On the Catalytic Action of Japanese Acid Earth. XII. The Relation between the Catalytic Activity and Adsorption. II. The Adsorption Isotherms of Water and Acetonitrile for the Earth.

By Koshiro ISHIMURA.

(Received May 14, 1941.)

Naphthalene produces β,β'-dinaphthyl when mixed with dry powdered Japanese acid earth and heated at about 300°C.(1) In this catalytic action, neutral substances containing oxygen such as water, alcohols, ethers and ketones exert a distinct promoting action, while nitrogen-containing substances such as ammonia, amines and nitriles behave as strong poisons. Carbon tetrachloride, chloroform and various hydrocarbons are indifferent to this catalytic action.(2)

In a previous paper it was reported by the present author(3) that with various specimens of the earth a parallel relation holds between the catalytic activity and the adsorptive powers for water, benzene and naphthalene.

It was thought that a promoter and a poison might show different behaviours, when they are adsorbed on the surface of the earth. An investigation was therefore made on the isothermal adsorption of the vapours of water and acetonitrile, one of which is a typical promoter and the other a typical poison.

Apparatus and Procedure. The essential part of the apparatus consists of McBain's sorption balance(4) suspended in a transparent silica tube which is installed in a thermostat of 25°C. (±0.01°C.) and connected with the reservoir of water or acetonitrile in another thermostat whose temperature may be varied from 0° to 25°C. (±0.01°C.). The spring of the sorption balance is made of a fine fused silica fibre, 0.14 mm in diameter. The diameter of the coils of the spring is 7 mm, the number of the coil is 49 and the total length of the spring without load is 77.16 mm. Previous to the employment the fibre is carefully annealed at 300°C. for 1 hour with the load of 0.3 g. The balance is calibrated throughout the working range by observing the deflections caused by known weights. A small platinum bucket (0.0238 g.) is suspended from the lower end of the spring and known weights are placed on it and the respective elongations of the spring are measured by a cathetometer. The instrument used is capable of giving readings accurate to 0.01 mm. The equation expressing the relation between the load (y in centigramme) and the elongation (x in mm.) is obtained by the method of least square as follows:—

$$y = x/0.9564.$$

---

(1) H. Inoue and K. Ishimura, this Bulletin, **9** (1934), 431.
(2) K. Ishimura, *Ibid.*, **9** (1934), 521.
(3) K. Ishimura, *Ibid.*, **9** (1934), 493.
(4) J. W. McBain and A. M. Baker, *J. Am. Chem. Soc.*, **48** (1926), 690.

The total weight of a sample weighing 0.2 g. can be determined within the experimental error of 0.1 per cent.

The Japanese acid earth designated D in the previous paper⁽⁵⁾ is dried in a desiccator of sulphuric acid, pulverised and sifted by a sieve of 200 mesh. It is kneaded with a small quantity of water to small balls, about 2 mm. in diameter. Eight balls thus formed are placed on the platinum bucket. The bucket is hung from the lower end of the silica spring and the whole is enclosed in a silica tube, and then heated gradually to 200°C. in an electric furnace and maintained at that temperature for 4 hours under the high vacuum of 0.001 mm., effected by a Cenco Hyvac pump. Then it is cooled and put in the first thermostat (25°C.). The weight of the dry earth is calculated from elongation of the spring.

In order to expel the gas dissolved in the liquid, the vapour of which is to be adsorbed, its reservoir is first cooled with ice and salt and evacuated and then the temperature is raised to the room temperature allowing any gas which has been dissolved to get free. It is again cooled and evacuated. This process of outgassing the liquid and evacuation is repeated until the dissolved gases are completely expelled. Then the reservoir is put in the second thermostat of the required temperature. Now the cock connecting the reservoir and the silica tube is opened and the adsorption experiment is commenced. The elongation of the spring is measured at intervals, until no increase is observed for 3 hours and thus the equilibrium is considered to be attained. Then the cock is closed and the temperature of the second thermostat is raised by some degrees, and the cock is again opened and the second adsorption experiment is carried out. Thus the velocity of adsorption as well as the amount of the substance adsorbed at equilibrium can be measured under varying vapour pressures of the adsorbate. Directly after a series of adsorption experiments is finished, desorption is carried out, which is followed by the second series of adsorption and desorption and so on.

To carry out the desorption the reservoir of the adsorbate is cooled for a while with ice water, or with a mixture of ice and salt. The vapour pressure in the system is thereby depressed and a portion of the adsorbed substance is set free. The cock between the reservoir and the balance room is closed and the system is left to attain the equilibrium. When no more change of the length of the spring is observed and the reading of the manometer become constant for 2 hours the desorption experiment is ended. After the vapour pressure is lowered considerably, the system is evacuated by the pump instead of cooling the reservoir, and the final desorption is carried out by working the pump for 5 hours or more under 0.001 mm. For the measurement of the pressures a Mcleod's gauge is used. The values of vapour pressure of water at various temperatures are adopted from Landoldt's "Physikalisch-Chemische Tabellen", while those of acetonitrile are calculated by applying Dühring's rule.⁽⁶⁾

Dühling expressed the relationship between the boiling points of two pure substances as follows:—

---

(5) H. Inoue and K. Ishimura, this Bulletin, **9** (1934), 431.

(6) R. Lorenz, *Z. anorg. allg. Chem.*, **138** (1924), 104; E. H. Leslie and A. R. Carr, *Ind. Eng. Chem.*, **17** (1925), 810; A. R. Carr and D. W. Murphy, *J. Amer. Chem. Soc.*, **51** (1929), 116. A. M. White, *Ind. Eng. Chem.*, **22** (1930), 230.

$$\frac{T_1 - T_2}{\theta_1 - \theta_2} = K$$

in which T_1 and T_2 are the boiling points of one substance at two different pressures, θ_1 and θ_2 the boiling points of the other at the same two pressures, K a constant. Vapour pressures of acetonitrie at 0°, 10° and 15°C. were measured by using the apparatus of the present experiment, varying the temperature of the reservoir of acetonitrile and it was confirmed that the Dühling's rule holds very well in this case too. Values of the observed vapour pressure together with that at 760 mm. are given below and the corresponding Dühling's line in Figure 1.

B. p. (°C.)	0	10	15	81.6
Vapour pressure (mm.)	25.2	41.9	55.5	760

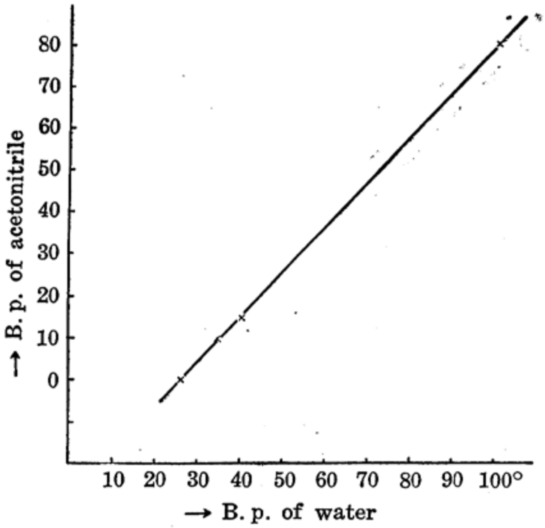

Fig. 1. Dühling's line of acetonitrile

From the above data the vapour pressures at various temperatures are obtained as follows:—

B. p. (°C.)	17.0	20.0	22.0	24.0	24.6	25.0
Vapour pressure (mm.)	58.0	67.6	74.5	82.1	84.6	86.3

In the case of water the experiment was extended to the third desorption, while in the case of acetonitrile to the fourth desorption which was immediately followed by the adsorption and desorption of water vapour.

Results of Experiments. (1) In every case a marked hysteresis has been observed, which is shown in Figures 2 and 3.

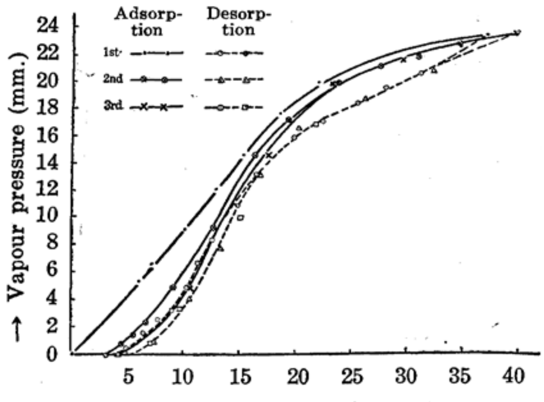

Fig. 2. Isotherm of water

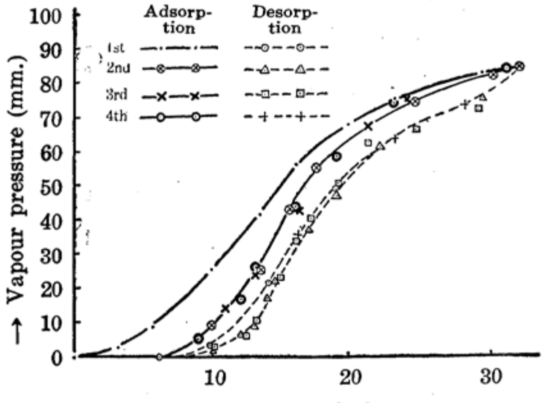

Fig. 3. Isotherm of acetonitrile

(2) It is clearly seen from Figures 2 and 3 that the vapour pressures corresponding to the definite quantities of the absorbed substances are greater in the first adsorption than in the second and the subsequent adsorptions.

(3) A small proportion of the adsorbed substance is very difficult to be expelled by evacuation; water remains undesorbed in the amount of 3.15% even after 5 or more hours' evacuation at 0.001 mm. and acetonitrile in the amount of 6.31% under the same condition. This very tenaciously held water or acetonitrile is that which has been designated by the present author "retained", and has been noticed to play an important rôle in the promotion and poisoning of the catalytic action of the earth.⁽⁷⁾

(4) It has been found that the first adsorption as well as desorption curves of water vapour in the presence of the "retained" acetonitrile considerably deviate from those without it, but the second adsorption and desorption curves are practically the same as those without the retained acetonitrile. The retained amount thereby decreased from 6.31 to 3.26%, th value very near to 3.15% ("retained" water on the earth without acetonitrile).

(5) The rate of adsorption increases as the process of adsorption and desorption is repeated. Figure 4 shows the amount of adsorbed water plotted against time in the first, second and third adsorption experiments under the pressure of 14.53 mm. (saturated vapour pressure at 17°C.).

The initial points of the three curves are made superimposed in order to render the comparison easy.

Similarly Figures 5 and 6 show the rate of adsorption of water under 4.58 mm. (saturated vapour pressure at 0°C.) and those of acetonitrile

---

(7) K. Ishimura, this Bulletin, **9** (1934), 522.

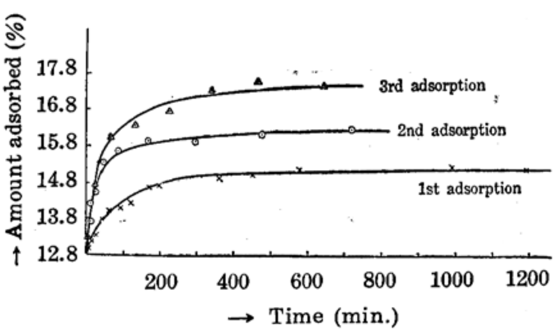

Fig. 4. Rate of adsorption of water at 17°C.

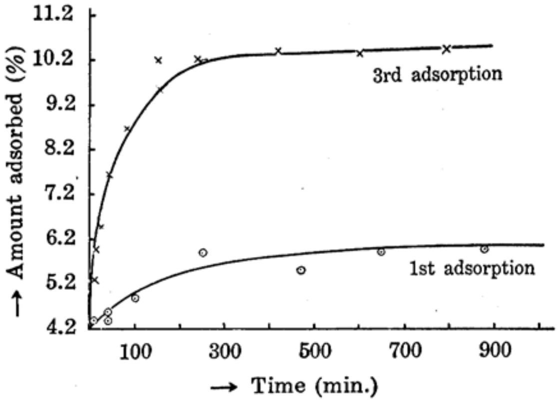

Fig. 5. Rate of adsorption of water at 0°C.

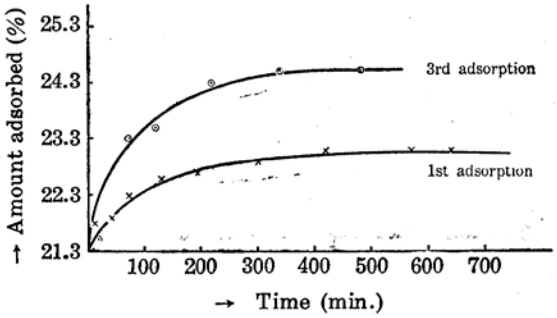

Fig. 6. Rate of adsorption of acetonitrile at 22°C.

under 74.5 mm. (saturated vapour pressure at 22°C.) respectively.

(6) It may be seen from Figures 4, 5 and 6 that not only the rate of adsorption but also the amount the the substance adsorbed at equilibrium increase as the adsorption and desorption are repeated.

(7) The rate of desorption could not be accurately measured under the condition of the present experiment. It can only be stated here that the time required for desorption is relatively short and shows little variation from one experiment to the other, usually about 1–2 hours' standing is enough to obtain the constant elongation of the spring and the constant reading of the manometer.

Discussion of Results.

It is well established that adsorbed films cannot be completely removd by evacuation, but that the treatment with a high pressure of gas at high temperature is much more efficient. For example, as H. S. Harned⁽⁸⁾ observed, simply heating charcoal up to 1200°C. in a vacuum will not suffice to produce an absolutely gas-free surface. When, however, charcoal is heated to over 700°C. in a vacuum, cooled in a vacuum, exposed to the gas until considerable quantities are adsorbed, and then again heated to above 700°C. in a gas, the surface of the charcoal seems to be first cleaned up, as the velocity of adsorption on the charcoal gives a reproducible value. Such process of "washing out" has most probably been effected on Japanese acid earth in the case of the present

---

(8) *J. Amer. Chem. Soc.*, **42** (1920), 372.

experiment at ordinary temperature. Thus as the process of adsorption and desorption of water or acetonitrile is repeated, the surface is successively washed out by these substances and consequently the adsorptive power of the earth gradually increase. The effect of the washing out process is clearly recognized from the increases in both the rate of adsorption and the amount of the adsorbed substances at equilibria, as shown in Figures 4, 5 and 6.

Though acetonitrile is capable of washing out the adsorbed foreign gas it hinders in its turn the adsorption of water vapour. It can however easily be flushed by the water vapour, as may be understood from the facts that the earth with "retained" acetonitrile adsorbs water vapour more slowly than the case without it, but after the first adsorption and desorption is finished the original rate of adsorption recurs and the upper region of the subsequent isotherm falls completely on the preceding one. At the same time the "retained amount" (6.31%) was found to be reduced to 3.26%, the value very near to the amount of retained water (3.15%) on the earth without acetonitrile. These facts suggest that water has a most strong affinity to the earth and capable of replacing acetonitrile from the surface.

The molecules of "retained water" visualized as above are those which are put in their original positions from where they were liberated when heated. As the present author⁽⁹⁾ has previously suggested, the active centres for the catalysis, which are formed when the three components, Al_2O_3, SiO_2 and water are suitably oriented, become inactive by loss of water, but recover their ability by regaining it in the original position. The "retained water" is not therefore that simply adsorbed on the surface; it is much more strongly held, it may be said quasi-chemically combined with other components of the earth.

The hysteresis observed in the isotherms above shown may be partly explained by taking the "washing out" process into consideration. The first adsorption lags more or less on account of the hindering effect of the foreign adsorbed substances. These are, however, more easily liberated than water vapour when desorption is commenced, giving rise to the observed "washing out" action of water vapour. The first isotherm shows therefore a marked hysteresis from the very initial stage of adsorption i.e. layer adsorption. An example of such hysteresis phenomenon due to the existence of the foreign adsorbed substance was given by R. Fricke and H. Marquardt.⁽¹⁰⁾ They reported that a marked hysteresis was observed in the adsorption of water vapour on human hair in the presence of air, while in the high vacuum of 0.0001 mm. no such hysteresis appeared.

Now in the case of the present experiment, most part of the foreign adsorbed substances are washed out by the first series of adsorption and desorption and hysteresis areas greatly decrease in the subsequent series. With acetonitrile curves of the second and the subsequent series overlap completely and the hysteresis covers the whole range, while with water the lower portion of the isotherm tends gradually to be reversible and accordingly the hysteresis tends to be restricted only to the upper region of the curve. This difference of the behaviours of the two substances may also

---

(9) K. Ishimura, this Bulletin, **9** (1932), 527.

(10) *Kolloid Z.*, **60** (1932), 124.

be attributed to the greater power of water vapour for the washing out process. By acetonitrile the foreign adsorbed substances cannot be removed by only repeating the process of adsorption and desorption and persist to stay on the surface.

The upper region of the hysteresis area, however, does not tend to decrease in both cases. Different mechanisms may, therefore, govern the hysteresis in the lower and the upper regions of the isotherms. The former, which tends to disappear, is most probably due to the existence of the foreign adsorbed substances as stated above, and in this region layer adsorption mainly takes place. The latter is associated with capillary condensation process which follows the layer adsorption. The boundary between the two types of adsorption can be ascertained, by the narrow part existing in the middle of the hysteresis area.

According to R. Zsigmondy,(11) during addition of vapour walls of pores are wetted incompletely and very slowly and therefore the radius of curvature of the meniscus is greater than that during desorption. Hence the vapour presure of a definite quantity of liquid held in pores is greater during adsorption than during desorption. A. G. Foster(12) studied equilibria between dehydrated gels (silica gel, and ferric oxide gel) and condensible vapours (water, benzene and ethyl alcohol). He attributed the higher pressures observed during adsorption to the liquid which is held in an unstable state on the walls of these pores in which the meniscus has not formed, the prssure of which masks the progress of the condensation process. During desorption all the adsorbed liquid is bound by the meniscus (with the exception of the strongly adsorbed layer which remains on the walls), and therefore show smaller vapour pressures.

The adsorption will come to an end when the pores of the adsorbent are all filled by liquid. This will occur under the vapour pressure of adsorbates, saturated at the temperature of absorbents, that is, when the temperatures of the two thermostats are the same. If the temperature of the adsorbate is raised over that of adsorbent, wetting process will begin to take place. At the end of the adsorption in the present experiment carried out under the saturated vapour pressure of adsorbate at 24.6°C., the temperature very near to that (25°C.) of the first thermostat in which the tube holding the silica spring with the earth is immersed, the adsorbed quantities of water and acetonitrile amounted to 39.82 and 32.16% of the weight of the earth respectively. Volumes of the two liquids at 25°C. to be adsorbed by 100 g. of the earth are therefore 39.8 c.c. of water and 40.7 c.c. of acetonitrile. The two values are very near. The difference between them will become smaller if the amounts adsorbed at the same humidity are taken instead of those at the same temperature. It is very probable therefore that the above values approximately represent the total volume of pores of 100 g. of the earth.

Summary.

Adsorption isotherms of water and acetonitrile for Japanese acid earth have been studied by using a McBain's sorption balance. A marked

---

(11) "Kolloidchemie," Leipzig, (1918), 214.
(12) *Trans. Faraday Soc.*, **28** (1932), 653.

hysteresis phenomenon has been observed in both cases. It has been found that as the process of adsorption and desorption is repeated, the lower region of the hysteresis area tends to be reversible in the case of water, while in the case of acetonitrile hysteresis covers the whole range of the isotherms even after the fourth series of adsorption and desorption. In both cases the upper region of the hysteresis area remains unchanged. The first type of the hysteresis, which tends to disappear, has been explained as due to the existence of the adsorbed foreign substances on the surface of the earth, while the second type is associated with capillary condensation process. The difference between the behaviours of water and acetonitrile can be attributed to the difference of affinity of the two substances to the earth. The total volume of pores of the earth has been calculated from the adsorbed amounts of the two substances and found about 40 c.c. for 100 g. earth.

The author's thanks are due to Dr. H. Inoue for his encouragement and advice.

The Tokyo Imperial Industrial Research Laboratory,
Hatagaya, Tokyo.