-1}}$. The activated carbon used in this work has a lower capacity compared to the reported value of 312.4 $\mathrm{mg \cdot g^{-1}}$ for granular activated carbon from a different source.[19]

The mean deviation D was calculated by eq 5

$$D = \frac{1}{N} \sum_{i=1}^{n} \left| \frac{q_i^{\mathrm{exp}} - q_i^{\mathrm{cal}}}{q_i^{\mathrm{exp}}} \right| \tag{5}$$

where N is the number of data points at a given temperature, and q^{exp} and q^{cal} are the experimental and calculated adsorption capacities, respectively. The Freundlich model had smaller mean deviation values (0.005 to 0.010) than the Langmuir model (0.020 to 0.025). Comparing Figure 2 with Figure 3, we find that the Freundlich equation gave a slightly better fit for the experimental isotherm curves of volatile C_6 alkanes than the Langmuir equation.

Table 5. Estimates of q_0 and b in Langmuir Equation, at 298 K, Using the Gravimetric Method[a]

sorbent	sorbate	q_0 ($\mathrm{mg \cdot g^{-1}}$)	b (Pa^{-1})	mean deviation D
activated carbon	n-hexane	237.53	0.0232	0.024
	cyclohexane	189.04	0.0259	0.020
	2-methylpentane	140.45	0.0284	0.025
	3-methylpentane	217.39	0.0238	0.022

[a] See eq 1, Table 3, and Figure 3.

Table 6. Estimates of K and n in THE Freundlich Equation, at 298 K, Using the Gravimetric Method[a]

sorbent	sorbate	K	n	mean deviation D
activated carbon	n-hexane	132.37	0.067	0.010
	cyclohexane	108.94	0.064	0.005
	2-methylpentane	86.258	0.055	0.005
	3-methylpentane	123.57	0.063	0.007

[a] See eq 3, Table 3, and Figure 4.

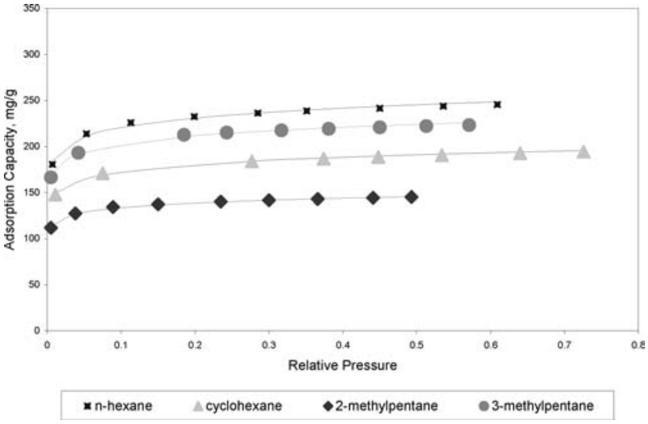

Figure 3. Experimental and predicted adsorption isotherms for C_6 alkanes on activated carbon, at 298 K, using the gravimetric method. Solid line, Freundlich model.

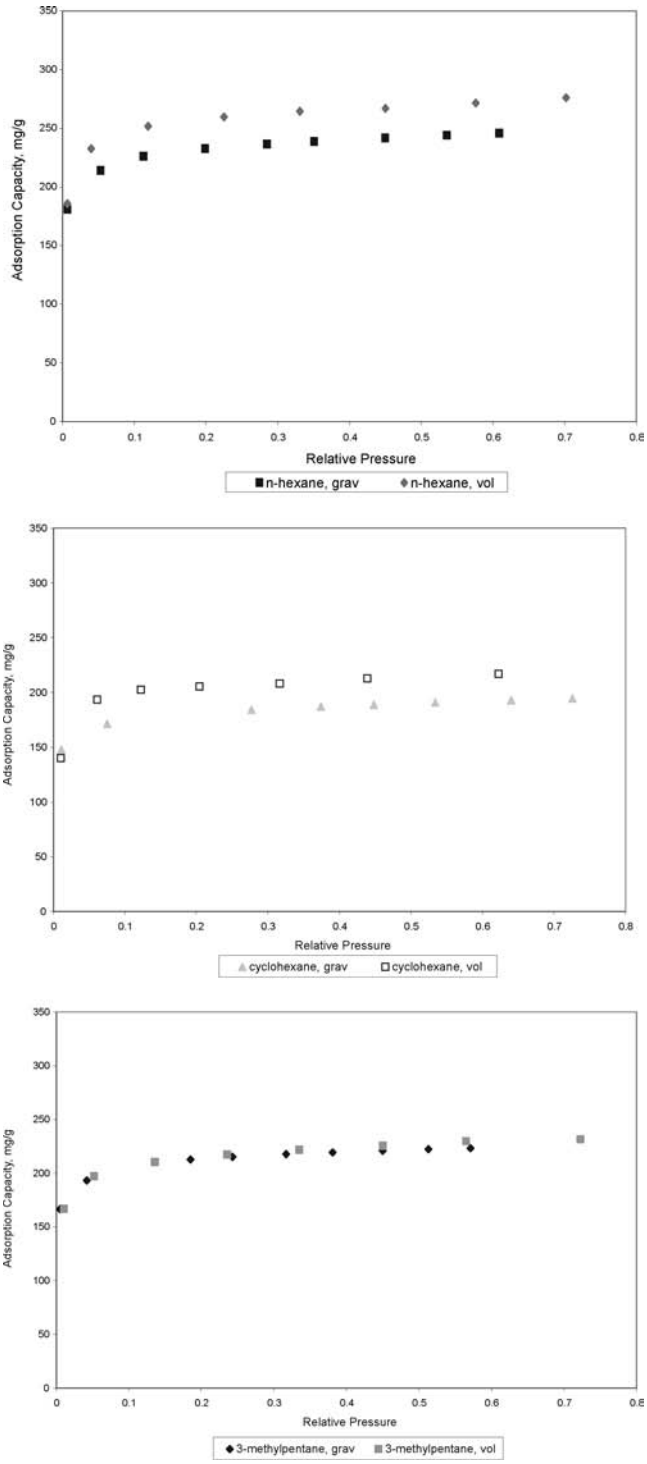

Figure 4. Comparison of gravimetric and volumetric methods, at 298 K.

Comparison of Gravimetric and Volumetric Methods. For comparative purposes, the adsorption capacities of n-hexane, cyclohexane, and 3-methylpentane on activated carbon at 298 K were measured once more but this time using a volumetric apparatus (Table 7). The equilibrium isotherms using the gravimetric and volumetric methods are shown in Figure 4.

The observed deviations of the two methods for n-hexane (9.9 %) and cyclohexane (10.7 %) were larger than the expected

Table 7. Experimental Data for Adsorption on Activated Carbon, at 298 K, Using the Volumetric Method

n-hexane		cyclohexane		2-methylpentane		3-methylpentane	
P/P^0	q^a (mg·g^{-1})	P/P^0	q^a (mg·g^{-1})	P/P^0	q^a (mg·g^{-1})	P/P^0	q^a (mg·g^{-1})
0.007	185.88	0.010	140.09	0.014	162.75	0.010	166.84
0.040	232.58	0.061	193.19	0.071	184.16	0.052	197.06
0.119	251.68	0.122	202.51	0.162	194.85	0.136	210.21
0.225	259.69	0.204	205.42	0.252	200.69	0.236	217.33
0.331	264.43	0.316	208.22	0.328	204.21	0.335	221.49
0.450	266.89	0.439	212.60	0.414	206.03	0.450	225.54
0.576	271.52	0.622	216.78	0.519	206.90	0.565	229.60
0.702	276.15			0.681	209.86	0.722	231.36

1-hexene		2,2-dimethylbutane	
P/P^0	q^a (mg·g^{-1})	P/P^0	q^a (mg·g^{-1})
0.032	174.824	0.006	134.35
0.081	213.198	0.030	156.708
0.135	234.689	0.084	169.644
0.205	244.355	0.202	176.405
0.281	252.682	0.286	179.911
0.384	262.065	0.394	181.305
0.503	271.315	0.518	183.457
0.648	277.710	0.696	185.027

acetone		2-butanone		2-pentanone	
P/P^0	q^a (mg·g^{-1})	P/P^0	q^a (mg·g^{-1})	P/P^0	q^a (mg·g^{-1})
0.0262	103.280	0.022	104.875	0.057	120.450
0.109	149.408	0.054	135.489	0.171	153.205
0.175	166.199	0.087	154.290	0.257	170.101
0.266	180.679	0.239	178.282	0.343	180.181
0.349	190.190	0.326	185.902	0.457	189.080
0.428	198.299	0.402	191.981	0.600	196.798
0.519	206.333	0.435	194.247		
		0.511	197.960		

[a] Uncertainty ± 1.6 %.

error (see Appendix for error analysis). This suggests that despite adherence to good experimental procedures there may have been a slight and undetectable leak from the compartments V_1 or V_3 in the volumetric experiments for *n*-hexane and cyclohexane. The observed deviation for 3-methylpentane (0.92 %) in Figure 4 is within the expected error. Considering the possibility of a small leak in a volumetric apparatus, together with the significantly smaller expected error for data from a gravimetric apparatus as discussed in the Appendix, it would seem to be that rigorous analytical work would require the more reliable gravimetric method. With proper regular calibration, the volumetric method may be sufficient for routine quality tests or monitoring for emissions.

Adsorption Capacity with Volumetric Apparatus. Data discussed in this section were obtained with the volumetric apparatus. The equilibrium isotherms of *n*-hexane and its isomers on activated carbon at 298 K are shown in Figure 5. The order of adsorption uptake was found to be *n*-hexane > 3-methylpentane > 2,2-dimethylbutane. This is consistent with Figure 2 which shows data from the gravimetric apparatus. The 2,2-dimethylbutane has two methyl groups, whereas 3-methylpentane only has one. The steric hindrance for 2,2-dimethylbutane is larger than 3-methylpentane, and its equilibrium uptake was smaller.

Figure 6 shows the equilibrium isotherms of *n*-hexane, cyclohexane, 1-hexene, and 2-pentanone at 298 K. The lower uptake for cyclohexane relative to *n*-hexane confirms the plot shown in Figure 3 using the gravimetric apparatus.

Figure 6 also shows that at low pressure the amount of adsorbed 1-hexene was smaller than *n*-hexane. However, there was almost no difference in the amount of adsorbed *n*-hexane and 1-hexene at $P/P^0 > 0.5$. The reason for this may be that the nonpolar activated carbon used in this work is good for the adsorption of nonpolar sorbates like *n*-hexane at low system pressure. It is possible that at higher system pressure the intermolecular interaction of 1-hexene molecules (dipole moment 0.4 D) may favor better packing of 1-hexene in the micropores of activated carbon.[20] The discussion given here must also take into account the observed deviation for isotherms from volumetric data (with respect to the gravimetric data) as mentioned above in the section Comparison of Gravimetric and Volumetric Methods.

The uptake *n*-hexane was greater than 2-pentanone at 298 K as shown in Figure 6 because activated carbon is nonpolar with more affinity for *n*-hexane.

Figure 7 shows the equilibrium isotherms of acetone, 2-butanone, and 2-pentanone in activated carbon at 298 K. The order of the adsorption uptake on activated carbon was 2-butanone >

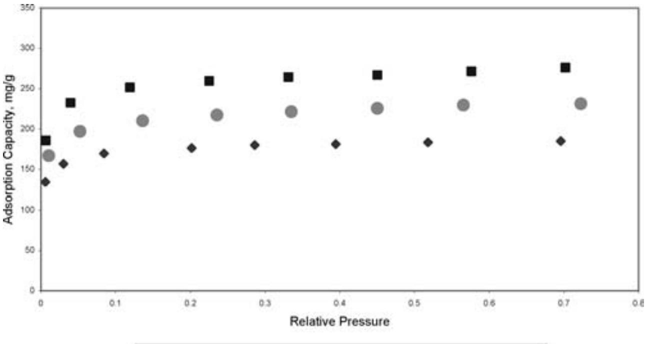

Figure 5. Experimental adsorption isotherms for *n*-hexane and its isomers on activated carbon, at 298 K, using the volumetric method.

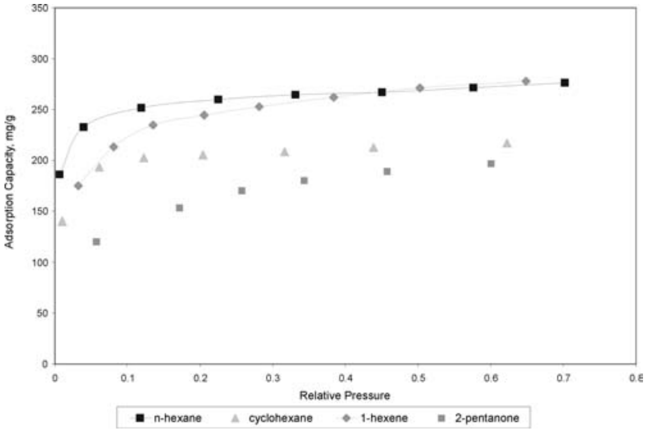

Figure 6. Equilibrium isotherms of *n*-hexane, cyclohexane, 1-hexene, and 2-pentanone on activated carbon, at 298 K, using the volumetric method.

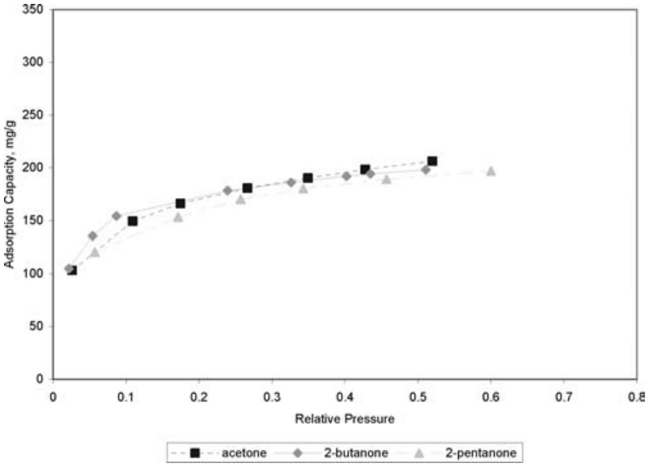

Figure 7. Equilibrium isotherms of acetone, 2-butanone, and 2-pentanone on activated carbon, at 298 K, using the volumetric method.

acetone > 2-pentanone in the low-pressure range. The order of the uptake switched to acetone > 2-butanone > 2-pentanone in the high-pressure range. It is noted that in the low-pressure range the order of the polarity of the three ketones is the same as the order of the uptakes.

A more detailed description of gas adsorption in activated carbon may soon become possible when the micropore and mesopore structures of the fine carbon particles are better known. Previous reports have used a slit model based on graphitizing carbon. More recent reports using high-resolution transmission electron microscopy describe activated carbon to have a fullerene-type structure composed of nongraphitizing sp^2 carbons.[21]

Temperature Effect on n-Hexane Isotherms. The equilibrium isotherms of *n*-hexane at different temperatures from (288 to 318) K are shown in Figure 8. The uptakes decrease as the temperature increases because VOC adsorption is an exothermic reaction. The isosteric heat of adsorption can be calculated from the Clausius−Clapeyron equation together with the isotherm model. This will be discussed in future work.

Conclusion

The adsorption isotherms of volatile C_6 alkanes in activated carbon were directly measured with a gravimetric apparatus at 298 K. Steric hindrance arising from molecular size and structure and the variation in boiling points are consistent with the observed sorption behavior. The Langmuir and Freundlich isotherm models provide good fits to the experimental data with acceptable mean deviations.

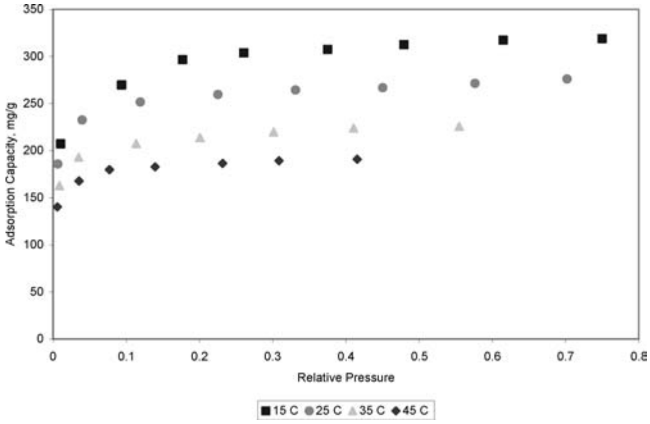

Figure 8. Equilibrium isotherms of *n*-hexane on activated carbon at different temperatures, using the volumetric method.

Using a volumetric apparatus, the uptake of *n*-hexane and its isomers was found to be in the order *n*-hexane > 3-methylpentane > 2,2-dimethylbutane. This is in agreement with results from data using the gravimetric apparatus. Steric hindrance was also observed in the higher adsorption of *n*-hexane compared to cyclohexane. Hexene adsorption was very similar to *n*-hexane. Acetone, 2-butanone, and 2-pentanone have adsorption uptakes that are well below *n*-hexane.

Nomenclature

D	mean deviation
q	adsorption capacity, mg of sorbate/g of sorbent
q_0	saturated adsorption capacity, mg of sorbate/g of sorbent
b	Langmuir adsorption equilibrium constant, 1/Pa
K	Freundlich constant
m_s	mass of adsorbent sample, g
n	exponent in Freudlich equation
n_{ads}	moles of adsorbed VOC
n_i	initial moles of VOC
n_f	final moles of VOC
N	number of data points at a given temperature
P	pressure, Pa
P^0	saturation vapor pressure, Pa
q^{exp}	experimental adsorption capacity, mg of sorbate/g of sorbent
q^{cal}	calculated adsorption capacity, mg of sorbate/g of sorbent
T	temperature, K
V	volume, cm^3
ν_a	molar volume, $cm^3 \cdot mol^{-1}$

Appendix

The error analysis provided in this Appendix gives the range of acceptable values of a measurement of adsorbate uptake which will include the “true value”. The error analysis takes into account the uncertainty of data measurement from each instrument (such as pressure gauge, temperature probe, and microbalance) used in the particular method.

I. Error Analysis for Volumetric Method

For a low-pressure system, the moles of VOC in volume V_1 (see Figure 1) is given by

$$n_i = \frac{V_1}{\nu_a(T, P_i)} \tag{A1}$$

where ν_a is the ideal gas molar volume of VOC at temperature T and pressure P_i. We get

$$\frac{dn_{\mathrm{i}}}{n_{\mathrm{i}}} = \frac{dV_1}{V_1} - \frac{d\nu_{\mathrm{a}}}{\nu_{\mathrm{a}}} \tag{A2}$$

The maximum error in n_i is

$$\left(\frac{\delta n_{\mathrm{i}}}{n_{\mathrm{i}}}\right)_{\max} = \pm\left(\frac{\delta V_1}{V_1} + \frac{\delta \nu_{\mathrm{a}}}{\nu_{\mathrm{a}}}\right) \tag{A3}$$

After uptake by the adsorbent, the final moles of VOC in ($V_1 + V_3$) is

$$n_{\mathrm{f}} = \frac{V_1 + V_3}{\nu_{\mathrm{a}}(T, P_{\mathrm{f}})} \tag{A4}$$

From eq A4, we get

$$\frac{dn_{\mathrm{f}}}{n_{\mathrm{f}}} = \frac{dV_1 + dV_3}{(V_1 + V_3)} - \frac{d\nu_{\mathrm{a}}}{\nu_{\mathrm{a}}} \tag{A5}$$

The maximum error in n_{f} is

$$\left(\frac{\delta n_{\mathrm{f}}}{n_{\mathrm{f}}}\right)_{\max} = \pm\left[\frac{\delta(V_1 + V_3)}{V_2 + V_3} + \frac{\delta \nu_{\mathrm{a}}}{\nu_{\mathrm{a}}}\right] \tag{A6}$$

The amount of adsorbed VOC is

$$n_{\mathrm{ads}} = \frac{n_{\mathrm{i}} - n_{\mathrm{f}}}{m_{\mathrm{s}}} \tag{A7}$$

where m_{s} is the mass of adsorbent sample. Using the same method as above, the expected error in n_{ads} is

$$\frac{\delta n_{\mathrm{ads}}}{n_{\mathrm{ads}}} = \pm\left[\left(\frac{\delta n_{\mathrm{i}}/n_{\mathrm{i}}}{(n_{\mathrm{i}} - n_{\mathrm{f}})/n_{\mathrm{i}}} \pm \frac{\delta n_{\mathrm{f}}/n_{\mathrm{f}}}{(n_{\mathrm{i}} - n_{\mathrm{f}})/n_{\mathrm{f}}}\right) + \frac{\delta m_{\mathrm{s}}}{m_{\mathrm{s}}}\right] \tag{A8}$$

In eq A8, we put a (±) between the first and second terms on the RHS to see the effect of these two terms.

It is shown in Part II of this Appendix that the gravimetric method can be significantly more accurate than the volumetric method. Therefore, for the error analysis given here in Part I, we will use the uptake for *n*-hexane in Table 3 as the "true" value.

Given the following values

$$m_{\mathrm{s}} = 50\ \mathrm{mg}$$

$$V_1 + V_3 = 68.24\ \mathrm{cm}^3$$

$$P_{\mathrm{f}} = 1.136 \cdot 10^5\ \mathrm{Pa}\ (\text{corresponding to } P/P^0 = 0.609)$$

$$T = 298\ \mathrm{K}$$

we obtain

$$n_{\mathrm{f}} = 3.1268 \cdot 10^{-3}\ \text{moles}$$

$$(n_{\mathrm{i}} - n_{\mathrm{f}}) = 1.4260 \cdot 10^{-4}\ \text{moles}$$

$$P_{\mathrm{i}} = 1.601 \cdot 10^5\ \mathrm{Pa}$$

The measurement errors for the volumetric apparatus are

$$\frac{\delta m_{\mathrm{s}}}{m_{\mathrm{s}}} = 0.002$$

$$\frac{\delta \nu_{\mathrm{a}}}{\nu_{\mathrm{a}}} = \frac{\delta T}{T} + \frac{\delta P}{P} = \frac{0.05}{298} + \frac{0.133}{11360} = 1.8 \cdot 10^{-4}$$

$$\frac{\delta V_1}{V_1} = 1.5 \cdot 10^{-4}$$

(using a mercury filling and weighing method)

(using a mercury filling and weighing method)

$$\frac{\delta(V_1 + V_3)}{V_1 + V_3} = 1.1 \cdot 10^{-4}$$

(using the same filling method as for V_1)

Therefore the expected error in n_{ads} is

$$\frac{\delta n_{\mathrm{ads}}}{n_{\mathrm{ads}}} = \pm\,(1.58 \cdot 10^{-2} \text{ or } 3.11 \cdot 10^{-3})$$

The error may become larger than 1.6 % if the uncertainties for T and P are found to be more than the manufacturers' specifications for the instruments. Another possible source of error is the error inherent in the manual filling method for determining V_1 and ($V_1 + V_3$). Obviously, a leak test is important for the system shown in Figure 1.

II. Error Analysis for the Gravimetric Method

In this method, the amount of adsorbed VOC is

$$n'_{\mathrm{ads}} = \frac{m_{\mathrm{f}} - m_{\mathrm{i}}}{M_{\mathrm{ads}} m_{\mathrm{s}}} \tag{A9}$$

where m_{i} is the initial mass (equal to the mass of adsorbent sample m_{s}); m_{f} is the final mass; and M_{ads} is the molecular weight of the VOC.

We get an error expression similar to eq A8. For this system, the measurement errors are

$$\frac{\delta m_{\mathrm{i}}}{m_{\mathrm{i}}} = 2 \cdot 10^{-6}$$

$$\frac{\delta m_{\mathrm{f}}}{m_{\mathrm{f}}} = 1.6 \cdot 10^{-6}$$

The expected error in n'_{ads} is

$$\frac{\delta n'_{\mathrm{ads}}}{n'_{\mathrm{ads}}} = \pm\,(1.82 \cdot 10^{-5} \text{ or } 2.03 \cdot 10^{-6})$$

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