

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Adsorption of Benzene and Cyclohexane by Graphite¹

BY R. NELSON SMITH, CONWAY PIERCE AND HERMAN CORDES

The similarity in the arrangement of carbon atoms in graphite to the arrangement of atoms in the benzene ring suggests that benzene might be particularly well adsorbed on graphite surfaces and that the packing of the atoms on the surface might be very close. No data have, to our knowledge, been reported for benzene on non-porous carbon surfaces. We have therefore determined the isotherm of benzene on Graphon, a partially graphitized carbon black. We have also determined, for comparison, the isotherm of cyclohexane.

Experimental

Graphon,² from the same lot as that used by Joyner and Emmett,³ and Beebe and associates^{4a,b} was used as adsorbent. The nitrogen area is given by Joyner and Emmett as 80 sq. m./g. Prior to use, we treated the sample with hydrogen at 1100°, to remove oxygen complexes if such were present. After sealing into the adsorption tube the sample was again degassed *in vacuo* at 400°.

Isotherms were determined at 28.6 and 5.5° by the gravimetric method previously described.⁵ The latter temperature was maintained at the freezing point of benzene by adding sticks of frozen benzene to pure liquid in a Dewar flask. All stopcocks were of the mercury seal type. Lubrication was with Silicone stopcock grease, which stood up quite well in contact with the organic vapors. From 0.8 to 1.2 g. of Graphon was normally used in a determination.

The benzene was a thiophene-free grade used without further purification. Cyclohexane was purified by distillation on a spinning band column having about 20 theoretical plates. Vapor pressures on a mercury manometer at room temperature were

	5.5°	28.6°
Benzene, mm.	34.9	112
Cyclohexane, mm.	37.0	114.5

Pressure readings for the isotherms were made on mercury manometers to *ca.* 0.2 mm. except for the lower pressure values of the 5.5° isotherms for which a McLeod gage was used.

The isotherms are shown in Figs. 1 and 2. The right hand curves are the complete 5.5° isotherms. The 28.6° data are not shown in these curves because the isotherms for the two temperatures are, at the higher relative pressures, too close together to show separately on the scale of the drawings. The left hand curves of the two figures show the low pressure regions of the isotherms on expanded scale with separate curves for the two temperatures.

An attempt was made to determine the isotherm of cyclohexane, but apparently the vapor polymerizes since it was found impossible to secure constant pressure readings.

(1) This is a progress report of work done under Contract N8-onr-54700 with the Office of Naval Research.

(2) Furnished by Dr. Walter R. Smith of the Godfrey L. Cabot Company, Boston, Massachusetts.

(3) L. G. Joyner and P. H. Emmett, *THIS JOURNAL*, **70**, 2353 (1948).

(4) (a) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, *ibid.*, **69**, 95 (1947). (b) R. A. Beebe, M. H. Polley, W. R. Smith and C. B. Wendell, *ibid.*, **69**, 2294 (1947).

(5) C. Pierce and R. N. Smith, *J. Phys. Coll. Chem.*, **52**, 1111 (1948).

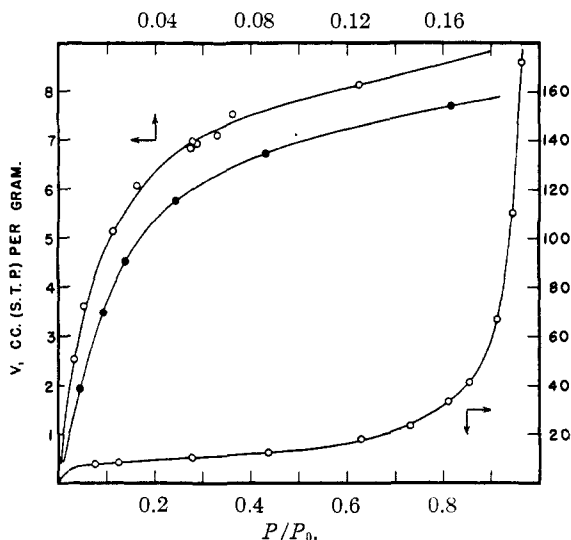


Fig. 1.—Isotherms of benzene on Graphon. The complete 5.5° isotherm is shown in the right-hand curve. The left-hand curves give the low pressure region on expanded scale at 5.5° (open circles) and 28.6° (closed circles).

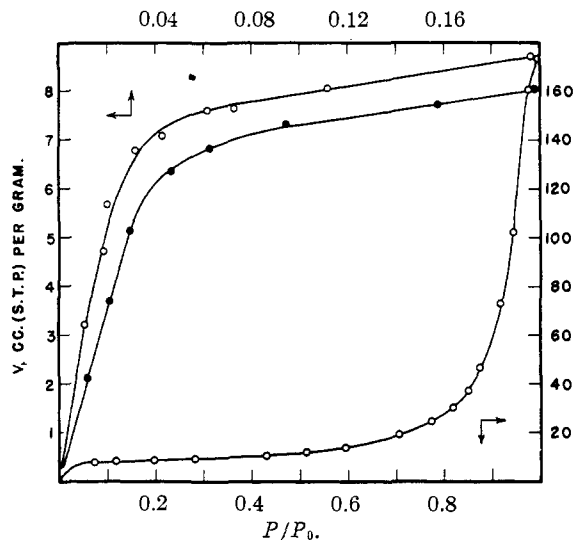


Fig. 2.—Isotherms of cyclohexane on Graphon. The complete 5.5° isotherm is shown in the right-hand curve. The left-hand curves give the low pressure region on expanded scale at 5.5° (open circles) and 28.6° (closed circles).

Discussion

Comparison of the isotherms for benzene and cyclohexane shows some interesting relations. At low relative pressure cyclohexane is more strongly adsorbed than benzene and its monolayer is completed at a lower relative pressure.

In the relative pressure region 0.1 to 0.9 the isotherms are practically identical. Above 0.9 benzene is appreciably more strongly adsorbed. At saturation 220 cc. of benzene is adsorbed but only 170 cc. of cyclohexane.

Areas of Adsorbate Molecules.—The variety of isotherms now available on Graphon and non-porous carbon blacks permits better comparisons of areas per molecule than previously, when tabulations such as those of Livingston⁶ had to rely upon data from a variety of adsorbents. In particular the data for benzene and cyclohexane are of interest because of their symmetrical shapes and high adsorbability.

We have listed in Table I the V_m and σ values for a number of adsorbates on Graphon and carbon black. For this comparison we have used the V_m values at point B rather than those computed by the BET equation, since the latter is not at all applicable to the methanol-Graphon isotherm. For some isotherms the BET value agrees closely with point B but for others it is somewhat higher.

TABLE I

AREA PER MOLECULE FOR ADSORBATES ON NON-POROUS CARBON SURFACES

Adsorbate	Adsorbent	V_m , cc./g.	σ , sq. Å./ mole- cule	Computed area From model	
				(V) ^{2/3}	
Nitrogen ²	Graphon	16.5	16.2		
Methanol ⁷	Graphon	19	14.1	16	14.7
Ethyl chloride ⁸	Graphon	9	29.7	24	26
Benzene	Graphon	6.5	41	28	41 (37, 40)
Cyclohexane	Graphon	7	38*	32	39
Butane ⁹	Carbon black	10.5	41.5	30	37.5
Pentane ¹⁰	Carbon black	9.5	46	33	42
Decane ¹⁰	Carbon black	4.5	97	47	72
Decane ¹⁰	Devolatilized carbon black	5.5	79	47	72

In computing σ we have used 16.2 Å.² as the N₂ area. The column headed (V)^{2/3} gives the approximate area as computed for symmetrical molecules. These values are, except for methanol and ethyl chloride, far too low. In the last column we give computed areas based upon models for unsymmetrical molecules lying flat on the surface. To compute these areas we have used dimensions from crystal structure, atomic radii and distances of closest approach for neighboring molecules which are computed from spreading areas of insoluble films.

Adam¹¹ gives an area of 20.5 Å.² for straight chain hydrocarbon molecules in insoluble films. This is the area perpendicular to the length of

(6) H. K. Livingston, *J. Colloid Science*, **4**, 447 (1949).

(7) C. Pierce and R. N. Smith, *J. Phys. Coll. Chem.*, **54**, 354 (1950).

(8) C. Pierce and R. N. Smith, *ibid.*, **54**, 784 (1950).

(9) G. L. Kington, R. A. Beebe, M. H. Polley and W. R. Smith, *This Journal*, **72**, 40 (1950).

(10) W. D. Schaeffer, M. H. Polley and W. R. Smith, *J. Phys. Coll. Chem.*, **54**, 227 (1950).

(11) N. K. Adam, "The Physics and Chemistry of Surfaces," Clarendon Press, New York, N. Y., (1930), p. 50.

the chain. Since such molecules are symmetrical in cross section this gives $\sqrt{20.5} = 4.55$ Å. for the thickness of the molecule. Dividing this into the volume per molecule gives the computed values of the last column for all the compounds with —CH₂ groups, including cyclohexane. The agreement for most is as good as the accuracy with which one can locate V_m from the isotherm. Decane on a carbon black is an exception but when a devolatilized black is used, the agreement is quite good. Apparently the hydrocarbons that were on the surface prior to devolatilization covered some of the adsorbing sites.

The area for benzene was computed in three ways. (1) For a flat hexagonal model the sum of the atomic radii gives a diameter of 4.94 Å. To this is added 1.5 Å. for the free space between adjacent molecules, giving a total of 6.44 Å. for the diameter of the molecule. This squared is 41 Å.² The free space value is obtained from the width of a hydrocarbon chain, 4.55 Å., by subtracting the actual width of a —CH₂ group. For the latter we used the sum of the atomic radii.

2. Adam gives 24 Å.² as the cross section for benzene in films, where the rings are standing on edge. The molecular volume is 146 Å.³ Dividing by 24 gives 6.1 as the height of the vertical molecule. This squared gives an area of 37 Å.²

3. If it is assumed that in the liquid benzene rings can be parallel to one another at the interplanar distance of graphite, 3.6 Å., the cross section is 146/3.6 = 40 Å.²

The good agreement between the three ways of estimating the area of a benzene ring and the observed value of 41 Å.² indicates that the ring must lie flat on the surface and that the surface is completely covered or nearly so at the V_m point, 6.5 cc.

When Hirschfelder models are constructed for benzene and cyclohexane molecules, it is found that the areas are approximately equal when both are lying flat (with benzene just a little larger). This is in agreement with the observed σ values.

It is interesting to note in the models that as the cyclohexane molecule lies on a plane surface, contact is made by only three H atoms, whereas the benzene model makes contact with a plane surface by all six C atoms directly. Yet it is observed in the isotherms (as pointed out above) that in the first layer cyclohexane is a little more strongly adsorbed than benzene. Calculation of the isosteric heats of adsorption near V_m (from the isotherms of Figs. 1 and 2) gives $E - E_L$ values near 5 kcal. per mole for both benzene and cyclohexane or total heats near 12–13 kcal. per mole (ca. 2 kcal. per C atom). The cyclohexane values are slightly higher than the benzene. These high values are of the same order as found by Beebe and associates for long chain hydrocarbons, ca. 2 kcal. per CH₂ group. This suggests

that the cyclohexane molecule is to some extent distorted on adsorption so that each CH_2 group has surface contact.

Summary

Isotherms are given for benzene and cyclohexane on Graphon at temperatures of 5.5 and 28.6°. The area covered per molecule is found to be *ca.* 38 Å.² for cyclohexane and 41 Å.² for benzene. Both indicate that the molecules lie

flat on the surface. The isotherms and isosteric heats of adsorption computed from them show that in the first layer cyclohexane is more strongly held than benzene. In the multilayer region benzene is the more strongly adsorbed.

Areas per molecule are given for a variety of adsorbates, as obtained from isotherms on Graphon and carbon blacks. These are compared with areas computed from models.

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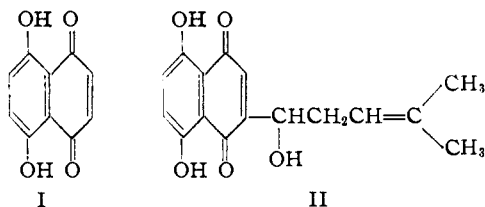
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[CONTRIBUTION FROM THE DEPARTMENTS OF RADIATION BIOLOGY AND BIOCHEMISTRY, UNIVERSITY OF ROCHESTER SCHOOL OF MEDICINE AND DENTISTRY]

Beryllium Complexes with Naphthazarin and Alkannin¹

BY A. L. UNDERWOOD, T. Y. TORIBARA AND W. F. NEUMAN

Previous papers^{2,3} have described the use of naphthazarin (I) and alkannin (II) as reagents for the spectrophotometric determination of microgram quantities of beryllium. It was of



interest, therefore, to know the nature of the materials formed by the interaction of beryllium with these dyes.

In certain instances, true compounds of the chelate type are formed from metal ions and so-called "lake-forming" dyes, but in others, the reaction appears to be non-stoichiometric with adsorption phenomena playing a predominant role.⁴ Dubsky, *et al.*,⁵ studied the products formed when beryllium solutions were mixed with naphthazarin or alkannin solutions in the presence of ethylenediamine; they concluded that ethylenediamine reacted with naphthazarin or alkannin to form ketimine compounds which then yielded chelate complexes with beryllium, but the data adduced to support this idea seem inconclusive. Thus, it appeared that the products formed from beryllium and alkannin or naphthazarin under the conditions of the analytical method² could not be characterized without further investigation.

(1) This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, N. Y. Presented before the Division of Physical and Inorganic Chemistry, Detroit, Michigan, April, 1950.

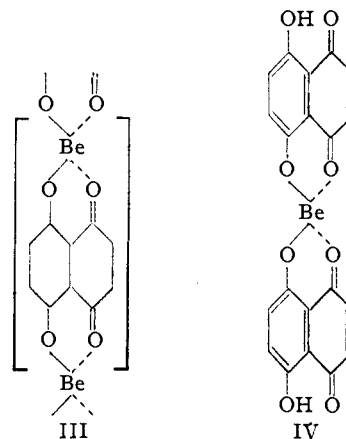
(2) Underwood and Neuman, *Anal. Chem.*, **21**, 1345 (1949).

(3) Toribara and Underwood, *ibid.*, **21**, 1352 (1949).

(4) For example, see Liebhafsky and Winslow, *THIS JOURNAL*, **69**, 1130 (1947); Porter and Weiser, *J. Phys. Chem.*, **31**, 1383, 1704 (1927).

(5) Dubsky, Langer and Wagner, *Mikrochemie*, **22**, 108 (1937).

It was found that beryllium reacts with naphthazarin or alkannin to form two definite complexes depending upon the ratio of the reactants in solution. The following structures (III) in which the ratio is one beryllium atom to one dye molecule and (IV) in which one beryllium atom reacts with two dye molecules are assigned using naphthazarin (I) as the dye.



The portion of structure III in the brackets is taken as the unit which probably forms a polymer. Certain chemical evidence favors this interpretation as well as the fact that the structure proposed is based on beryllium's maximum coordination number of 4.

The evidence for the structures of these complexes was obtained from spectral studies, use of the method of continuous variations^{6,7,8} and *pH* titrations.

Experimental

Apparatus.—All spectrophotometric data were obtained with a Beckman model DU quartz spectrophotometer, using matched Corex cuvettes. *pH* titration curves were obtained with a Beckman model H 2 glass electrode *pH* meter.

(6) Job, *Ann. Chim.*, [10] **9**, 113 (1928).

(7) Job, *ibid.*, [11] **6**, 97 (1936).

(8) Vosburgh and Cooper, *THIS JOURNAL*, **63**, 437 (1941).