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A Model for the Formation of Airborne Particulate Matter Based on the Gas-Phase Adsorption on Amorphous Carbon Blacks

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This paper reports the physicochemical properties that describe the adsorption of a series of solutes onto the surfaces of amorphous carbon blacks. Adsorption was studied at concentrations that correspond to low surface coverages and in the presence of volatile solvent diluents. The adsorbates and adsorbents were selected for their relevance as models for environmental agent-particle complexes originating from incomplete combustion. The data clearly show that the major factors that determine the strength of adsorption are the surface properties of the adsorbent and the intermolecular forces between the surface and the adsorbing molecule. The heat of adsorption data have been used to predict the lifetime of the absorbate-adsorbent complexes.

Introduction

The combustion of organic materials can produce a variety of compounds that are dependent upon the stoichiometry of the flame reactions, the chemical composition of the fuel, and the fuel-to-oxidizer ratio. Fuel-rich combustion produces carbon-rich species, whereas fuel-lean combustion produces oxygen-rich species. Additionally, if the combustion charge is heterogeneous, i.e., the fuel is a liquid or solid, then the fuel-to-oxidizer ratio can change as combustion progresses, and products will be produced that have a variety of oxidation states. Such compounds as particulate carbon, heterocyclics, aliphatic, aromatic, and polycyclic aromatic hydrocarbons can be produced by substoichiometric and pyrolytic reactions. Additionally, nitro and oxygenated derivatives of these compounds are formed during combustion or by subsequent gas-phase collisions.

During and after combustion, gas phase or volatile species will collide with the carbon particles and may remain adsorbed on the particle surface. The resulting adsorbate-adsorbent complex, if of respirable size, has been implicated as a potential health hazard. Many studies have characterized the adsorbed species in the particulate complexes from a variety of combustion sources, e.g., cigarette smoke, diesel emissions, etc., (*1–4*). Other studies have determined the chemical compositions of particulate complexes and related the concentrations of specific adsorbed compounds to the resulting biological effects (*5–8*). Although these studies have reported important results, they have failed to develop a clear comprehension of the nature and involvement of the particle surface in the resulting health effects studies.

Static and dynamic experimental approaches are the classical means to study the interactions of adsorbate molecules with the surface of adsorbents (*9–11*). Although both methods should provide similar results, the selection of the method is dependent upon the physical state of the adsorbate molecule. The static method (*9,10*), based upon gravimetric or volumetric measurements, is ideally suited for gaseous or volatile adsorbates, whereas the dynamic method (*11*), based on gas solid chromatography, can be used for any adsorbate that interacts reversibly with the adsorbent and elutes in a reasonable time. The implicit assumption of both methods is that equilibrium is reached before the measurement is made, and therefore the interactions can be characterized thermodynamically.

Previous gas-solid chromatographic studies have suggested that interactions between gas-phase molecules and the surfaces of graphitized carbon blacks are nonspecific, and the magnitudes of the adsorption energies could be predicted on the basis of the total polarizability of the adsorbing molecule (*11*). This statement is only true if the surfaces are nonpolar and contain very low concentrations of active sites.

Prior studies (*12,13*) from this laboratory have used both static and dynamic methods to characterize the adsorption of various adsorbates onto the surfaces of Spheron 6 (a graphitized carbon black) and particles collected from diesel engines operated on different fuels. The results of these studies show that all the particles

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were similar, although the surface properties of diesel particles were moderated by adsorbed lubricant-derived molecules, which were not easily removed. This inability to remove involatile substances from the surface of diesel particles has prompted the use of carbon blacks as models for environmentally significant particles.

This paper describes the adsorption of various adsorbate molecules on a series of carbon blacks. The formation processes are relatively similar for all carbonaceous particles, whether they are produced in flames, diesel engines, or by the commercial processes utilized to form carbon blacks. In each case the intrinsic particle is an agglomerate of aciniform carbon. The carbon blacks used in this study are furnace carbon blacks which are produced from the thermal decomposition of oil feed stocks. They have imperfect graphitic structure, are devoid of long-range order, and are considered amorphous (*14*). The advantage of using these types of particles as opposed to environmental particles is that the carbon blacks are manufactured under well-defined conditions and are, therefore, more reproducible from particle to particle. Therefore, by changing the carbon black, the parameters contributing to the surface properties may be studied independently. The blacks selected have different surface areas and degrees of surface oxidation, which are important properties for defining the surface activities of airborne particles. Oxidized carbon blacks are produced by oxidization with ozone, nitric acid, or the oxides of nitrogen.

The adsorbates used in this study fall into two groups: those that contain many of the functional groups common to the adsorbed molecules found on particles emitted during the combustion of organic materials (e.g., polycyclic aromatic hydrocarbons and their nitro or oxygenated derivatives). Selection of simpler molecules has two distinct advantages. Simple molecules can be expected to elute reversibly under typical gas-solid chromatographic conditions using these active solid supports. It was hoped that these simple molecules could be used as probes for specific functional groups to generate predictive data for the more complex environmentally relevant compounds based on the concept of linear free energy additivity. The second group of adsorbates was selected because they were to be used as mobile phases for a simultaneous HPLC study.

Theory

The physical adsorption of a gas-phase molecule onto an adsorbent is governed by the intermolecular forces between the molecule and the surface. If adsorption reaches equilibrium, then the concomitant change in free energy quantifies the interactions between adsorbate molecules and the adsorbent surface. Generally, it is reasonable to ignore the change in entropy that accompanies physical adsorption, as it is small (approaches unity) and is not expected to differ significantly as a function of the identity of the adsorbate. Therefore, the energy change that accompanies adsorption can be quantified by the change in enthalpy of the system. The intermolecular forces that contribute to the heat of adsorption in order of magnitude are: dipole-dipole (hydrogen bonding), dipole-induced dipole, and London or dispersion interactions.

The classical description of the adsorption process is that adsorbate molecules adsorb onto the adsorbent surface at the most active sites, and subsequent molecules continue to adsorb at less active sites or pool at the active sites until a monolayer of adsorbent molecules is produced. An adsorption isotherm is a graphical representation of the distribution of the adsorbate between the gas phase and the adsorbent surface for a given quantity of adsorbent and a given temperature. Adsorption isotherms can be linearized in the region of the monolayer (θ = 0.5 to 1.5 of a monolayer) by the Brunauer, Emmett, Teller (BET) equation. This is the region where adsorption occurs at the less active sites of the surface. If adsorption isotherms are obtained at different temperatures, then points from these isotherms can be inserted into the Clausius Clapeyron equation to generate the relationship between the heat of adsorption and surface coverage. If this plot shows a significant variation in the values of the heat at low coverages, then the surface contains adsorption sites of different energies.

Surfaces have been classified as type I, II, or III (*9*). A type I surface interacts nonspecifically with adsorbates via London or dispersion forces. A type II surface has specific active sites with localized positive charges that will interact most strongly with adsorbates containing localized areas of electron density via dipole-dipole interactions. A type III surface has specific active sites with localized areas of electron density that will interact most strongly with adsorbates containing localized positive charges via dipole-dipole interactions. type II and III surfaces will also interact nonspecifically with adsorbates via London or dispersion forces. Graphitized carbon is an example of a type I surface, silica an example of a type II surface, and alumina is an example of a type III surface. A type III surface can be obtained by depositing a dense layer of molecules that have the desired polarity and structure onto a type I surface. Similarly, type II or type III surfaces can be converted to a type I surface by the removal of specific active sites. For example, silica can be converted to a type I surface by dehydroxylation with various silane derivatives, which is the procedure used for the deactivation of diatomaceous earths for use as solid supports for packed column gas chromatography or the production of C18 column packing materials for reverse-phase HPLC. An example of the conversion of a type II to a type III surface is the use of a suitable reagent to convert the hydroxyl groups on silica to nitrile groups for reverse phase column packing materials.

Classical gas-phase adsorption can be used to describe the sorption of pollutants onto the surfaces of airborne particles. If the airborne particle is a type I surface, then as a result of collisions with gas-phase molecules, its surface will become covered with molecules on the

basis of their total polarizabilities (nonselective adsorption). The total polarizability of a molecule can be calculated using the Lorenz-Lorentz equation. Similarly, if the surface of the airborne particle is type II or III, it may retain selectively polar molecules as compared to nonpolar molecules; however, it is reasonable to propose that airborne particles will have heterogeneous surface properties because their production is uncontrolled. Heterogeneous surfaces will become covered with molecules with varying polarities. The adsorption energies of molecules sorbed onto nonpolar, polar, and heterogeneous surfaces will be dependent upon the energies of the active sites and the chemical properties of the adsorbing molecules. However, the importance of the energies of these active sites to adsorb polar molecules selectively decreases as coverages approach the monolayer. After monolayer coverage is achieved, the adsorption energy decreases as the square of the distance between adsorbing molecule and the adsorption site (*10*). The energy of multilayer adsorption approaches the energy of vaporization (i.e., the interactions between sorbed molecules). Therefore, if molecules are bound to the surface by physical adsorption, then the surface defines selective adsorption until the coverage approaches a monolayer or until all the active sites are covered by sorbed molecules. Coverage is defined by the surface area of the particle and the adsorption cross-section of the adsorbing molecule. Therefore, determination of dose on the basis of the quantity of molecules adsorbed onto respirable particles that can be extracted by an organic solvent does not include the contributions of the surface areas or the surface properties of the particles, which are major factors in defining the dose of the adsorbed agent that is bioavailable to lung tissue and physiological fluids.

A perhaps more meaningful way of expressing the adsorption of molecules on the surface of airborne particles is in terms of the time the molecule remains adsorbed (*15*). If a molecule collides with a surface it can rebound immediately, or it can remain associated with the surface for varying periods of time. If the surface has an affinity for the striking molecule, the time the molecule remains associated with the surface will be dependent upon strength of this affinity. Therefore, the time of adsorption (τ) can be calculated from the enthalpy of adsorption using the equation proposed by Frenkel (*16*), which assumes that the entropy contributions of adsorbed molecules are not significantly different:

$$\tau = \tau_o \exp \Delta H_a/RT \qquad [1]$$

where τ_o is the time of oscillation(s) of the atoms in the adsorbent with particular reference to vibrations perpendicular to the surface, ΔH_a is the heat associated with adsorption (kJ), T is the temperature (K), and R is the molar gas constant (kJ deg^{-1} mole^{-1}). Values of τ_o can be obtained using the relationship proposed by Lindemann (*17*):

$$\tau_o = 4.75 \times 10^{-13} \{[M(V)^{0.667}]/T_s\}^{0.5} \qquad [2]$$

where 4.75×10^{-13} is a constant [S (K mole/g)$^{0.5}$ (mole/cm^3)$^{0.667}$], M is the molecular weight (g/mole), V is the molar volume (cm^3/mole) and T_s is the melting point temperature (K) of the adsorbate molecule. Although there may be uncertainty attached to the use of these two equations, they can be used to compare the relative adsorption times for molecules on the surface of adsorbents. Also, these equations can be used to compare adsorption times as a function of coverage, since as the coverage exceeds the monolayer, the heat of adsorption approaches the heat of vaporization.

Experimental

Materials

The following adsorbates (99+% purity, Aldrich or Burdick and Jackson) were used as received: 1-hexane, cyclohexane, toluene, aniline, dichloromethane, tetrahydrofuran, ethyl acetate, methanol, water, pyridine, benzaldehyde, acetophenone, nitrobenzene, benzofuran, thiophene, quinoline, benzene, phenol, naphthelene, *p*-benzoquinone, and hydroquinone.

The adsorbents studied are oil furnace carbon blacks, and their ASTM classifications are as follows: N765, N339, N110, N339 oxidized (N339OX), Black Pearls 2000 (BP 2000) (Cabot Corporation).

Procedure

A gas chromatograph with a flame ionization detector (Varian 3700 series) was used to investigate the adsorption phenomena of all adsorbates except water, which was monitored using a thermal conductivity detector (Varian 920). The lengths (5 cm–2 m) and internal diameters (1.0–2.1 mm) of the chromatographic columns (6 mm OD), were varied to suit the chromatographic elution properties of the solute under investigation. Helium, which had been passed through molecular sieves, was used as the carrier gas and a constant flow rate was maintained at approximately 0.5 mL/s. The samples of carbon were sieved to obtain various sized fractions with minimum size distributions before being packed in the columns. The gas chromatographic columns containing known amounts of the pelletized carbon blacks were packed using vibration with vacuum assistance.

Known aliquots of adsorbates were introduced directly onto the columns, (containing the carbon blacks), either as pure liquids, solutions in various solvents, or as gas samples. An alternative method of sample introduction was developed in which the adsorbate was injected as a pure liquid onto a precolumn of (6 feet long, 3 mm OD) 10% SP2100 on 80–100 mesh Supelcoport. This column was connected to a second flame ionization detector via a pneumatically actuated high temperature gas sampling valve with a 1.0-μL loop (C14W-T1 Valco Instruments). When this valve was actuated, a portion of the eluting solute peak of interest was injected onto the column containing the carbon black. The quantities of adsorbates injected via this sampling

loop were determined from calibration curves. After a measurement of the retention datum for an adsorbate had been made isothermally, the oven was temperature programmed to cycle from the column operating temperature to 320°C with a 30 min hold between each run. This heating protocol ensured that the surface of the carbon was cleaned from the previous analysis. Retention volumes were measured isothermally at three different column temperatures. The dead volume of the system in all chromatographic configurations was determined by injection of methane without a column, followed by injection with the column empty. This retention volume minus the volume occupied by the known weight of carbon contained in the column, (based on the helium density), was used to calculate the dead volume of the column. The dead volume was found to be negligible in comparison with retention volumes for columns up to and including 20 cm in length.

Gas chromatographic retention data were recorded on a computing integrator (Spectraphysics SP4270) used in the usual mode to collect retention data as a function of time. It has been well-established that the isosteric heat of adsorption can be obtained from the slope of a plot of the logarithm of the specific retention volume versus the absolute column temperature for any adsorbate-adsorbent system, providing that the adsorbate elutes in a reasonable period of time (*11*). This relationship is only valid when the concentration of the solute approaches infinite dilution and therefore falls within the Henry's Law region of the adsorption isotherm. The limiting concentration of this region is generally considered to be 1% of a monolayer coverage ($\theta = 0.01$), since below this coverage solute molecules are thought to interact with the adsorbent surface independently of other adsorbed molecules. Additionally, the integrator was programmed to transmit area slices as a function of time to a microcomputer (Apple IIe). Software was developed which converted the area slice data to adsorption isotherms using the method proposed by Saint-Yrieix (*18*).

Physical Characterization of Carbon Blacks

The apparent densities of the sized carbons were determined by weighing the quantity of particles occupying a known volume. True (or helium) densities were determined by expanding known volumes of helium into a sample cell with and without known masses of particles. The nitrogen surface areas (*19,20*) of the carbon blacks were determined using a Monosorb Surface Area Analyzer (Quantachrome Corp.) or an Omnisorb 360 Surface Area Analyzer (Omnichron Corp.). The latter instrumentation was used for Black Pearls 2000. The carbon blacks were submitted for elemental analyses for carbon, hydrogen, and oxygen (Galbraith Laboratories).

The particle sizes of the sieved, pelletized blacks were determined by optical photomicroscopy at 50×. Scanning electron microscopy at 250× and 1000× was used to examine the particle agglomerates after the pellets had been ultrasonically disrupted.

Results and Discussion

Physical Properties of Carbon Blacks

The carbon blacks used in this study are pelletized agglomerates of aciniform particles whose fundamental aggregate size is 2 to 20 nm (J. W. Riehl, personal communication). This spherical aggregate is an inherent, stable, invariant characteristic of oil furnace carbon black, and the pelletization process does not alter the intrinsic surface properties of the carbon black.

The physical properties of the carbon blacks are listed in Table 1. Comparisons of the apparent and helium densities suggest that these pelletized carbon blacks may have extensive pore structures and that the carbons do not contain extensive long-range graphitic structure (pure graphite has a density in the range 2.09–2.23 g/cm^3). The only differences in particle shape and size between these particles that could be discerned from photomicroscopy were that the Black Pearls 2000 particles were spherical whereas the other particles had irregular shapes. The results obtained with scanning electron microscopy after the pellets had been disrupted provided no additional information apart from determining the spherical shape and size of the carbon black aggregates. The physical properties of these carbon blacks confirm that the particles (N765, N339, N339 oxidized, and N110) are similar in structure but different from the particles of Black Pearls 2000, which are more porous. Also, Black Pearls 2000 had an apparent density significantly less than that of the other carbon blacks. This difference is due to the spherical shape of this pelletized carbon black, which limits its packing density. The surface areas varied from 45m^2/g (N765) to 1538 m^2/g (Black Pearls 2000).

Carbon, hydrogen, and oxygen analyses show (Table 2) that all the particles are mainly composed of carbon with quantifiable levels of hydrogen and oxygen. These carbon blacks also contain significant amounts of other, not quantified, elements (*21*), [(probably metal carbonates) (J. W. Riehl, personal communication)]. The only carbon black that is significantly different in terms of the elements quantified is N339 oxidized, for which the increased percentage of oxygen is balanced by a reduction in the percentage of carbon. Black Pearls 2000 has more inorganic residue than the other blacks. Other features that may be significant are the increased car-

Table 1. Physical properties of carbon blacks.

Carbon black	Bulk density, g/cm^3	Helium density, g/cm^3	Average particle size, mm	Surface area, M^2/g
N765	0.381	1.92	0.21	45
N339	0.385	1.95	0.24	109
N339 ox	0.376	1.70	0.21	112
N110	0.362	2.00	0.20	159
BP 2000	0.141	2.11	0.20	1538

Table 2. Elemental analysis of carbon blacks.

Carbon black	Carbon, %	Hydrogen, %	Oxygen, %	Residue, %	Empirical formulae
N765	96.35	0.50	1.96	1.19	$C_{669}H_{42}O_{10}$
N339	95.36	0.49	3.61	0.54	$C_{346}H_{21}O_{10}$
N339 oxidized	92.33	0.57	5.39	1.71	$C_{208}H_{13}O_{10}$
N110	96.01	0.26	2.13	1.6	$C_{602}H_{20}O_{10}$
BP 2000	95.47	0.30	1.76	2.47	$C_{724}H_{27}O_{10}$
Diesel (model fuel) (*13*)	95.35	0.65	3.97	0.03	$C_{274}H_{26}O_{10}$
Diesel (regular fuel) (*13*)	89.85	2.66	6.98	0.71	$C_{170}H_{60}O_{10}$

bon/hydrogen ratios for N110 and Black Pearls 2000, perhaps signifying that the surfaces of these particles are composed of less energetic sites than the other blacks. However, this reduced surface activity may be counteracted by the increased surface area of N110 and Black Pearls 2000. The chemical composition of the carbonaceous residue of two samples of diesel particulate matter after Soxhlett extraction with dichloromethane are included to show their similarities (*13*).

Isosteric Heat of Adsorption

Small beds of adsorbents had to be used to determine the retention volumes for the adsorbates studied, since the carbon blacks used in this study were expected to interact strongly with all the solutes. This requirement placed severe limitations on the injection volume because it was essential that the amount injected approach infinite dilution. Initially, adsorbates were injected in minimal volumes as solutions in volatile solvents, but it was found that the retention volume varied extensively with slight changes in amount injected. The heat of adsorption varied by as much as 20 kJ (Fig. 1). Since the surface coverage did not change significantly ($\theta = 2 \times 10^{-3}$ to 9×10^{-3}) and the coverage was in Henry's Law region ($< \theta = 0.01$), these data suggest that the adsorbate was interacting with adsorbed solvent rather than with the adsorbent surface. This conclusion

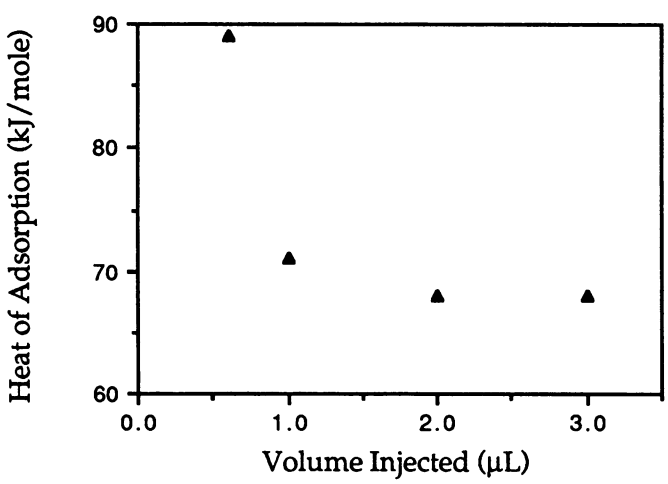

FIGURE 1. Heat of adsorption from retention data for 0.1% (v/v) benzaldehyde in dichloromethane on N765 as a function of injection volume at surface coverages ranging from 2×10^{-3} to 9×10^{-3} θ.

was confirmed by using different volatile solvents as diluents, and the resulting isosteric heat was found to vary with the diluent (Table 3). The variation is not as large as was expected, which suggests that these carbon blacks do not contain large numbers of active sites. The next approach was to use gas samples in helium and to spike each sample with a low concentration of methane. This study also demonstrated that the volume injected and the methane concentration affected peak retention time for the adsorbates that exhibit reasonable vapor pressures (Table 4). There was an 18 kJ difference in the heat of adsorption for benzene as gas or liquid samples.

All these results suggested that there may be distributions of energy levels of the adsorption sites on the surfaces of these carbon blacks, and, therefore, great care was used to ensure that adsorption was studied with clean adsorbent surfaces. The isosteric heats of adsorption were obtained for very low quantities of pure adsorbates (1×10^{-8} to 1×10^{-10} M) using the precolumn and pneumatic injector (Table 5). Also included in this table are the heats of vaporization for the adsorbates (*22*) and the heats of adsorption obtained on graphitized carbon blacks (*11*). These data indicate that surface area is not a significant parameter for defining adsorption at these low coverages, although it will define the concentration required to produce a monolayer. Of the carbons investigated, N765 had the lowest surface activity, demonstrated by lower enthalpies of adsorption and by the elution of a larger number of adsorbates. Adsorbates with low volatilities could not be studied because they were not eluted from these carbons at temperatures up to 330°C. The number of adsorbates that could be eluted at low concentrations was considerably smaller than when the surface had been partially

Table 3. Variation of the heat of adsorption from retention data for solutions of benzaldehyde in various solvents on N765.[a]

Solvent	Heat of adsorption, kJ/mole
1-Hexane	81
Cyclohexane	80
Toluene	91
Dichloromethane	89
Tetrahydrofuran	78
Ethyl acetate	79
Methanol	83
Water	87

[a]Coverage $\theta = 2 \times 10^{-3}$. Solutions of benzaldehyde 0.1% (v:v) in various solvents. Solvents, 0.6 μL injected.

Table 4. Heats of adsorption from retention data for solutions of adsorbates in methanol, dichoromethane, or gas samples with 1 Torr methane for N765.[a]

Adsorbate	Heat of adsorption, kJ/mole
Gases	
1-Hexane	57
Cyclohexane	52
Benzene	68
Toluene	71
Dichloromethane	58
Tetrahydrofuran	—
Ethyl acetate	86
Methanol	71
Pyridine	76
Thiophene	66
Solutions	
Benzene	50
Quinoline	83
Benzaldehyde	89
Acetophenone	80
Nitrobenzene	82
Benzofuran	72
Phenol	92
p-Benzoquinone	72
Hydroquinone	91
Naphthalene	74
Water	87

[a]Solutions of adsorbates 0.1% (v:v) in various solvents. Solvents 0.6 μL injected, coverage $\theta = 2 \times 10^{-3}$. Gas samples, 10–20 Torr, 10 μL, coverage $\theta = 3 \times 10^{-4}$.

Table 5. Dipole moments (μ) and total molar polarizabilities (P) of adsorbate molecules.

Adsorbate	μ, Debye	$P \times 10^{24}$, cm^3
1-Hexane	0	11.8
Cyclohexane	0	11.0
Toluene	0.36	12.3
Dichloromethane	1.60	6.5
Tetrahydrofuran	1.63	7.9
Ethyl acetate	1.78	8.8
Methanol	1.67	3.2
Water	1.85	1.5
Pyridine	2.2	9.6
Benzaldehyde	2.77	12.8
Acetophenone	3.01	14.4
Nitrobenzene	4.21	12.9
Benzofuran	0.79	14.1
Thiophene	0.63	9.6
Quinoline	2.29	16.6
Benzene	0	10.3
Phenol	1.45	11.0
Naphthalene	0	16.5
p-Benzoquinone	0	NA[a]
Hydroquinone	2.47	NA

[a]NA = refractive index not available.

deactivated by the addition of diluent solvent (compare Tables 4 and 6). These data confirm that the use of solvents for sample introduction modified the energies of interaction between the adsorbates and adsorbents. There were only minor differences in enthalpies for the other carbon blacks (N339, N110, N339 oxidized and Black Pearls 2000), which suggests that there are not significant differences in their surface properties. These enthalpies of adsorption, which correspond to surface coverages in the range of 1×10^{-5} to 1×10^{-6} of a monolayer, are significantly larger than the heat of vaporization. Also, these heats of adsorption are larger than those obtained for graphitized carbon blacks by other workers (*11*). The more homogeneous surfaces present in graphitized carbon blacks are expected to be less polar and contain fewer numbers of active sites due to their ordered graphitic structure than the surfaces present in the amorphous carbon blacks used in this study. The less ordered structures of the amorphous carbon blacks have more surface defects and short-range graphitic structures, which may result in a greater number of active sites. Additionally, the heats of adsorption for the graphitized carbon blacks were obtained by injection of the solutes in volatile solvents, which may have further reduced the residual active sites on the graphitized carbon blacks.

When these data were compared with the dipole moments and total molar polarizabilities calculated from their refractive indices (*22*) using the Lorenz-Lorentz equation (Table 5), it was apparent that the surfaces of amorphous carbon blacks contained low concentrations of surface groups that were active, as the data could not be correlated to total molar polarizabilities for solutes that do not contain dipole moments. These results suggest that the active sites on the carbon blacks are inducing dipoles into the adsorbate molecules, and these types of interactions are not directly additive to London or dispersion forces. Since amorphous carbon blacks used in this study are more representative of the airborne particles derived from the combustion of organic materials than graphitized carbon blacks, it is impossible to generate the expected model based on the additivity of free energy to predict the heat of adsorption of environmental pollutants at submonolayer coverages. However, since most environmental particles have supramonolayer coverages, it is possible to develop a predictive model of adsorption for those molecules contained at monolayer coverages based on the heat of vaporization. The selectivities of active sites are significantly reduced by adsorbed molecules and therefore, once the surface is partially covered, it becomes less selective for adsorbates.

The elution characteristics of all the adsorbates studied show that the particles generated during the combustion of organic matter will become rapidly coated with gas-phase adsorbates which will be retained strongly by the surface. Also, molecules will be retained on the basis of their volatilities and by any selective interactions with surface active groups. Therefore, since most particles of environmental origins have supra-monolayer coverage of adsorbed molecules, any molecule that is contained at submonolayer coverage will not be easily removed from the surface by physical processes unless the energy available for release is greater than the energy of adsorption.

Adsorption Isotherms from Gas Chromatographic Data

The adsorbate cross-sectional adsorption surface areas were calculated from density or by computer pro-

Table 6. Heat of adsorption calculated from retention data for pure gaseous adsorbates on five carbon black adsorbates and heat of vaporization.

Adsorbate	Heat of adsorption, kJ/mole					ΔH_v	ΔH_a[a]
	N765	N339	N110	N339 ox	BP 2000		
1-Hexane	53.0	81.0	86.5	83.3	80.1	31.9	43.5
Cyclohexane	47.3	68.3	78.8	76.2	74.1	32.8	36.4
Toluene	54.7	79.9	85.2	92.9	90.1	35.9	48.5
Dichloromethane	45.7	54.0	58.6	57.9	56.9	31.7	
Tetrahydrofuran	75.1	52.3	61.7	63.7	61.9	34.2	
Ethyl acetate	79.3	82.2	86.4	88.7	55.2	34.7	
Methanol	71.4	66.8	65.9	78.4	56.8	37.6	22.2
Water	39.7	29.1	36.4	34.4	45.3	47.3	
Pyridene	68.0	—[b]	—	—	—	40.4	42.3
Benzaldehyde	85.7	103	90.1	93.0	97.3	48.8	
Acetophenone	101	—	—	—	—	49.1	54.4
Nitrobenzene	87.8	98.1	109	132	105	50.9	59.4
Benzofuran	106	101	104	108	104	43.6[c]	
Thiophene	59.7	70.6	64.3	71.0	65.2	36.6	37.7
Quinoline	128	—	—	—	—	52.6	
Benzene	53.5	60.6	62.9	80.2	72.3	34.1	41.0
Phenol	—	—	—	—	—	49.8	54
Naphthalene	—	—	—	—	—	51.5	72.4
p-Benzoquinone	—	—	—	—	—	—	
Hydroquinone	—	—	—	—	—	78.4	52.7
Aniline	—	—	—	—	—	47.3	54

[a] Heat of adsorption for graphitized carbon black (*11*).
[b] —, not eluted.
[c] Calculated from boiling point using Trouton's rule.

Table 7. Adsorbate cross-sectional adsorption surface areas.[a]

Adsorbate	Calculated from density[b]	Calculated from atomic radii	Literature
1-Hexane	38	59	51.5
Benzene	28	60	40
Pyridene	28	55	
Tetrahydrofuran	29	—	
Phenol	30	66	
Naphthalene	35	94	
Benzaldehyde	33	71	
Acetophenone	36	81	
Nitrobenzene	33	74	
p-Benzoquinone	28	66	
Hydroquinone	29	68	
Thiophene	28	51	
Quinoline	36	92	
Toluene	34	69	
Methanol	18	21	10
Dichloromethane	25	27	
Ethyl acetate	32	61	
Benzofuran	35	77	
Cyclohexane	34	60	39
Water	10	—	10.6

[a] Surface area, Å^2.
[b] Calculation assumes 12 neighbors in bulk phase and 6 neighbors absorbed.

gram from atomic radii (Table 7). Although these values were different from the available literature values (*11*) (only 5 out of 20 were available), the calculated values based on density (*23*) were used in all subsequent studies, since it was assumed that the error would be consistent. Enthalpies of adsorption as a function of coverage for all adsorbates were obtained from the shapes of the chromatographic peak. These data and the cross-sectional areas of the adsorbates and the surface areas of the adsorbents were used to calculate the heat of adsorption versus coverage (Table 8). For certain adsorbates, these enthalpies were found to vary significantly, which confirms that the carbon blacks contained small numbers of active sites and suggest that these are type II surfaces. Also, these data demonstrated that the surface of Black Pearls 2000 was more homogeneous and approached a type I surface more closely than the other carbons (Figs. 2 and 3). These observations are consistent with the fact that the gas chromatographic peaks of all adsorbates on Black Pearls 2000 approached Gaussian, whereas the other carbons exhibited tailing. There was acceptable agreement between the two methods used to calculate the enthalpies of adsorption only when the chromatographic peaks were Gaussian.

Relative Adsorption Times

The preceding discussion is the classical description of the adsorption interactions as a function of the adsorbate, adsorbent, and the surface coverage of the adsorbent. However, it is difficult to relate these data to the capture of gas-phase pollutants by airborne particles. Therefore, the data listed in Table 6 have been expressed in terms of adsorption times using Equations 1 and 2 (Table 9). Also listed in Table 9 are the oscillation times for molecules when not adsorbed on surfaces (τ_o) and the adsorption times for the same molecules at a coverage that corresponds to greater than a monolayer (τ_v) calculated using the heat of vaporization. The former are the oscillations of the atoms in the adsorbate with particular reference to the adsorbent surface, whereas the latter are the minimum times that these

Table 8. Heat of adsorption for pure gaseous adsorbate on five carbon blacks from isotherm data.

Adsorbate	Heat of adsorption, kJ/mole				
	N765	N339	N110	N339 ox	BP 2000
1-Hexane	60.1–66.8	60.6–78.1	70.3–82.1	80.8–83.0	81.6–82.7
Cyclohexane	47.1–47.8	35.4–61.8	68.9–73.7	51.9–66.3	69.2–78.1
Toluene	55.4–63.1	55.7–69.6	75.3–87.9	64.5–73.3	65.5–90.6
Dichloromethane	29.9–53.9	55.9–56.3	48.2–55.1	64.4–66.1	55.2–57.8
Tetrahydrofuran	47.6–64.6	54.7–65.0	56.2–65.5	73.2–87.5	53.2–61.1
Ethyl acetate	70.0–73.9	54.5–71.2	63.0–73.2	81.6–83.0	36.7–59.5
Methanol	55.8–69.9	33.7–51.6	46.1–55.3	22.7–36.7	39.0–51.6
Water	32.8–49.9	9.1–31.7	18.3–36.0	20.5–38.1	23.3–37.8
Pyridene	38.0–72.5	—[a]	—	—	—
Benzaldehyde	22.6–58.4	104.0–122.0	85.7–94.4	101.0–177.0	94.4–102.0
Acetophenone	84.7–85.4	—	—	—	—
Nitrobenzene	85.9–99.7	55.1–80.9	40.8–80.1	72.8–76.5	113.0–119.0
Benzofuran	40.1–49.3	71.3–106.0	98.0–110.0	65.1–69.10	73.5–101.0
Thiophene	55.6–60.6	64.8–69.5	62.8–64.0	59.1–72.4	60.7–68.4
Quinoline	69.7–93.1	—	—	—	—
Benzene	49.1–63.1	47.2–50.2	41.6–59.9	61.7–72.2	77.0–77.6

[a]—Not eluted.

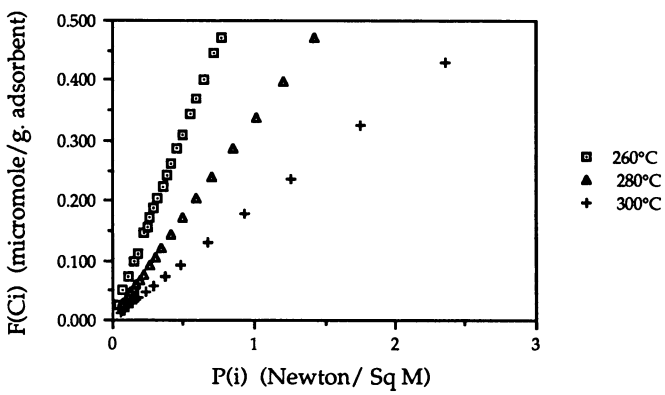

FIGURE 2. Adsorption isotherms of benzene on Black Pearls 2000.

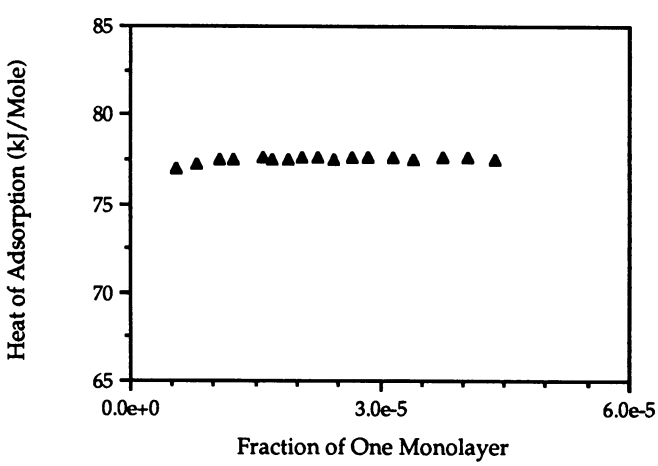

FIGURE 3. Heat of adsorption versus surface coverage for benzene on Black Pearls 2000.

molecules will remain sorbed on any surface, as it is reasonable to expect that the heat of vaporization will be less than the heat of adsorption. These data should be compared to the data that correspond to the adsorption times for these same molecules based on the enthalpies of adsorption at low coverages (Table 6). The data contained in Table 9 show the selectivities of the carbon black surfaces in terms of relative adsorption times as a function of coverage (low versus greater than monolayer coverage). Clearly, these values show that the carbon blacks are interacting strongly with certain molecules. For example, 1-hexane interacts with the surface very strongly and is retained relatively longer than would be immediately obvious from examining the enthalpy data contained in Table 6. These results show dramatically how the use of solvents to dilute solutes can result in the measurement of the interactions between solute molecules and adsorbed solvent molecules as opposed to the interactions between the solute and the adsorbent surface, as even volatile solvents will have significant adsorption times. Depending upon the extent of the interactions between the solvent and the adsorbent, the relative magnitudes of the enthalpies can be markedly different.

Water is sorbed for the minimum time on all the carbon blacks. The dominant intermolecular force exhibited by water is hydrogen bonding, and clearly this force is not a major contributor to the adsorption on carbon blacks. However, the relative adsorption times for pyridine and quinoline (and aniline by default) suggest that the carbons contain residual quantities of acidic groups (type II), because these solutes are not eluted from most of the carbon surfaces. It is reasonable to propose, based on the presence of quantifiable amounts of oxygen, that these acidic sites could be quinones (π acids), carboxylic acids, or phenols. However, since there is no evidence of hydrogen bonding, the active sites on the carbons must be quinones. Additionally, it is proposed that the carbon black N765 contains the smallest number of qui-

Table 9. Oscillation times (τ_o) and adsorption times at low coverages (τ_a) as function of carbon black and adsorption times at coverages greater than a monolayer (τ_v).

Adsorbate	$\tau_0(S)$	$\tau_a(S)$, 25°C					$\tau_v(S)$
		N765	N399	N110	N399 ox	BP 2000	
1-Hexane	1.7×10^{-12}	3.3×10^{-3}	2.7×10^{2}	2.5×10^{3}	6.8×10^{2}	1.9×10^{1}	6.6×10^{-7}
Cyclohexane	1.2×10^{-12}	2.3×10^{-4}	1.1×10^{0}	7.8×10^{1}	2.7×10^{1}	1.2×10^{1}	6.7×10^{-7}
Toluene	1.6×10^{-12}	6.2×10^{-3}	1.6×10^{2}	1.4×10^{3}	3.1×10^{4}	9.9×10^{3}	3.4×10^{-6}
Dichloromethane	1.3×10^{-12}	1.3×10^{-4}	3.8×10^{-3}	2.4×10^{-2}	1.8×10^{-2}	1.2×10^{-2}	4.7×10^{-7}
Tetrahydrofuran	1.4×10^{-12}	2.0×10^{1}	2.1×10^{-3}	9.2×10^{-2}	2.1×10^{-1}	9.9×10^{-2}	1.4×10^{-6}
Ethyl acetate	1.5×10^{-12}	1.2×10^{2}	3.8×10^{2}	2.1×10^{3}	5.3×10^{3}	7.1×10^{-3}	1.8×10^{-6}
Methanol	6.9×10^{-13}	2.3×10^{0}	3.5×10^{-1}	2.5×10^{-1}	3.8×10	6.2×10^{-3}	2.7×10^{-6}
Water	3.2×10^{-13}	2.9×10^{-6}	4.0×10^{-8}	7.7×10^{-7}	3.4×10^{-7}	2.8×10^{-5}	6.3×10^{-5}
Pyridine	1.2×10^{-12}	1.0×10^{0}	—	—	—	—	1.4×10^{-5}
Benzaldehyde	1.5×10^{-12}	1.6×10^{3}	1.7×10^{6}	9.3×10^{3}	3.0×10^{4}	1.7×10^{5}	5.4×10^{-4}
Acetophenone	1.5×10^{-12}	7.6×10^{5}	—	—	—	—	6.1×10^{-4}
Nitrobenzene	1.5×10^{-12}	3.7×10^{3}	2.4×10^{5}	1.9×10^{7}	2.1×10^{11}	3.5×10^{6}	1.3×10^{-3}
Benzofuran	1.5×10^{-12}	5.7×10^{6}	7.6×10^{5}	2.5×10^{6}	1.3×10^{7}	2.5×10^{6}	6.6×10^{-5}
Thiophene	1.2×10^{-12}	3.5×10^{-2}	2.8×10^{0}	2.2×10^{-1}	3.3×10^{0}	3.2×10^{-1}	3.1×10^{-6}
Quinoline	1.7×10^{-12}	4.7×10^{10}	—	—	—	—	2.8×10^{-3}
Benzene	1.1×10^{-12}	2.6×10^{-3}	4.6×10^{-2}	1.2×10^{-1}	1.3×10^{2}	5.2×10^{0}	1.0×10^{-6}
Phenol	1.2×10^{-12}	—	—	—	—	—	6.4×10^{-4}
Naphthalene	1.4×10^{-12}	—	—	—	—	—	1.5×10^{-3}
p-Benzoquinone	1.1×10^{-12}	—	—	—	—	—	ND[a]
Hydroquinone	1.0×10^{-12}	—	—	—	—	—	5.5×10
Aniline	1.2×10^{-12}	—	—	—	—	—	2.3×10^{-4}

[a]ND, compound sublimes.

none active sites as compared to the other blacks, as quinoline can be eluted from this black. By comparing the lifetimes of the substituted benzenes to benzene it is possible to propose that surface interactions due to functional groups are not additive, as the substituent groups sterically hinder the interactions between the aromatic π electrons in the adsorbate molecules and the short range π electrons in the graphitic structures of the amorphous carbon adsorbents. There appear to be no active sites that have basic character (type III) on the carbon blacks investigated. The data presented in Table 6 also support this hypothesis; if the surface is deactivated by adsorbed solvent, it is possible to elute a greater number of adsorbates from these carbons. Additionally, there was not a major difference in retention, since none of the solvents had basic character. Studies are in progress which will attempt to use basic solvents and to use alternative approaches to quantify and confirm the presence of quinone-type surface groups on the carbons. However, it is clear that if the amorphous carbon blacks are reasonable models for airborne particles that are produced by combustion sources, they can selectively collect those compounds that have low volatility and that have basic properties. Potential health effects caused by the release of these adsorbed molecules, which represents another aspect of this research, will be dependent upon the physiological tissue, cell, or fluid that contacts the inhaled particle.

Conclusions

The data reported in this paper suggest that the use of extracts from the surfaces of airborne particles for chemical analysis or for *in vitro* bioassays should be treated with considerable caution. Soxhlet extraction using organic solvents may remove most adsorbed molecules regardless of their heats of adsorption and may not remove molecules present at low coverages. However, the amount and composition of the extract will be dependent upon the extracting solvent. These conclusions suggest that it is impossible to relate Soxhlet extraction of airborne particles to the release of surface adsorbed molecules by physiological fluids or tissues.

These results suggest that inhalation studies based on the addition of radiolabeled biologically active compounds to diluted diesel exhaust may be in error. For example, if one assumes that diesel particulate matter has a nitrogen surface area of 100 m^2/g (*13*), contains adsorbates of molecular weight of 100 and adsorption cross-sections of 40×10^{-20} m^2, a monolayer would be achieved when the particulate matter is only 4% extractable; however, diesel particulate matter is typically > 17% extractable. The radiolabeled biologically active materials will only be interacting with adsorbed molecules, and not the carbonaceous surface. These compounds are only retained by their heats of vaporization and will be more biologically available than any compound that is adsorbed during the formation of the diesel particulate matter. Therefore, such results are not suitable for the prediction of the potential health effects of inhaled diesel particulate matter.

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