Surfaces of Solids. XVI. Adsorbed Films of Water and Normal Heptane on the Surface of Graphite

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Introduction

The surface of a solid has been considered as hydrophilic if the contact angle of water with the surface of the solid is zero, and as hydrophobic if the angle is greater than zero. Most solids are hydrophilic.[1] Talc, stibnite, graphite and paraffin are *hydrophobic*. The contact angle of water against these solids, is, respectively, 87.9, 84.2, 85.7°,[2] and for different paraffins, from 104 to 111°.

In two recent papers Harkins and Jura[3,4] have reported in detail the energy changes of the surface of anatase caused by the adsorption of water. The above indicated system is typical of those in which the contact angle is zero. In the present contribution the writers give the results obtained by the adsorption of water on graphite. It is not known at this time whether or not the results are typical of the entire class of hydrophobic solids. Graphite was chosen because: (1) it has a known crystal structure, (2) it can be obtained in a high state of purity, (3) it can be subdivided finely enough to give sufficient area for precise work, (4) its relation to charcoals and carbon black, which have been extensively studied, is known, and (5) its industrial use is extensive. Since *n*-heptane spreads on the surface of graphite, the surface is oleophilic.

Experimental

The preparation and purity of the water and of the *n*-heptane, and the apparatus used for the determination of the adsorption isotherms have been described in an earlier paper.[4] Two samples of graphite were used. The first[5] contained less than 0.004% ash by weight and had been formed at 1100° in a reducing atmosphere to prevent the formation of an oxygen–carbon compound or complex on its surface. The second sample[6] contained 0.46% ash by weight. Nothing is known concerning the presence of an oxygen complex on its surface.

The degassing procedure used was as follows: the samples were evacuated at room temperature for several hours in a vacuum of 10^{-5} mm. before they were heated. The samples were then heated for twelve–fourteen hours at 500–550° in the vacuum. X-Ray diffraction patterns were photographed by the use of copper Kα radiation in a camera whose radius is 2.96$_8$ cm.

Areas and Isotherms

The areas of the samples were determined by the adsorption of nitrogen at $-195.8°$ and from

n-heptane isotherms at 25° by the use of both the relative method of Harkins and Jura[7] and the method of Brunauer, Emmett and Teller.[8] The results are summarized in Table I.

TABLE I

AREAS OF THE GRAPHITE SAMPLES IN SQUARE METERS PER GRAM

Graphite	Relative method		BET method (under assumptions below)[a]	
	N_2	n-C_7H_{16}	N_2	n-C_7H_{16}
Less than 0.004% ash	4.22	4.37	4.31	4.42
0.46% ash	6.22	6.47	6.22	6.85

[a] The areas given as by the BET method were obtained by the use of 16.2 and 64.0 sq. Å. as the effective cross-sectional areas for nitrogen and *n*-heptane, respectively. These areas were obtained by a combination of the relative method of Harkins and Jura with the BET method. The values of the areas used for subsequent calculations in this paper are 4.22 and 6.22 m.²g.⁻¹, as obtained by the relative method from isotherms for the adsorption of nitrogen.

X-Ray diffraction patterns were taken of the two samples as received, and, in addition, the sample containing 0.46% ash after it had been saturated with water and with *n*-heptane. All four patterns gave the same values, 2.45$_5$ and 6.70 Å. for a_0 and c_0. This indicates that there cannot be any appreciable penetration of the graphite by either water or *n*-heptane and, therefore, that all of the vapor which disappears is adsorbed in each case wholly as a surface film.

The water isotherms for the entire pressure range of p/p_0 up to unity are exhibited in Fig. 1, while in Fig. 2 the values are given for pressure from $p/p_0 = 0.0$ to $p/p_0 = 0.1$. In Fig. 1 values obtained by Boyd and Livingston[9] are also included. Their sample contained 10% ash by weight. The results are given in molecules adsorbed cm.⁻² as a function of the relative pressure, so the values are independent of the areas of the various samples.

The curves exhibit several features of interest. The high ash graphite (10%) investigated by Boyd and Livingston gave results that are much too high as compared with the two graphites of low ash content. Thus the ash increases very greatly the amount of water adsorbed. Of the two latter samples the purer adsorbs much less gas in the low pressure region, but at high relative pressures the films are polymolecular, reaching an average thickness of at least three layers at

(1) Many organic liquids give zero contact angles with a large number of solids. Such solids are commonly designated as *oleophilic*.

(2) F. M. Fowkes and W. D. Harkins, THIS JOURNAL, **62**, 3377 (1940).

(3) W. D. Harkins and G. Jura, *ibid.*, **66**, 919 (1944).

(4) G. Jura and W. D. Harkins, *ibid.*, **66**, 1356 (1944).

(5) Prepared by the National Carbon Company through the courtesy of Dr. Lester L. Winter.

(6) Obtained through Dr. Raymond Szmanowitz of the Acheson Colloid Corporation.

(7) W. D. Harkins and G. Jura, THIS JOURNAL, **66**, 1366 (1944).

(8) S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

(9) G. E. Boyd and H. K. Livingston, *ibid.*, **64**, 2383 (1942).

relative pressures of 0.98. Whether a part of this thickness is due to a slight porosity was not determined, but the isotherms in the high-pressure region with *n*-heptane are exactly similar to those obtained with materials which are known to be non-porous.
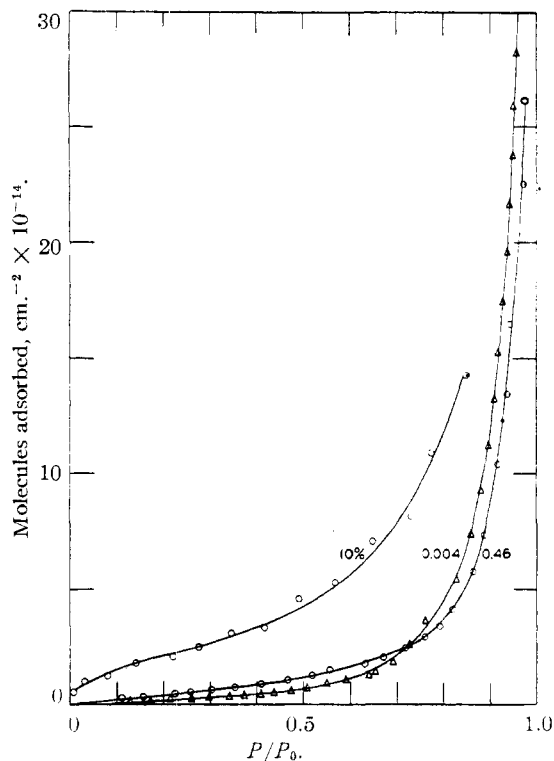

Fig. 1.—Adsorption isotherms of water at 25° on graphites with 10, 0.46 and less than 0.004% ash by weight, the last of these produced with no oxygen complex on the surface.

The second point of interest is exhibited in Fig. 2. The shape of the water isotherms in Fig. 1 corresponds to Type III in Brunauer's classification.[10] Fig. 2, however, shows that the adsorption has, in general, the same form as that exhibited by the Type II curves. The difference between the two is that the curve flattens out, when water is adsorbed on graphite, where only a small fraction of a monolayer is adsorbed, whereas in the Type II curve this occurs at approximately the completion of a monolayer. Also, in the Type II curve the point of inflection occurs at lower relative pressures.

Figure 2 also illustrates another point of interest in connection with the graphite with 0.46% ash. This is a discontinuity which appears, as the pressure is increased, at a value of 1.750 mm. This is a first order phase transition in the film formed by the water on the surface of graphite. Similar discontinuities are found when *n*-heptane is the adsorbate on either of the two samples of

(10) S. Brunauer. "The Adsorption of Gases and Vapors." Princeton University Press, Princeton, 1943, p. 150.

graphite. With that which contains 0.46% ash the discontinuity occurs at 0.006 mm., but for the low ash graphite, at a pressure of 0.014 mm. This phenomenon is described in detail in other papers by Jura, Loeser, Basford and Harkins.[11,12]
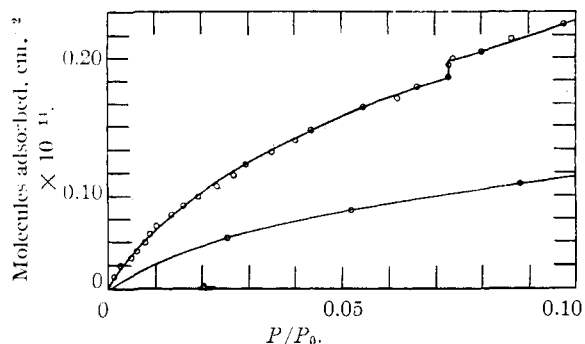

Fig. 2.—Isotherms of water on graphites of 0.46% and less than 0.004% ash for values of relative pressure from 0.0 to 0.1. The sample containing 0.46% ash exhibits a finite discontinuity at a pressure of 1.750 mm.

Figure 3 exhibits the isotherms of *n*-heptane on the two graphites. These results are typical of all other systems in which the contact angle is zero. Figure 4 gives isotherms for the adsorption of water and *n*-heptane on the sample with 0.46% ash. In spite of the larger size of the *n*-heptane molecule, more heptane than water molecules are adsorbed per unit area at a given relative pressure. When the contact angles of both liquids are zero, then the reverse is true, for example, on titanium dioxide, where at a given relative pressure more water than heptane molecules are adsorbed.[4]

Results and Discussion

The spreading coefficient $S_{L/S}$, free energy of emersion $f_{E(SL)}$, and work of adhesion $w_{A(SL)}$ are given by the equations

$$S_{L/S} = \gamma_S - \gamma_{SL} - \gamma_L \qquad (1)$$
$$f_{E(SL)} = \gamma_S - \gamma_{SL} \qquad (2)$$
$$\text{and } w_{A(SL)} = \gamma_S - \gamma_{SL} + \gamma_L \qquad (3)$$

respectively, where γ_S, γ_{SL}, and γ_L are the free surface energies per unit area of the surface of the clean solid, of the solid–liquid interface and of the liquid. The quantity $\pi_e = \gamma_S - \gamma_{S_e}$ can be obtained from the adsorption data by integrating the Gibbs adsorption equation as suggested by Bangham.[13,14,15] The relation is expressed by the equation

$$\pi_e = \gamma_S - \gamma_{S_e} = \frac{RT}{V_M \Sigma} \int_0^{p_a} \frac{v}{p}\, dp \qquad (4)$$

The evaluation of this integral has been dis-

(11) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *J. Chem. Phys.*, **13**, 535 (1945).

(12) G. Jura, *et al., ibid.*, **14**, March (1946).

(13) D. H. Bangham, *Trans. Faraday Soc.*, **38**, 805 (1937).

(14) D. H. Bangham and R. I. Razouk, *ibid.*, **33**, 1463 (1937).

(15) D. H. Bangham and R. I. Razouk, *Proc. Roy. Soc., London*, **A166**, 572 (1938).
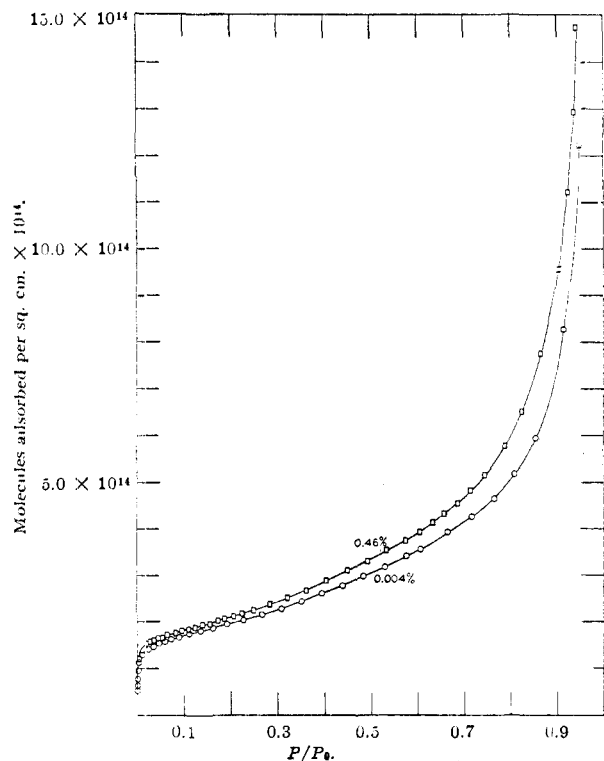
Fig. 3.—Isotherms of *n*-heptane at 25° for graphites of 0.46% and less than 0.004% ash. The experimental values shown extend only to relative pressures of 0.95. The data, however, extend to pressures of 0.985, where the amount of gas adsorbed is double the maximum of 15×10^{14} molecules cm.$^{-2}$ shown in this figure, or 30×10^{14} molecules cm.$^{-2}$.

cussed in an earlier paper.[4] Then, from the relationship[16]

$$\gamma_{S_0} = \gamma_{SL} + \gamma_L \cos \theta \qquad (5)$$

the energy relations expressed by equations 1, 2 and 3 are

$$S_{S/L} = \gamma_L (1 - \cos \theta) + \frac{RT}{V_M \Sigma} \int_0^{p_0} \frac{v}{p} dp \qquad (6)$$

$$f_{E(SL)} = \gamma \cos \theta + \frac{RT}{V_M \Sigma} \int_0^{p_0} \frac{v}{p} dp \qquad (7)$$

and

$$w_{A(SL)} = \gamma_L (1 + \cos \theta) + \frac{RT}{V_M \Sigma} \int_0^{p_0} \frac{v}{p} dp \qquad (8)$$

Since the isotherm obtained showed the adsorption of such large amounts of water near the saturation pressure, the contact angle was redetermined with even more care than in the earlier work, but with the same apparatus. Inside the cover, filter papers were suspended in dishes of water, and the cover of the apparatus was sealed with tape and wax. This procedure should ensure the saturation of the atmosphere with water vapor. A half hour after the tape was sealed, the contact angle was found to be 85.7°

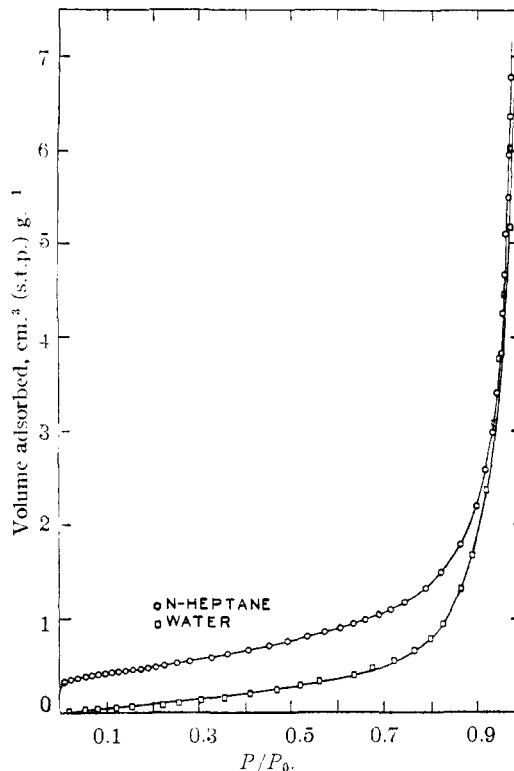(16) W. D. Harkins and H. K. Livingston, *J. Chem. Phys.*, **10**, 342 (1942).

Fig. 4.—Isotherms for water and *n*-heptane at 25° on graphite with 0.46% ash. At a given value of the relative pressure more molecules of *n*-heptane than of water molecules are adsorbed. This is in marked contrast to the isotherms obtained with the same vapors when the contact angles of both liquids are zero. In such a case, more molecules of water than of heptane are adsorbed.

(almost the same as the 85.5° of Fowkes and Harkins) and remained constant for six hours. The same angle was obtained, whether the liquid was advancing or receding, over the surface. Thus, the angle must be the equilibrium angle under the conditions used, *i. e.*, water and air in contact with graphite. Since the adsorption of nitrogen and oxygen is so small at room temperature, it is doubtful whether the value observed for the contact angle is seriously affected by the presence of these gases.

In Table II, *A* summarizes the free energy changes for the film of water, while *B* gives the results for *n*-heptane. For purposes of comparison, the values of Boyd and Livingston for graphite containing 10% ash are also given.

All the values in Table II, except that for π_e, depend upon the value of the contact angle used. The lowest value of the contact angle of water against graphite thus far reported in the literature is that of Rehbinder and associates,[17] who obtained values ranging from 55 to 60°. The application of these values of the contact angle would affect the magnitudes of the spreading

(17) P. Rehbinder, M. Lipetz, M. Rimskaja and A. Taubman, *Kolloid Z.*, **65**, 268 (1933).

Graphite (ash content), %	π_e	$S_{L/S}$	$f_{E(SL)}$	$w_{A(SL)}$
	A.	Water		
10	56	−10	62	134
0.46	19	−47	25	97
Less than 0.004	19	−47	25	97
	B.	Normal Heptane		
10	60	60	80	100
0.46	69	69	89	109
Less than 0.004	63	63	83	103

coefficient, free energy of emersion, and work of adhesion for the two pure graphites but would not change the negative sign of the spreading coefficient. In order that the spreading coefficient should change sign for the two pure graphites, it would be necessary for the contact angle to be less than 42°.

The relations observed with water, are somewhat unexpected; i. e., a contact angle not zero, the adsorption of more than a monomolecular film, presumably not caused by capillary condensation, and the low value of the decrease of free surface energy. While all of these facts are compatible with the known thermodynamic relationships, it is difficult to conceive from a molecular point of view, how a thick film can be formed which is not duplex, i. e., the contact angle equal to zero. It is hoped that when our calorimetric study of the water–graphite system is completed,

additional facts may aid in clarifying the picture of the water-graphite system. For this reason, a detailed discussion is deferred until the facts become available.

Summary

1. The adsorption isotherms of water and n-heptane have been determined on two samples of graphite containing 0.46% ash by weight and less than 0.004% ash by weight. The latter sample had also been treated so that the surface should be free of any oxygen–carbon "complex."

2. The films of water became thicker than a monolayer at relative pressures above 0.9, attaining an average of thickness of three layers at the maximum pressures measured, 0.98.

3. A detailed study of the curve for low values of p/p_0 show that the adsorption curves are convex rather than concave to the pressure axis. The curves, however, flatten out when only a small fraction of a tightly packed monomolecular film has been adsorbed, whereas, for hydrophilic solids this occurs when enough gas to form a monomolecular layer has been adsorbed.

4. The spreading coefficient free energy of emersion and work of adhesion of water are found to be −47, 25 and 97 ergs cm.$^{-2}$, respectively, while for n-heptane the corresponding values are 69, 89 and 109 ergs cm.$^{-2}$.

5. The X-ray diffraction patterns of clean graphite were found to be identical with those for the solid saturated with water and n-heptane. The cell constants found are $a_0 = 2.455$ Å. and $c_0 = 6.70$ Å.
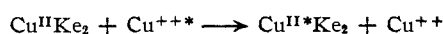
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The Stability of Chelate Compounds. III. Exchange Reactions of Copper Chelate Compounds

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In previous papers of this series[1a,2] experiments were reported in which the relative stabilities of a series of copper chelate compounds were determined on the basis of measurements of chemical equilibrium. The present paper contains a report of experiments designed to determine the relative stabilities of the same series of copper chelates from kinetic measurements of the rate of their reactions. The reaction selected was the exchange reaction between the chelate and copper ion, the copper ion being marked by containing a radioactive copper isotope

$$Cu^{II}Ke_2 + Cu^{++*} \longrightarrow Cu^{II}*Ke_2 + Cu^{++}$$

indicated by the superscribed asterisk. Ke represents one equivalent of chelating substance usually filling two coördination positions of the metal.

A number of scattered experiments of this type are already in the literature[3,4,5,6] usually in connection with other problems, and no exchange between metal ions and a chelated metal has been studied in sufficient detail to determine its kinetics.

Experimental

Chelate Compounds.—The chelate compounds were made by the general methods of Pfeiffer.[7] Several not

(1) Abstracted from the thesis submitted by R. B. Duffield to the University of California, Berkeley, in 1943, in partial fulfillment of the requirements for the Ph.D. degree.

(1a) Calvin and Wilson, This Journal, **67**, 2003 (1945).

(2) Calvin and Bailes, **68**, May (1946).

(3) Long, This Journal, **61**, 570 (1939); **63**, 1353 (1941).

(4) Flagg, ibid., **63**, 557 (1941).

(5) Ruben, Kamen and Frankel, J. Phys. Chem., **46**, 710 (1942).

(6) Ruben, Kamen, Allen and Nahinsky, This Journal, **64**, 2297 (1942).

(7) Pfeiffer, Breith, Lubbs and Tsumaki, Ann., **503**, 84 (1933).