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M. F. Burke[ab]; A. K. Moreland[a]; L. B. Rogers[a]
[a] Department of Chemistry, Purdue University, Lafayette, Indiana [b] Department of Chemistry, University of Arizona, Tucson, Arizona

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Surface Area Study of Pretreated Silica Gels*

M. F. BURKE,† A. K. MORELAND, and L. B. ROGERS
DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

Summary

The surface areas of a series of pretreated silica gels were measured by a frontal-analysis chromatographic technique using benzene for which the cross-sectional area had been obtained by adsorption measurements on a sample of Sterling MT carbon black as a standard. Much smaller surface areas were found than when nitrogen was used. The chromatographic equilibrium constants for aromatic adsorbates, calculated using the surface areas measured with benzene, point to a change in the adsorption mechanism which was not apparent when nitrogen surface areas were used.

The gas chromatographic behavior of silica gels pretreated by dehydration under various boiling aromatic liquids has been reported (*4*). While the exact nature of the interaction of the organic liquids with the silica gels was not clear, it was shown that the decreases in capacity ratios observed for pretreated gels could be explained qualitatively by changes in surface areas measured by adsorption of nitrogen, as Kiselev et al. had done for carbon black adsorbents (*6*). For an adsorbent with an irregular, porous surface, such as silica gel, it seems reasonable to question whether the surface area available to nitrogen is a valid measure of the area available to a larger molecule (*3,8*). Any difference in the surface areas available to different adsorbates would profoundly affect their rela-

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† Present address: University of Arizona, Department of Chemistry, Tucson, Arizona.

tive chromatographic retentions. With the hope of obtaining more nearly quantitative correlation, the present study was undertaken to determine the surface area available to benzene, one of the adsorbates previously studied chromatographically, on the same series of pretreated silica gels (*4*).

The surface area of a solid is usually determined by application of the BET equation to the adsorption isotherm for a particular adsorbate and temperature (2). The most common system is nitrogen at its boiling point, but the method is equally applicable for many other adsorbates.

The determination of an adsorption isotherm is accomplished by measuring the equilibrium amount of material adsorbed at different concentrations of the adsorbate. The crucial step is the measurement of the amount adsorbed, which can be done statically by either measuring pressure changes in a vacuum system or weighing the adsorbent with a suitably sensitive balance. Both of these methods have been used entensively for solids having relatively large surface areas at moderate-to-high adsorbate concentrations. However, the methods are not very suitable for solids having small surface areas, and the required apparatus is relatively cumbersome and complex. In the present case such measurements would be complicated further by the fact that the adsorbates of interest are not permanent gases but organic liquids having boiling points above room temperature.

A method utilized recently for measurement of adsorption isotherms is frontal-analysis chromatography (*1,5,11*). Its use appeared to be particularly attractive because it would permit measurements to be made conveniently under conditions very similar to those that existed during the measurement of retention times and, if desired, on the same portions of column packings. For those reasons an apparatus capable of providing adsorption data for a wide variety of volatile liquids was constructed. In addition, because many chromatographic studies in our laboratories involve solids having specific surface areas of 1 m^2/g or less, changes were made in the apparatus reported in the literature (*11*) so as to permit more reliable measurements to be made of small amounts of adsorbed material.

For our study to be internally consistent, we used as a reference adsorbent a sample of graphitized carbon black, an adsorbent which has been reported to have a nearly homogeneous, nonporous surface (7). The nitrogen surface area of the carbon black was deter-

mined using the adsorption–desorption approach of Nelson and Eggertson (*10*). The surface area was then determined using the organic adsorbate by frontal analysis. Assuming that the total surface area available to each organic species and to nitrogen was the same, the cross-sectional molecular area of each organic compound was calculated. That molecular area was then used to calculate the surface areas of the silica gels from the frontal-analysis data.

EXPERIMENTAL

Adsorbents

The carbon black used as a reference was a graphitized thermal black, designated as Sterling MT D-5, supplied by the Cabot Corporation Laboratories and was similar to those described elsewhere (*12*). The carbon black, which was a very fine powder, was pelletized by rolling in a ball mill without the addition of water or a binder. The 60–80 mesh fraction was then packed in a column.

The silica gels were precipitated from aqueous sodium silicate solution by acidification with HCl and then dehydrated by refluxing under different aromatic liquids. In all cases samples were taken from the same preparations used in the earlier gas chromatographic study (*4*).

The columns used for the carbon black were $4 \times \frac{1}{4}$ in. o.d. stainless steel. Those used for the silica gels were $\frac{1}{8}$-in. o.d. stainless steel, and the length was varied to provide sufficient adsorbent to give retention times greater than 200 sec.

Apparatus and Procedures

A block diagram of the apparatus is shown in Fig. 1. Both helium tanks were regulated by Matheson two-stage pressure regulators. They were set to deliver 50 psi for maximum efficiency of the differential flow controllers. A Heise pressure gauge was used to monitor the output pressure of the regulator. The gauge had a range of 0 to 75 psi and a pressure could be estimated to the nearest 0.02 psi. The change in the regulator output pressure at a constant gas flow was found to be less than 0.3 psi at 50 psi over several days. The flow through the sample stream was maintained constant by means of a Brooks Model 8795 differential flow controller. The controller was mounted securely and wrapped with insulation to mini-

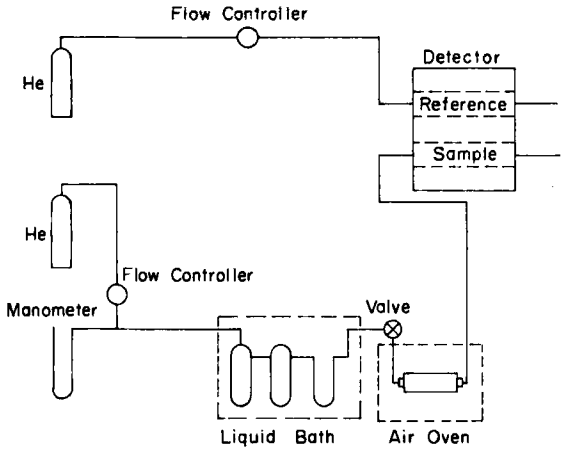

FIG. 1. Frontal-analysis apparatus.

mize temperature fluctuation. For a given output pressure of 50 psi of helium, the flow could be held constant within 0.3% at any flow rate between 2 and 50 ml/min. For our work, flow rates between 3 and 10 ml/min were used.

The pressure changes on the line supplying the reference side of the detector were not monitored since variations in that pressure had little effect on the results. This flow was controlled by a Moore differential controller.

A pair of gas-dispersion tubes, 7 cm long and 1.4 cm in diameter, were connected in series to saturate the helium stream with organic vapor. Each tube was filled with liquid to a height of 6 cm. Because the temperature of the liquid determined the partial pressure of the adsorbate, the saturation system was immersed in an ethylene glycol bath held constant to the nearest 0.01°C by means of a Sargent heater and pump assembly controlled by a mercury-contact thermoregulator. In addition, a 20-cm length of 6-mm glass tubing, packed with glass wool, was placed immediately after the bubblers to collect any aerosol (fog) formed.

A Varian-Aerograph 6-way gas-sampling valve used in the saturated stream was heavily wrapped with insulation and was heated by means of a Glasco heating tape to approximately 100°C. When the valve plunger was out, the saturated stream was vented to the atmosphere through a fine needle valve. When the plunger was in, the adsorbate stream was directed through the column to the de-

tector. The purpose of the needle valve was to permit adjustment of the pressure drop across the vent so that it was equal to that across the column of adsorbent. Equalization of the pressure drops assured that when the stream was switched from the vent to the column no significant change in the flow rate would occur. When the pressure drops differed, there was an interval during which the flow rate was above or below the desired value while the flow controller adjusted the pressure throughout the dead volume of the system. A mercury manometer was used to indicate the pressure drops.

A Carle Microcell thermal conductivity detector held at about 200°C in a Dewar flask was used to detect the chromatographic front. The detector was extremely stable at the sensitivities employed, which were about 2% of the maximum sensitivity available.

The column of adsorbent was maintained at a constant temperature in a Becker Model 1452 chromatographic oven where the temperature was controlled to better than ±0.2°C over long periods of time. However, by measuring the temperature with an iron-constantan thermopile, the temperature during a run was found to be constant within ±0.02°C.

For replicate runs on a column, the oven temperature was increased to approximately 180°C for 20 min, with pure helium flowing through the column to remove the adsorbate. Then the column was cooled to 80.1°C for the next run. The exact conditioning temperature was not found to be critical over the 150–200°C range, nor was the conditioning time critical in the 10–30-min range.

Calculations

Assuming that an equilibrium exists for a gas–liquid chromatographic process, one can relate the retention volume of an adsorbate to the equilibrium constant K through the capacity ratio k, which is defined as

$$k = (V_R/V_A) - 1 \tag{1}$$

V_R is the corrected retention volume of the adsorbate, and V_A is the retention volume of an unadsorbed species and is a measure of the interstitial gas volume (free space) in the column. The equilibrium constant is defined as

$$K = C_S/C_g \tag{2}$$

where C_S is the concentration in the stationary phase and C_g the concentration in the mobile phase. In practice, k is measured experimentally and then converted to the equilibrium constant by the relationship

$$K = k(V_A/V_S) \tag{3}$$

where V_S is the volume of the stationary phase.

In gas–solid chromatography, instead of the volume of the stationary phase, the amount of surface area A_S available to the given adsorbate is involved. The proper expression for K is then

$$K = k(V_A/A_S) \tag{4}$$

showing that k, the measured quantity, depends on the surface area of the solid. The interstitial gas volume V_A depends on the density of the adsorbent and the amount of adsorbent in the column, i.e., the packing density. Although Kiselev et al. (*6*) had shown the usefulness of correcting for surface area differences, the use of V_A had not been previously tested, so a simple experiment was run in the present study to verify its usefulness.

The volume of adsorbed material was calculated for the frontal analysis from the breakthrough time by means of the equation

$$V = (273rtPp)/[760T(P - p)] \tag{5}$$

where V is the volume adsorbed in milliliters at STP, P the atmospheric pressure in millimeters of Hg, p the vapor pressure of the adsorbed substance at the temperature of the saturator in millimeters of Hg, r the nitrogen flow rate into the saturator, t the breakthrough time in minutes, and T the room temperature in °K. The correction for the dead volume of the apparatus was on the order of 10–15% of the breakthrough time for the low-area carbon black, and it was practically negligible for the silica gels. The volume adsorbed was then plotted as a function of the partial pressure of the adsorbate using the BET equation:

$$p/V(P_s - p) = (1/V_m)[(C + 1)/C](p/P_s) + 1/V_mC \tag{6}$$

where P_s is the saturation pressure of the adsorbate for the temperature at which the measurement was made, V_m the volume of a monolayer of the adsorbate, and C a constant which is much greater than unity.

Therefore Eq. (*7*) can be expressed as

$$p/V(P_s - p) = (1/V_m)(p/P_s) \tag{7}$$

This equation usually gives a linear plot for values of p/P_s between 0.1 to 0.3, the slope of which is the reciprocal of the volume of a monolayer. The surface area is then found from the number of molecules present, after assuming a cross-sectional area for the adsorbate molecule.

An approximate method, based on the assumption that the BET plot passes through the origin, was used to determine some of the surface areas from data at a single partial pressure (*10*). Assuming that the constant C approaches infinity, the monolayer coverage V_m is given by

$$V_m = V(1 - p/P_s) \tag{8}$$

RESULTS

Preliminary Studies

The surface area of the Sterling MT carbon black was found to be 9.8 $m^2/g \pm 2\%$ using nitrogen in a system similar to that proposed by Nelson and Eggerston (*10*). The values for the amount of nitrogen adsorbed at various partial pressures determined on this carbon black by the frontal technique and the adsorption–desorption method agreed within 4%, but this comparison was done using a flow controller of lower stability than that used in the rest of the study. Our values agree well with the 9.7 m^2/g reported by Smith (*13*).

The preliminary part of the investigation was devoted to testing the validity of Eq. (4). Two carbon black columns were packed, one with much gentle tapping to assure close packing and the other with no tapping. These procedures resulted in packing densities of 0.577 and 0.436 g/ml, respectively. A chromatographic study of these columns using butane samples with helium as the carrier gas at 25°C produced capacity ratios of 12.57 and 8.76, respectively. However, when these values were corrected for the ratio V_A/V_S, the resultant K values were 15.67 and 15.32, indicating that Eq. (4) was valid.

Benzene was used to test the reproducibility and precision of the frontal-analysis apparatus. The standard deviation for a set of five replicate runs on a column containing 1.12 g of carbon black was $\pm 1\%$, while the fit to the BET equation gave a standard deviation of 2%. The limiting factor appeared to be the accuracy with which the impedance of the vent through the needle valve could be matched with that of the column.

When the commonly accepted value of 16.2 Å² was used for the cross-sectional area of nitrogen, the cross-sectional area needed to make the benzene surface area agree with that for nitrogen was 47.2 Å². The latest review of such values for adsorbed molecules gives a value of 43.6 ± 9.8 Å² for benzene, so that our value is well within this range (9).

Silica Gels

The surface areas of the pretreated gels measured by nitrogen adsorption, and by benzene adsorption, using the cross-sectional area measured on the carbon black, are compared in Table 1. These data assume that a benzene molecule has the same orientation on both adsorbents. Such comparisons might not be valid for adsorbates for which there are two or more highly probable orientations on the surface and where the preferred orientation might be a function of the adsorbent. The range for the areas of the first four gels was less than a factor of 2, but that for the last three gels was much larger.

Equilibrium constants calculated from the packing densities and both the benzene and nitrogen surface areas are shown in Table 2. If the only difference between members of a series of adsorbents is the surface area, the capacity ratios for a given adsorbate will increase in proportion to the surface areas of the adsorbents, and the calculated equilibrium constants will be the same. Conversely, if the surface area is not the only factor involved, then the equilibrium constants will not be the same for different adsorbents. Table

TABLE 1

Surface Areas of Pretreated Silica Gels Determined Using Nitrogen and Benzene

Gel	Area, m²/g	
	Nitrogen	Benzene
Control	730	590
Benzene	424	310
Toluene	381	279
Ethylbenzene	400	299
o-Xylene	227	66
m-Xylene	200	59
Naphthalene	148	29

TABLE 2

Chromatographic Equilibrium Constants Calculated Using Nitrogen and Benzene Surface Areas

	Equilibrium constants					
	Nitrogen values			Benzene values		
Gel	Benzene	Toluene	Ethyl-benzene	Benzene	Toluene	Ethyl-benzene
Control	0.11	0.27	0.55	0.11	0.26	0.53
Benzene	0.13	0.27	0.56	0.20	0.43	0.82
Toluene	0.12	0.27	0.49	0.16	0.37	0.66
Ethylbenzene	0.12	0.27	0.48	0.17	0.37	0.65
o-Xylene	0.11	0.20	0.31	0.37	0.91	1.42
m-Xylene	0.12	0.22	0.33	0.52	0.70	0.87
Naphthalene	0.09	0.16	0.23	0.45	0.80	1.17

2 shows that, except for ethylbenzene, equilibrium constants calculated using the nitrogen surface areas were fairly constant, although they do exhibit a decrease down the series. However, when benzene surface areas were used to calculate the equilibrium constants, the results were strikingly different. In each case the control gel exhibited the smallest K and in no case were the K values nearly constant for the series. The increase in K for a treated gel reflects an increase in the relative adsorption which was not apparent before correcting the capacity ratio for the smaller benzene surface areas.

Two other effects of the pretreatment were also apparent. One effect, reported earlier (*4*), was the decrease in α for a given column temperature as one proceeded down the series of gels from the control to the naphthalene-treated gel. Such a decrease in the selectivity signifies a change in the type of interaction between the adsorbates and adsorbents. Another effect was found in a qualitative study of the sample-size dependence of the capacity ratio. When compared with untreated solids having similar surface areas, pretreated gels, especially the xylene and naphthalene gels, had much wider ranges of sample sizes over which the capacity ratios were nearly constant. In fact, the symmetries of the eluted peaks were also better on the pretreated gels. Such behavior suggests that the modified surfaces were more nearly homogeneous.

To put the above results in perspective, it is well to remember

that, over the years, a large number of publications have dealt with pretreatment of adsorbents in general and, in recent years, with supports for gas–liquid chromatography. Pretreatment has usually been aimed at minimizing the tailing of chromatographic peaks or decreasing long retention times with little or no attention to the accompanying changes in selectivity. The goal has been to deactivate partially an adsorbent by chemical reaction (esterification or silanization of OH groups, treating with acid or base, etc.) or by allowing a relatively nonvolatile polar liquid to "neutralize" the more active sites by physical adsorption.

In contrast, we have treated a freshly precipitated gel with unreactive, relatively nonpolar, volatile aromatic hydrocarbon liquids. The effects of pretreatment on selectivity were then studied by examining changes in absolute and relative chromatographic retention times. The work most similar to ours is that of Vysotskii et al. (*14*), who dried silica gels in the presence of vapors of benzene and toluene, rather than under the respective boiling liquids. They then noted selectivity by comparing adsorption isotherms for several adsorbates on pretreated and untreated samples.

However, the most important aspect of the present study is not the method of pretreatment but the need for considering the effects of a difference in surface area available to an organic adsorbate and to nitrogen on a particular column of adsorbent. Although capacity ratios for the organic adsorbates on pretreated silica gels appeared to have decreased much more than the surface area, based upon nitrogen measurements (*4*), the capacity ratios per unit of surface area based upon benzene measurements actually increased.

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