and appeared to be a hydrate; a sample dried at 40° and 1 mm. analyzed correctly for a hemihydrate.

Anal. Calcd. for $C_{17}H_{25}ON_3 \cdot 2HCl \cdot 0.5H_2O$: C, 55.28; H, 7.64; N, 11.38; Cl, 19.20. Found: C, 55.76; H, 7.36; N, 11.66; Cl, 19.12.

A mixed m. p. of this sample of X with X prepared by alkylation (equation 2; Table II, m. p. 177–179°) was 172–173°.

The dipicrate prepared from this sample of X, recrystallized from 4:1 ethanol–acetone and dried at 70° and 1 mm. had a m. p. of 137–138° (with previous softening) and was not depressed on mixture with X dipicrate prepared from the alkylation product (equation 2; Table III, m. p. 140.5–141°).

Anal. Calcd. for $C_{29}H_{31}O_{15}N_9$: C, 46.71; H, 4.19. Found: C, 46.76; H, 4.44.

Summary

A number of derivatives of 6-methoxy-8-aminoquinoline have been prepared which are substituted on the 8-amino group by primary or secondary aminoalkyl side chains. A rearrangement proceeding through a tertiary ethyleneimine intermediate has been observed to occur in the alkylation of 6-methoxy-8-aminoquinoline with 1-alkylamino-2-chloropropane hydrochlorides (equation 1). 6-Methoxy-8-(alkylaminoalkylamino)-quinolines of known structure have been synthesized by first attaching primary aminoalkyl side chains to the 8-amino group through intermediate phthalimido compounds, and then reductively alkylating the primary aliphatic amino group with acetone and with cyclohexanone in the presence of Adams platinum catalyst and hydrogen. A 6-methoxy-8-(nitroalkylamino)-quinoline also has been reductively alkylated with these ketones under the same conditions.

RECEIVED AUGUST 26, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Adsorption of Water Vapor on Activated Charcoal

BY EDWIN O. WIIG AND A. J. JUHOLA[1]

There will be presented in the papers that follow a method for measuring pore size distribution of charcoal which assumes that water on charcoal is held by capillary condensation. The main support for this assumption is that the pronounced hysteresis in the adsorption isotherm can best be accounted for by explanations based on the capillary condensation theory.[2,3,4,5] The results reported in this paper of studies of the changes in the density of adsorbed water with change in relative pressure and of the changes in the dimensions of an activated charcoal during adsorption and desorption lend further support to this theory.

I. Linear Expansion of Charcoal

The change in length of charcoal rods as water and also various other vapors are adsorbed has been studied by numerous investigators.[6] In most of these investigations, which will be discussed later, relatively large carbon rods were employed whereas in the present work an activated gas mask adsorbent was used.

This charcoal, N-19, was prepared from hardwood sawdust, zinc chloride activated, extruded as rods 1/16 inch diameter, calcined at 600°, washed and calcined at 850°. It had an ash content of 0.2%, an apparent density of 0.48, a particle density of 0.80, a carbon density (by helium) of 2.09 and a surface area of 1300–1700 sq. m./g.

Determination of Linear Expansion of Charcoal.—The principal part of the apparatus for measuring the linear expansion of charcoal during adsorption and desorption is shown in Fig. 1. The inner tube A is filled with the extruded charcoal rods, 2–5 mm. long and 1.6 mm. diameter, placed end to end. The ends of each granule were squared off with emery cloth before being placed in the tube. B is a short piece of wire with squared-off ends placed on top of the charcoal column. Changes in length of the column during adsorption and desorption were observed by following with a cathetometer the movement of the upper edge of the wire with respect to a reference mark on the inner tube. The length of the charcoal column was 960 mm. and its weight was 0.920 g.

The tube assembly, which was weighed at intervals to determine the water content, was attached to an apparatus similar to that shown in Fig. 4 for the necessary evacuation of the sample, adsorption, desorption, measurement of the relative vapor pressure, etc. The charcoal column was thermostated at 24.4° with a water-cooled jacket.

Fig. 1.—Apparatus for measuring linear expansion of charcoal.

Results

The per cent. change in length of the charcoal column as a function of the relative pressure is shown in Fig. 2. It will be observed that, starting with dry char, as the humidity is increased the charcoal first contracts and then at $p/p_0 \sim 0.68$ begins to expand

---

(1) Present address: The Barrett Division, Allied Chemical and Dye Corp., Philadelphia, Pennsylvania.

(2) E. O. Kraemer in H. S. Taylor's "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1931. Chap. XX.

(3) McBain, THIS JOURNAL, **57**, 699 (1935).

(4) Cohan, *ibid.*, **66**, 98 (1944); includes an excellent bibliography.

(5) Emmett and DeWitt, *ibid.*, **65**, 1253 (1943); Emmett and Anderson, *ibid.*, **67**, 1492 (1945).

(6) Meehan, *Proc. Roy. Soc.* (*London*), **115A**, 199 (1927); Bangham and Fakhoury, *ibid.*, **A130**, 81 (1930); *J. Chem. Soc.*, 1324, (1931); Bangham, Fakhoury and Mohamed, *Proc. Roy. Soc.*, **A138**, 162 (1932); **A147**, 152 (1934); **A147**, 175 (1934); Bangham and Razook, *ibid.*, **A166**, 572 (1938); McBain, Porter and Sessions, THIS JOURNAL, **55**, 2294 (1933); Haines and McIntosh, *J. Chem. Phys.*, **15**, 28 (1947); Schwab and Karkalos, *Z. Elektrochem.*, **47**, 345 (1941).

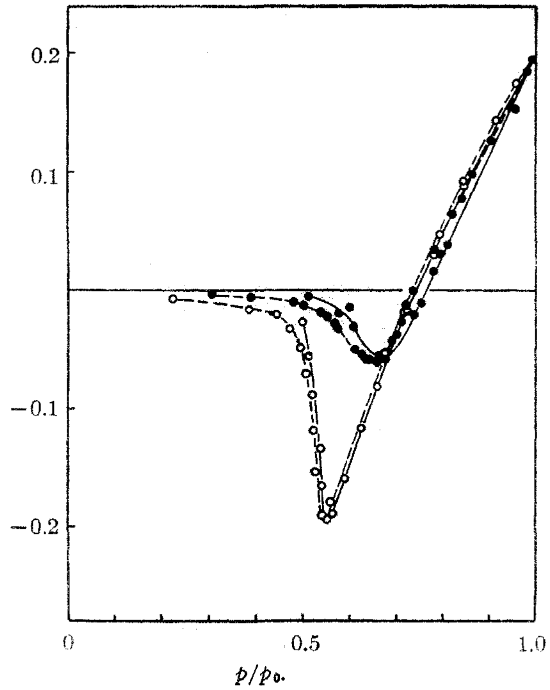

Fig. 2.—Percentage linear expansion L of charcoal N-19 as a function of the relative vapor pressure of adsorbed water: ●, adsorption points; ○, desorption points; solid curve, first adsorption and desorption; broken line curve, second adsorption and desorption.

until at $p/p_0 \sim 1$ it is 0.2% longer than at the start. Determinations on the adsorption wave were repeated to make certain the contraction was real. Contraction was again observed but the second set of determinations (broken line curve) did not quite coincide with the first. This displacement of the curve to the left may be due to the same cause as the displacement to the left of the second and subsequent adsorption curves of isotherms as in Fig. 5. On desorption a much greater contraction is obtained.

Except for the results of Haines and McIntosh,[6] which appeared while this work was in progress and with which the present observations are in essential agreement, the contraction obtained here would seem to disagree with the expansion noted by earlier workers. The experimental conditions are quite different, however, and appear to account for the differences in behavior. Most of the charcoals were not as highly activated as are modern chars. Meehan's[5] charcoal was prepared from three-inch cubes of yellow pine which were slowly dried and then heated uniformly for approximately four hours in a charcoal packed cylinder having small gas vents in its ends. After gradual cooling the charcoal so obtained was trimmed to approximately two-inch cubes. Some of the experiments of Bangham,[6] *et al.*, were carried out with rods cut from this charcoal. It would appear doubtful that such cubes could be completely carbonized near the center. Any oxygen structure remaining in the charcoal might easily produce immediate swelling as in wood itself. The oft quoted observation of Bangham and Fakhoury[6] that the first traces of water admitted to their char caused a marked expansion was made on an 80 × 8 × 8 mm. rod of German willow charcoal of pre-World War I manufacture. Again there is no way of knowing how thoroughly carbonized such charcoal might be. This charcoal was untreated except that between experiments it was "submitted to prolonged vacuum-heating at 220°" in the extensometer. On heating one of Meehan's charcoals to 1000° Bangham observed on adsorbing methanol at 20° that no measurable expansion occurred until 0.059 g. of methanol per g. of carbon had been adsorbed, then marked expansion set in at 0.07 g. per g., followed by a steady increase thereafter. This is in contrast with greater expansion on less rigorously treated samples.

McBain, Porter and Sessions[6] report only expansion for a rod (60 mm. long × 25 mm. diameter) of activated sugar charcoal. However, in the lower relative pressure range, where contraction was observed in the present investigation, these workers chose to hold the water vapor pressure constant and heated the charcoal to 37–61° to reduce the relative humidity. Since the surface tension changes with temperature, any contraction that might have occurred at lower temperatures may have been missed. Bangham observed no expansion by water vapor absorbed at 100° and a decrease in expansion by methanol at 50° compared to 0°. Also, Haines and McIntosh[6] found an expansion with dimehtyl ether at 20° but an initial contraction with a more sensitive extensometer at 6.5°. Using relatively large rods of a zinc chloride activated charcoal similar to that employed here, Haines and McIntosh observed no change in length with increase in water vapor pressure until $p/p_0 = 0.75$ was reached, after which expansion increased regularly. On subsequent desorption contraction below the original length and then expansion to the original length occurred as reported here. However, in a footnote they report that with their more sensitive electrical condenser arrangement for measuring the change in length of the charcoal rod a slight initial *contraction* was observed in the lower relative pressure range, analogous to the larger contraction in the present work.

The thermal effects which Haines and McIntosh observed on admitting vapors to charcoal might also contribute to the difference in behavior of the large rods of other investigators and the very small rods used here. With long relatively thick rods the vapor penetration must advance crosswise radially. The thermal effects should consequently be lengthwise. If the temperature is lower toward the center of the rod then perhaps contraction sets in crosswise and expansion, due to the higher temperature, lengthwise. Eventually the rod should reach equilibrium but the attainment of equilibrium between a radial contraction and a lengthwise expansion might be slow, especially when one considers that charcoal is, as X-ray data indicate,[7] probably composed of small graphite platelets. At any rate, in the second condenser arrangement of Haines and McIntosh, where the thermal effect was smaller, a slight contraction rather than expansion was observed with water.

II. The Density of Adsorbed Water

The density of water adsorbed on silica gel has been reported by Ewing and Spurway[8] to vary from 0.5408 for larger amounts of water to 1.0285 for smaller quantities. Danforth and DeVries[9] found densities for carbon tetrachloride adsorbed on activated charcoal which began at about 1.9, fell to a minimum of 1.36 and then rose to 1.58 as the vapor pressure was increased. Similar results were obtained with acetone. Morrison and McIntosh[10] have recently reported the density of water adsorbed on several activated charcoals. Their values, however, are quite different from those reported here.

Two charcoals were used in the present work: N-19, on which the linear expansion measurements were made; N-291-AY-1, a zinc chloride activated wood charcoal which was extruded through a seven-inch die in one step of its preparation and later crushed to small particles. The pore size distribution, etc., of this char are reported in detail in the following paper.

Determination of the Density of Adsorbed Water.—In principle the determination consisted of measuring by helium displacement the volume of a known weight of dry charcoal followed by similar volume measurements with varying amounts of adsorbed water.

The charcoal (16–20 mesh) contained in adsorption tube T, Fig. 3, was degassed at 360° for several hours, stopcock A closed and the thermostat water jacket J placed around T. In the case of charcoal N-291-AY-1 the adsorption tube had a volume of about 32 cc. and held 7.380 g. char. To obtain much greater accuracy the sample was increased tenfold for N-19. Gas buret B, with the mercury level at one of the constrictions between the bulbs, and the system to A were filled with helium to nearly atmospheric pressure, usually about 740 mm. as measured by mercury manometers 1 and 3. The pressure on both sides of the dibutyl phthalate null manometer 5 was adjusted to that of B. Stopcock A was opened to admit helium to the charcoal and the mercury level in B raised to increase the helium pressure to the initial pressure as determined by the null manometer. After equilibrium was reached, mercury was drained from B until the initial level was obtained and the mercury weighed. The volume of the weighed mercury was the volume of T, with or without charcoal as the case might be.

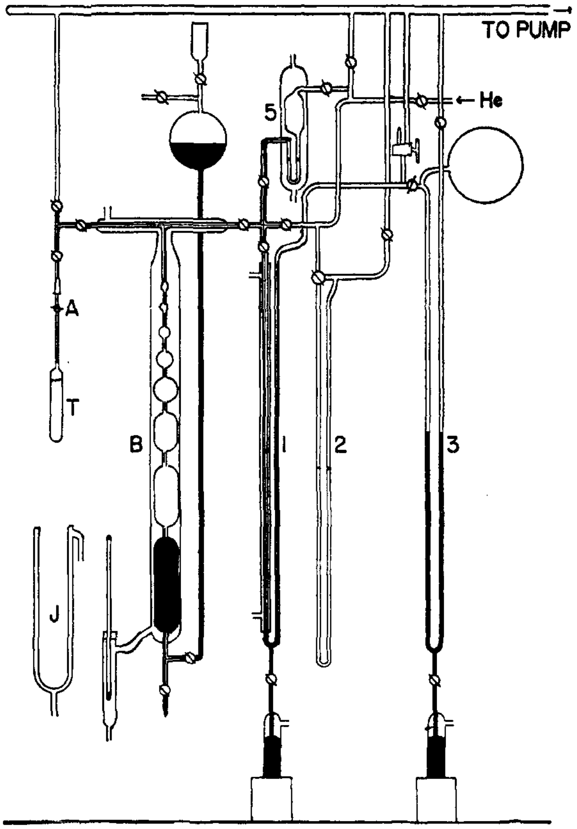

Fig. 3.—Apparatus for measuring apparent volume of adsorbed water.

When the charcoal contains adsorbed water a slightly different procedure was followed since a vapor pressure correction was necessary in the calculations. The water vapor was allowed to expand from T into B and over to dibutyl phthalate manometer 2, where its pressure was measured after attainment of equilibrium. Dead space corrections were negligible. The buret system to stopcock A was evacuated and from this point on the determination was the same as for dry char. Tube T contained a fine capillary below A which prevented diffusion of water vapor through the helium into B. The vapor pressure correction was introduced into the calculations through the relationship

$$V_t = \frac{P}{P - p} V_h$$

where P is the helium pressure, p the vapor pressure of the adsorbed water, V_h the volume of weighed mercury, and V_t the volume of tube T. An indication of the accuracy of the measurements is given by two sets of experiments with smaller than 16 mesh Pyrex glass particles in place of charcoal in tube T. The volume by helium displacement of, *e. g.*, 2.5 and 5.0 g. water on the glass

---

(7) Clark and Johnstone, O. S. R. D. Formal Report, Dec. 9, 1942; Hofman, Ragoss and Sinkel, *Kolloid Z.*, **96**, 231 (1941).

(8) Ewing and Spurway, THIS JOURNAL, **52**, 4635 (1930).

(9) Danforth and DeVries, *ibid.*, **61**, 873 (1939).

(10) Morrison and McIntosh, *Canadian J. Res.*, **24**, 137 (1946).

gave 0.997 for the density of water at 24° as compared to the accepted value of 0.9973.

Determination of Water Adsorption Isotherms.—The apparatus for determining the isotherms, which are needed in connection with both the density of adsorbed water and the linear expansion of charcoal, is shown in Fig. 4. Manometers M and N contained dibutyl phthalate, M measured P, the vapor pressure of adsorbed water, and N measured P_0, the saturation vapor pressure of water. A and C were three-way stopcocks with one of the outlets sealed to a capillary tube as shown in the diagram. During evacuation the stopcocks were turned so that gases passed through the larger outlets while during adsorption or desorption the stopcocks were turned so the water vapor passed through the capillaries. The purpose of the capillaries was to slow down the adsorption or desorption process sufficiently so that the pressure of the vapor surrounding the charcoal was not greatly different from the equilibrium pressure. The amount of water adsorbed was determined by weighing tube T. Flask B, containing water, and T were submerged in a waterbath maintained at about 24°, slightly below room temperature. While precautions were taken to prevent rapid changes in temperature, no effort was made to keep the bath at exactly constant temperature, since Coolidge[11] has shown that the water adsorption isotherm is not affected by temperature changes near room temperature.

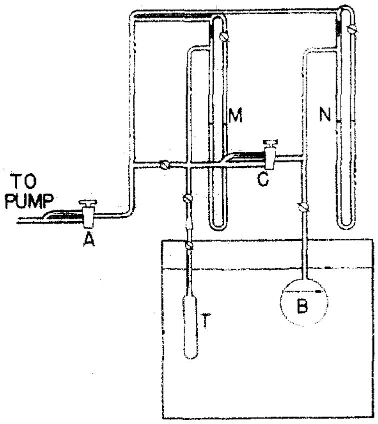

Fig. 4.—Apparatus for measuring water adsorption.

Results

For the two charcoals studied the water adsorption isotherm is presented in Figs. 5 and 6, the apparent volume of adsorbed water in Figs. 7 and 8 and the density of adsorbed water in Table I. The latter, consistently less than unity, is in disagreement with the values 1.01 to 1.16, 0.95 to 1.04, 0.99 to 1.15 and 0.98 to 1.17 obtained by Morrison and McIntosh on four different charcoals but in line with their values of 0.95, 0.94 and 0.93 at 100% relative humidity. The present data would appear to be reliable; the high results mentioned could be caused by either or both of two possible sources of error.[12] At first sight it might appear strange that the volume (or density) of adsorbed water does not reach the normal

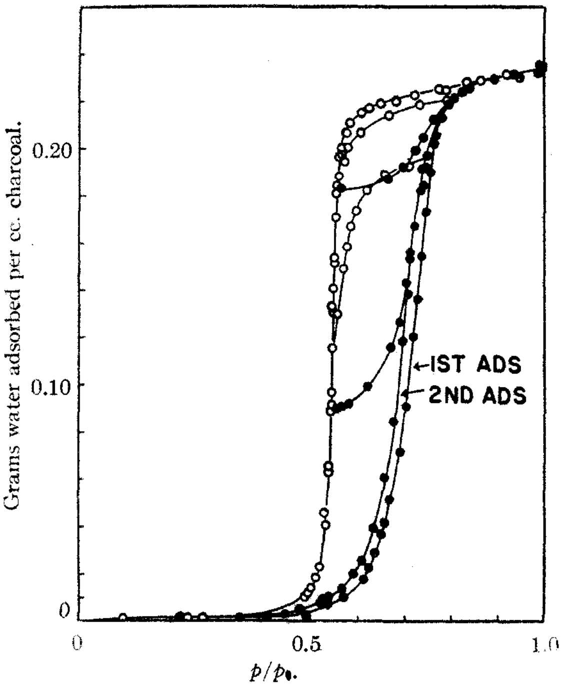

Fig. 5.—Water adsorption isotherm, charcoal N291-AY-1: ●, adsorption; ○, desorption.

TABLE I

DENSITY OF ADSORBED WATER ON THE ADSORPTION AND DESORPTION BRANCHES OF THE ISOTHERM

Relative pressure	N-291-AY-1 Adsorp.	N-291-AY-1 Desorp.	N-19 Adsorp.	N-19 Desorp.
0.35				0.90
.40			0.79	.82
.50		0.85	.82	.85
.60	0.90	.90	.85	.89
.70	.91	.91	.89	.91
.80	.92	.92	.91	.91
.90	.93	.93	.92	.92
.99	.93	.93	.92	.92

---

[11] Coolidge, THIS JOURNAL, 49, 708 (1927).

[12] Small amounts of acid spray from the sulfuric acid solutions (stirred to hasten equilibrium) which were used to control the water vapor pressure might, as suggested by Emmett (private communication) have contaminated the water adsorbed on the charcoal. A more likely source of error is to be found in the method used to determine the volume of the adsorbed water by helium displacement. In making this determination helium, at high pressure and mixed with water vapor of the same partial pressure as that over the charcoal, was admitted to the charcoal tube. This has the effect of yielding a total water vapor pressure in the charcoal tube greater than the original partial pressure. Some of this extra water vapor should be adsorbed, resulting in a somewhat greater pressure drop, hence a smaller volume for the adsorbed water and an increased density. Though the system was open for twenty-four hours to allow attainment of equilibrium, the back diffusion of water vapor through two stopcocks and tubing filled with helium at relatively high pressure would be very slow. As the water content of a given char increases the effect of the extra pressure decrease will be smaller and the density will decrease, as was observed in general. *Cf.* Tuck, McIntosh and Maass, *Canadian J. Res.*, **26**, 20 (1948).

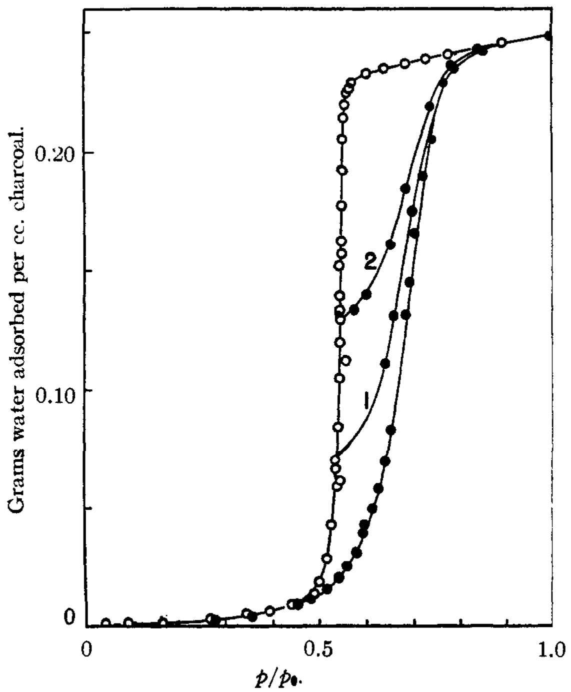

Fig. 6.—Water adsorption isotherm for charcoal N-19: ● adsorption; ○ desorption; 1 and 2 scanning curves.

value for liquid water at P_0. However, since the water molecules in general cannot exactly fit the pores, there will be larger voids between water molecules in pores than are present in the normal liquid state. Since these chars have a large volume of small pores, the voids prevent the attainment of the normal density.

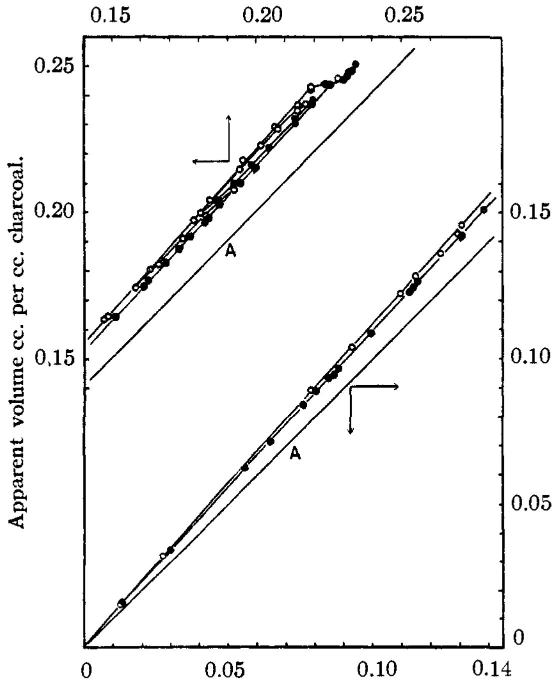

Fig. 7.—Apparent volume of adsorbed water at 24° on charcoal N291: ●, adsorption points; ○, desorption points; curve A, normal volume of water.

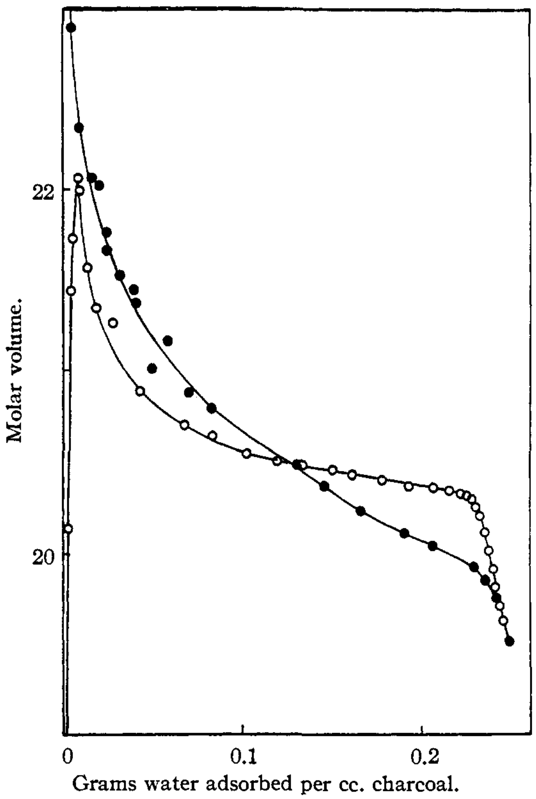

Fig. 8.—Molar volume of adsorbed water in equilibrium with vapor pressures on the main hysteresis loop of the isotherm: ●, adsorption; ○, desorption; charcoal N-19.

Discussion

The results of the measurements of the linear expansion of charcoal suggest that the expansion is a function of the relative vapor pressure and the weight of adsorbed water. It was found that the experimental data approximately obey the equation

$$L = kw(\ln p/P_0 - B) \qquad (1)$$

where L is the per cent. linear expansion, B is $\ln p_a/P_0$ where p_a is the vapor pressure when $L = 0$ (*i. e.*, where L changes from negative to positive), w is the weight of adsorbed water per cc. of charcoal and k is a constant. When the quantity $w(\ln p/P_0 - B)$ is plotted against L as shown in Fig. 9, an essentially straight line is obtained, the slope of which gives k a value of 2.8. The greatest deviation from this equation, indicated by the dotted line curve, occurs during contraction on adsorption at low partial pressures; the rest of the experimental points obey the equation quite well.

The contraction of the carbon structure can readily be accounted for by the capillary condensation theory which requires a contraction pressure or tension on the adsorbent. When the latter predominates—as in the intermediate pressure

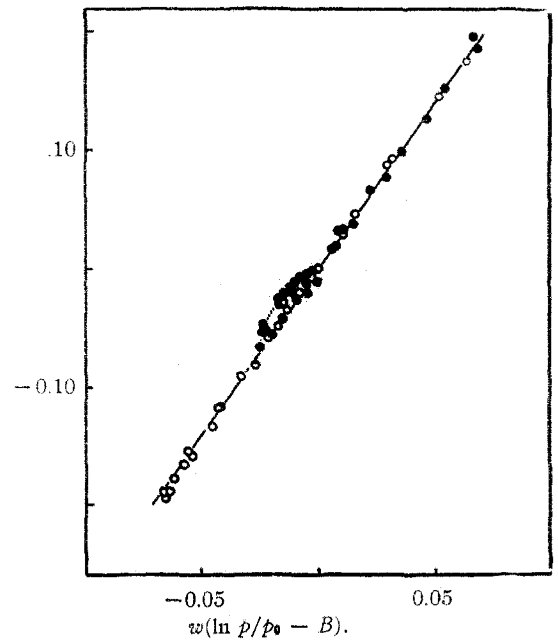

Fig. 9.—Percentage linear expansion L of charcoal as function of logarithm of relative vapor pressure and weight of adsorbed water w per cc. of charcoal: B constant; ●, adsorption points; ○, desorption points.

range, in which the pores are filled but in which the curvature of the menisci is still appreciable—contraction results but, as the tension is reduced, owing to decreased curvature of the menisci, the swelling pressure predominates and a net expansion results which increases to P_0. The constant B may then be considered due to the swelling pressure similar to the swelling of any solid by a liquid.

A helpful picture which fits in with the data in the succeeding papers is as follows. The water molecules in pores behave as rigid spheres and due to the relative size of the pores as compared to the water molecules, there are larger voids between the molecules than exist in the normal liquid phase. Owing to their mutual attraction (hydrogen bonding), the molecules tend to squeeze into these voids and the result is an outward pressure exerted against the pore wall which appears as expansion of the charcoal. When the meniscus of the condensed water is in small pores, the meniscus exerts a negative pressure on the liquid which partially balances the mutual attraction between the molecules and, therefore, they do not tend to squeeze into the voids. The result is that the charcoal does not expand but rather contracts. As more water is adsorbed, the meniscus moves to larger pores, thereby decreasing the negative pressure (or increasing the hydrogen bonding since the molecules approach each other closer), and as a result the charcoal expands. It follows that if there were no voids between the water molecules there would be no expansion of the charcoal at the higher relative pressures. The length of the charcoal column during adsorption would pass through a minimum and come to its normal length at saturation.

According to the capillary rise equation a liquid is under a tension or negative pressure P which varies inversely with the pore diameter D

$$P = -\frac{4\sigma \cos \theta}{D} \qquad (2)$$

where σ is the surface tension and θ the contact angle of the liquid with the wall. Assuming adsorption of water by capillary condensation and the validity of the Kelvin equation

$$D = \frac{4V\sigma \cos \theta}{RT \ln P_0/p} \qquad (3)$$

where V is the molar volume of adsorbed water, and substituting for D in equation (2) one obtains

$$P = \frac{RT}{V} \ln p/P_0 \qquad (4)$$

During the contraction of charcoal the pressure on the carbon is equal to the pressure on the adsorbed liquid, equation (4), with the sign changed. If the per cent. linear expansion, L, is directly proportional to this negative pressure and to the amount of water adsorbed, then at constant temperature

$$L = k'\frac{w}{V} \ln p/P_0 \qquad (5)$$

This differs from equation (1) in that it contains the variable V and constant B is lacking. In the adsorbed water density studies it was observed that the maximum variation of V was less than 5%, hence for approximate calculations V may be considered constant. If then constant B is attributed to the void effect mentioned earlier, equation (1) has some theoretical foundation.

If the water adsorption isotherms of the two charcoals in Figs. 5 and 6 are compared with the volume curves of adsorbed water on the same char in Figs. 7 and 8, it is evident that over nearly the complete range the volume (or density) is some function of the relative pressure. According to equation (4) any change in the relative pressure produces a change in pressure P on the adsorbed liquid. The change in volume per unit volume of adsorbed water depends on this change in pressure on the liquid and the coefficient of compressibility β

$$\beta(P_2 - P_1) = -\frac{v_2 - v_1}{v_1} \qquad (6)$$

By proper combination of equations (4) and (6) one obtains

$$\beta RT\left(\frac{1}{V_2} \ln \frac{p_2}{P_0} - \frac{1}{V_1} \ln \frac{p_1}{P_0}\right) = -\frac{v_2 - v_1}{v_1} \qquad (7)$$

Values of β are available only for positive pressures. Since β increases with increasing tension or negative pressure, this change in β was estimated from calculations based on the van der Waals equation, using a = 7003 and b = 0.811, and on equation (6). In making these calculations it was assumed that the van der Waal's P–V relationship would be an extension into the negative pressure range of its known behavior in the positive pressure range.

To test the relationship in (7) on charcoal N-291-AY-1 the value of the right side of the equation was calculated from the curves in Fig. 7. For a given weight of adsorbed water the volume on the desorption curve was taken as v_2 and on the adsorption curve as v_1. This gave the change in volume per unit volume when the relative vapor pressure was decreased from p_1/P_0 on the adsorption side of the isotherm to p_2/P_0 on the desorption side. The molar volumes V_1 and V_2 were calculated from v_1 and v_2, respectively.

In Fig. 10 the calculated values of the right side of equation (7) are presented graphically by the lower curve and the left side of the equation by the upper curve. Although the experimental accuracy of the volume measurements, shown by the vertical lines through the experimental points, does not warrant a quantitative comparison, the similarity in shape of the two curves does give a qualitative indication that equation (7) may be essentially correct.

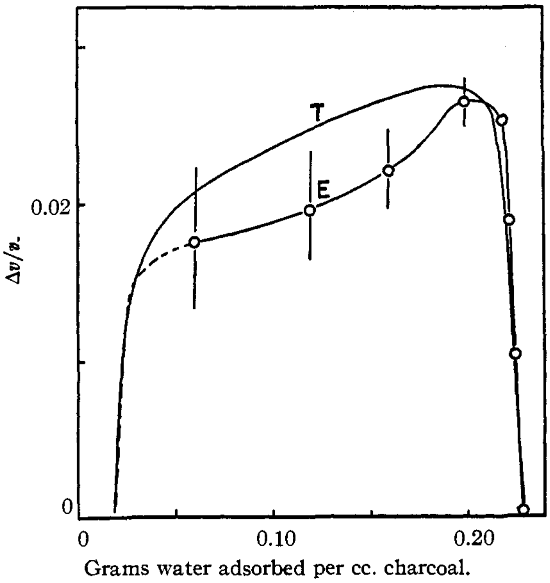

Fig. 10.—Change in volume per unit volume $\Delta v/v$ of the apparent volume of adsorbed water as observed experimentally and calculated from the isotherm: E, experimental; T, calculated; charcoal N291-AY-1.

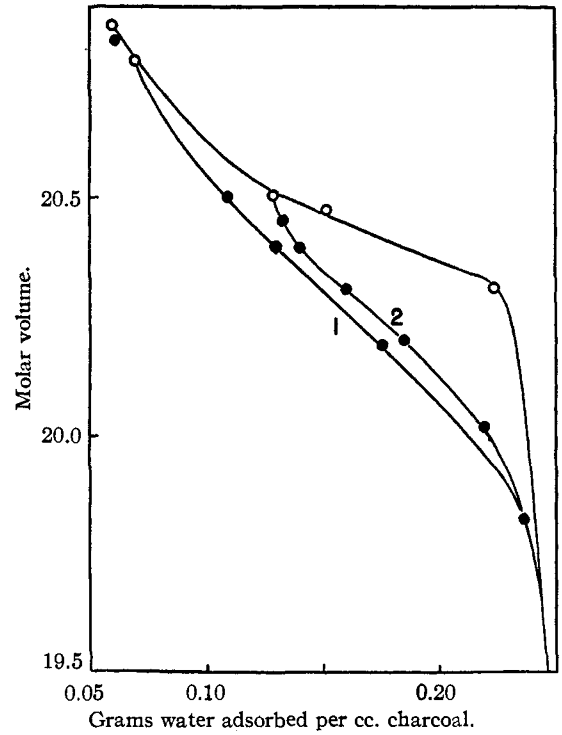

Fig. 11.—Molar volume of adsorbed water in equilibrium with relative vapor pressures on the main desorption and two scanning curves of the isotherm: ●, adsorption; O, desorption; charcoal N-19.

The water density data obtained on N-19 were treated in a somewhat different manner. Figure 11 shows the molar volume of adsorbed water in equilibrium with relative water vapor pressures on the main desorption branch and the two scanning curves of the isotherm (Fig. 6) as a function of weight of water adsorbed. In Fig. 12 the solid line curves are the accumulated change in volume per unit volume of adsorbed water, starting at saturation in Fig. 11 and proceeding to lower moisture contents along the desorption and scanning curves 1 and 2. The broken line curves were calculated from the left side of equation (7) as for

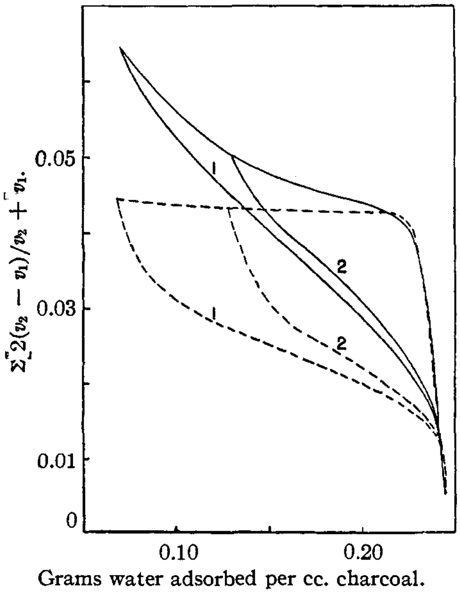

Fig. 12.—Change in volume per unit volume of adsorbed water in equilibrium with the desorption side and scanning curves of the isotherm: solid curves, experimental; broken line curves, theoretical; charcoal N-19.

charcoal N-291-AY-1. The agreement is good between the theoretical and experimental volume change in the range 0.21 to 0.25 g. water adsorbed per cc. charcoal but at lower moisture contents the experimental and theoretical curves begin to diverge.

The choice of N-19 for this study may have been an unfortunate one since an extra variable, which apparently did not exist in N-291-AY-1, appears to influence the molar volume of adsorbed water on this charcoal. For N-291-AY-1 the molar volume on the desorption side for a given weight of adsorbed water was always found to be greater than on the adsorption side. On N-19, however, the molar volume on adsorption at moisture contents below 0.13 g. was found to be greater than on the desorption side, as shown by the curves in Fig. 8. This crossing of the two curves may be attributed to the water adsorbed below 0.01 g. of moisture content, desorption side, having a very low molar volume. It appears that on adsorption, as more and more water is adsorbed, the previously adsorbed water molecules rearrange themselves into a closer packed state which is retained on desorption.

In order to avoid the complicating effects due to this rearrangement of the water molecules in the determination of the effect of the relative pressure on the molar volume, calculations were made only with data from the main desorption branch of the hysteresis loop and the two scanning curves. In Fig. 13 the differences between the curves in Fig. 12 were plotted against weight of water adsorbed in an attempt to cancel out the contribution of the submicro volume (which is apparently the volume of voids between water molecules in small pores) to the molar volume. Curve 1 in Fig. 13 was obtained by plotting the difference between scanning curve 1 and its desorption curve in Fig. 12 against the weight of water adsorbed. The other curves were obtained similarly. These curves represent the change in volume per unit volume for a given weight of adsorbed water when the relative pressure is increased from points on the desorption branch of the isotherm to points on the scanning curves. For N-19, Fig. 13, as for N-291-AY-1 in Fig. 10, a similarity exists between the theoretical and experimental curves, and again the magnitudes of the theoretical values are greater. These studies would appear to show that a definite relationship does exist between the relative vapor pressure and the molar volume of adsorbed water but the exact quantitative relation is complicated by the factors discussed above.

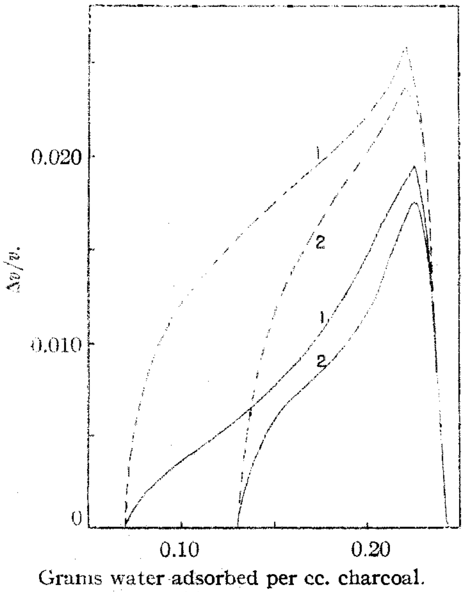

Fig. 13.—Change in volume per unit volume of the adsorbed water when the relative vapor pressure is decreased from the adsorption to the desorption side of the isotherm: solid curves, experimental; broken line curves, theoretical, charcoal N-19.

The evidence presented in this paper for the initial contraction of charcoal on exposure to water vapor, for a density of adsorbed water close to that of liquid water and for the similarity of experimental adsorbed water volume relationships with those calculated on the basis of capillary condensation would seem to constitute rather strong support for the capillary condensation theory. Additional support for the theory has recently been claimed by Broad and Foster[13] through their observation that isotherms of water and deuterium oxide on charcoal are identical (within 3%).

Acknowledgment.—The authors wish to express their thanks to the Chemical Corps Technical Command for sponsoring this work and in particular for a fellowship held by one of us (A. J. J.). They are also indebted to Professor T. L. Hill for valuable suggestions.

Summary

Charcoal exposed to water vapor has been found to undergo an initial contraction followed by a subsequent expansion as the vapor pressure is increased. The per cent. linear expansion of the charcoal has been shown to be a function of the relative vapor pressure and the amount of water adsorbed. This relationship is expressed approximately by the equation

$$L = k'w\,(\ln p/P_0 - B)$$

which was partially justified on theoretical grounds by the capillary condensation theory.

The change in the volume per unit volume of adsorbed water was found to vary with the relative vapor pressure qualitatively according to a relationship derived from theoretical considerations based on the capillary condensation theory. For the density of water adsorbed on charcoal a value slightly less than unity was obtained.

RECEIVED JULY 23, 1948

---

(13) Broad and Foster, *J. Chem. Soc.*, 372 (1945).