

Conductance of Water-sorbed Activated Carbon: Differentiation of Flow Direction

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ABSTRAK

Kekonduksian sebatang karbon yang telah diaktifkan telah disukat semasa terendam dalam air pada beberapa suhu yang berlainan. Pengaliran air ke arah atas, bawah dan juga mengufuk dalam batang yang sama dapat dibuat secara menyusun semula radas. Kadar kenaikan kekonduksian diertikan sebagai kadar pengaliran air ke dalam liang karbon.

ABSTRACT

The conductance of a piece of activated carbon immersed in water has been measured at several different temperatures. The upward and downward flow of water as well as the flow in the horizontal direction in the same piece was made possible by using various arrangements of the apparatus. The rate of increase in the conductance has been interpreted as the rate of flow of water into the pores of activated carbon.

INTRODUCTION

The dependence of the conductance, σ , of a solid on its length, h , and cross-sectional area, A , is given by

$$\sigma = \kappa A/h \quad (1)$$

where κ is the conductivity. In a perfect crystal, the atomic nuclei are the primary scattering centres for the electron flowing under the influence of an electric field. In a non-perfect crystal, additional scattering due to the presence of defects and impurities also takes place effectively reducing its conductance.

Activated carbon can be regarded as aggregates of graphite crystallites separated by pores. These pores which penetrate the carbon throughout are the main scattering centres. Generally, the more pores there are, the more

active the carbon will be. Thus the activity of activated carbon can be reflected by its conductivity compared to graphite, for example.

In a recent publication, it was shown that the conductance of activated carbon increased with time of immersion in water (Badri *et al.*, 1984). The increase was suggested to be due to the presence of hydrogen ions in solution in the pores. When water seeped into the pores through the openings on the surface, S , of the activated carbon, *Fig. 1*, the various functional groups located on the wall of the pores ionized to yield hydrogen ions which acted as charge carriers in the solution in the pores. As more pores were filled, the number of ions increased resulting in the increase in the conductance of the sample. In such a situation the dependence of σ on the depth of penetration of water should be in the form

$$\sigma = \kappa Ah \quad (2)$$

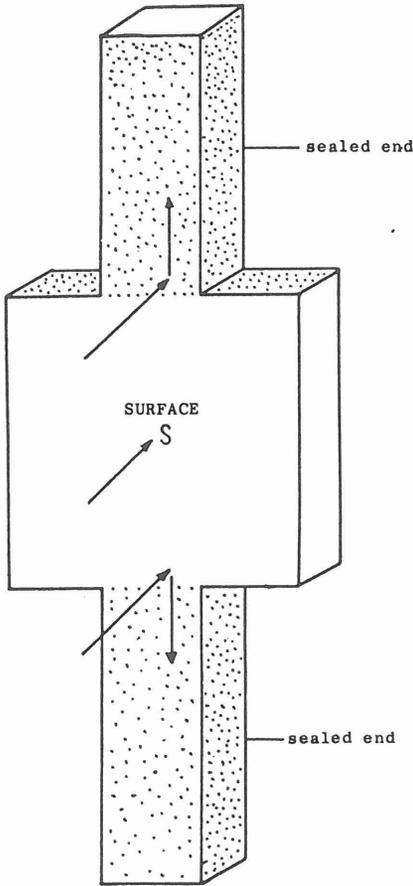


Fig. 1: Carbon conductor showing simultaneous flow in horizontal and vertical directions. Arrows indicate the directions of flow.

Referring to Fig. 1 it is obvious that the horizontal flow of water into the sample through the surface S and the vertical flow into the sealed ends took place simultaneously after the initial sorption by the surface. Fortunately it was possible to show that the two rates of flow have similar mathematical expressions especially at the beginning of the experiment. However, it would be more convenient for discussion if these directions of flow could be separated. In this communication such an attempt will be described.

By covering the sides of a parallelepiped conductor as shown in Fig. 2, penetration of

water would take place only through its top square end. The direction of flow could be changed by appropriate positioning of the conductor either upward, downward or sideways. Thus, for any configuration the area of contact, A, between the conductor and water would remain constant. Hence the conductance of the sample would increase in accordance with the depth of penetration of water, h. Therefore from (2)

$$d\sigma = \kappa A. dh \tag{3}$$

For a capillary rise of water in glass, Bikerman (1970) has given the following expression

$$\frac{dh}{dt} = \frac{\rho g r^2}{8\eta} \left[\frac{h_f - h}{h} \right] \tag{4}$$

where ρ and η are the density and viscosity of water respectively at a given temperature, g is the gravitational constant, r is the radius of the capillary, h is the height of water column and h_f is its final height in the capillary. By assuming that the conductance is proportional to penetration height, a similar expression for σ with respect to time, t, would be

$$\frac{d\sigma}{dt} = \kappa A \frac{\rho g r^2}{8\eta} \left[\frac{\sigma_f - \sigma}{\sigma - \sigma_o} \right] \tag{5}$$

where σ_o and σ_f are the initial and final conductance of the sample respectively. By intergration we would arrive at:

$$\ln \left[\frac{\sigma_f - \sigma_o}{\sigma_f - \sigma} \right] - \left[\frac{\sigma - \sigma_o}{\sigma - \sigma_o} \right] = \frac{\rho g r^2}{8\eta h_f} t \tag{6}$$

For a horizontal flow of water into a glass capillary, Bikerman has also given

$$\frac{dh}{dt} = \frac{\gamma r}{4\eta h} \tag{7}$$

where γ is the surface tension of water. Substituting (7) into (3) we get

$$\frac{d\sigma}{dt} = \kappa A \frac{\gamma r}{4\eta \sigma} \tag{8}$$

which upon integration would yield

$$\left[\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o} \right]^2 = \frac{\gamma r}{2\eta h_f^2} t \quad (9)$$

For a downward flow of water through a capillary, Rosenthal and Asimov (1974) gave the relationship

$$\frac{dV}{dt} = \frac{\pi \rho g r^4}{8\eta} \quad (10)$$

where V is the volume of the flow. Assuming that the pores are cylindrical $V = \pi r^2 h$ and $dV = \pi r^2 \cdot dh$

$$\therefore \frac{dh}{dt} = \frac{\rho g r^2}{8\eta} \quad (11)$$

By substituting (11) into (3) we get

$$\frac{d\sigma}{dt} = \kappa A \frac{\rho g r^2}{8\eta} \quad (12)$$

which upon integration would yield

$$\left[\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o} \right] = \frac{\rho g r^2}{8\eta h_f} t \quad (13)$$

If the interaction of water towards the pores were similar to its interaction towards a glass capillary, plots of the quantities on the left hand sides of (6), (9) and (13) against time would individually give straight lines. Furthermore, the average radius of the pores could then be estimated from the slope of the graph since all other quantities are known.

MATERIALS AND METHOD

Activated carbon was prepared by the method described earlier (British Patent, 1983). A fairly flat piece was ground with fine sand paper into a parallelepiped measuring about $2 \times 2 \times 15$ mm. It was soaked in 2M HCl for about a week and washed with distilled water in a Soxhlet apparatus for another week. After that it was dried in an oven at 70°C . It was then

sealed in a 10 mm long sleeve of rubber tubing with Araldite epoxy resin leaving 5 mm exposed on one end. Platinum wire was tied around this end of the carbon before the carbon-rubber assembly was sealed into a 15 mm long ground glass cone (B7) using epoxy resin also. This created a 5 mm long groove between the carbon and the glass. To ensure good electrical contact of the platinum with carbon, a drop of mercury was placed in this groove. Some resin was then carefully added to the top of the mercury, filling the groove and enclosing the mercury. A piece of wire insulator was sealed to the platinum lead. When the assembly, henceforth referred to as the conductor, *Fig. 2a*, was dry, both ends of the carbon were sanded slightly and the conductor was cleaned and then dried in a vacuum desiccator at 70°C for five hours before use.

For a conductivity measurement, the conductor was connected to a J-tube fitted with a ground glass socket, *Fig. 2b*. Some mercury was placed in the J-tube to establish good electrical contact. A piece of platinum wire was used as the other lead. The whole assembly was placed in a container and equilibrated to the working temperature. When the conductivity reading was constant, distilled water at the working temperature was poured slowly into the container to a level just enough to submerge the conductor. Conductance readings were taken until maximum value was reached after a few days. Wyne Kerr Autobalance Universal Bridge B642 was used. Drops of distilled water were added as necessary to keep the water level constant.

Conductance measurement for upward flow and horizontal flow of water into the pores was done by modifying the J-tube into an L-shape or vertical tube. Otherwise the same procedure was followed. After each experiment the conductor was dried as described above.

RESULTS

Upon sorption of water, the rate of increase in the conductance of activated carbon differed depending upon the direction of flow in the following order,

downward > horizontal > upward

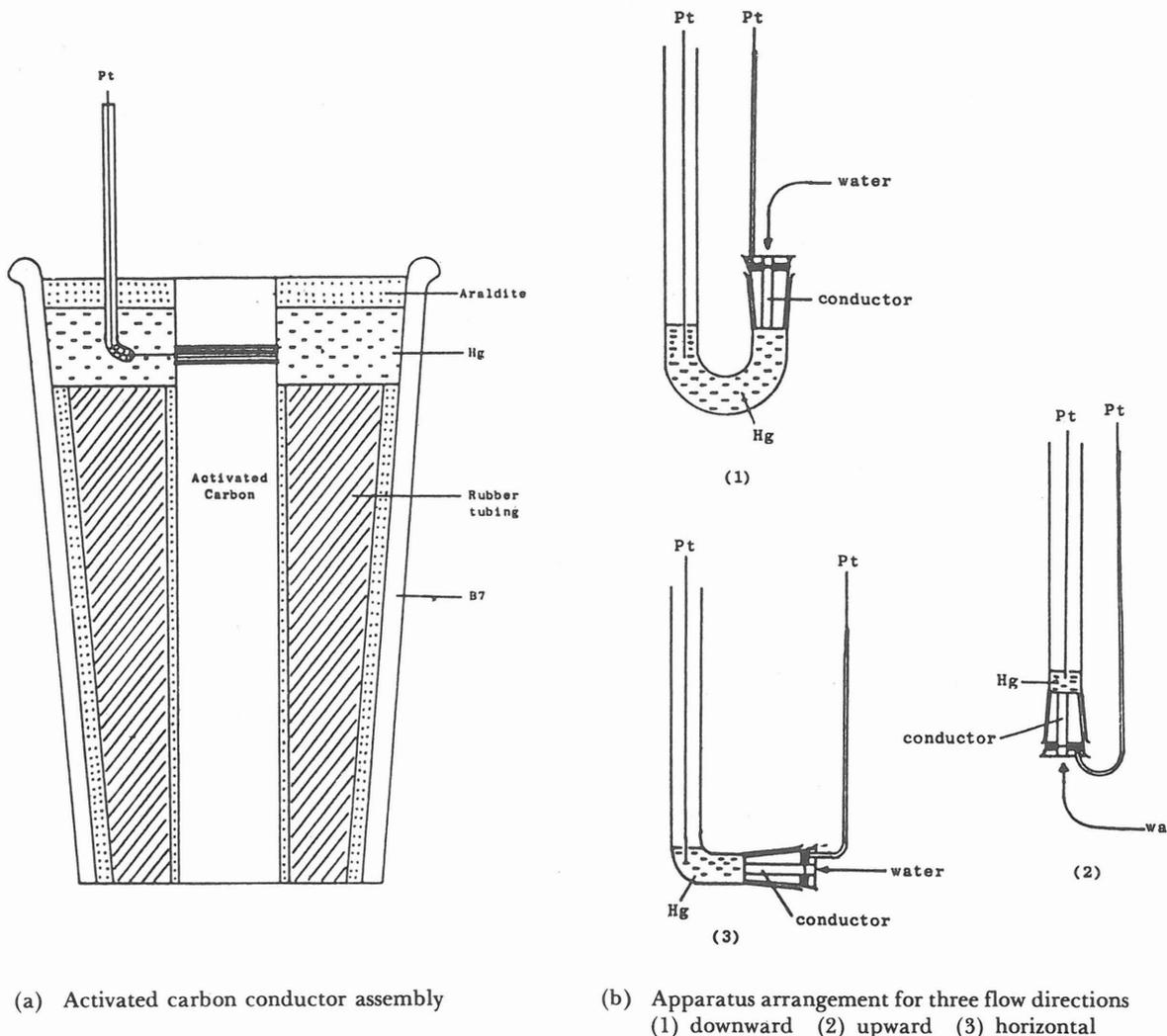
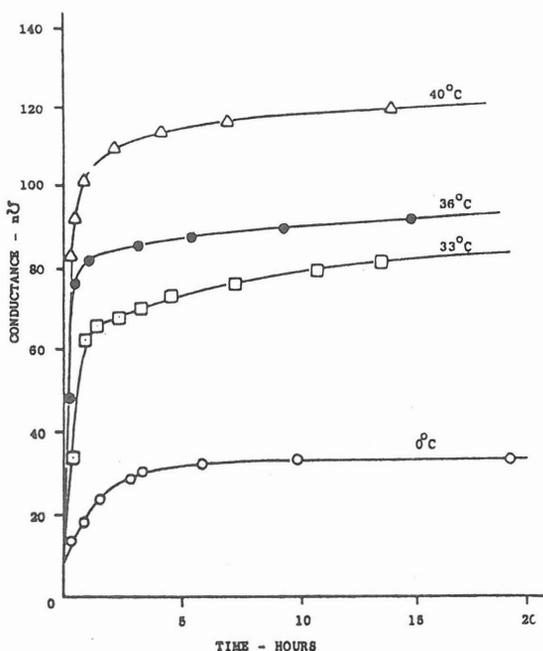


Fig. 2: Apparatus assembly for conductivity measurement.

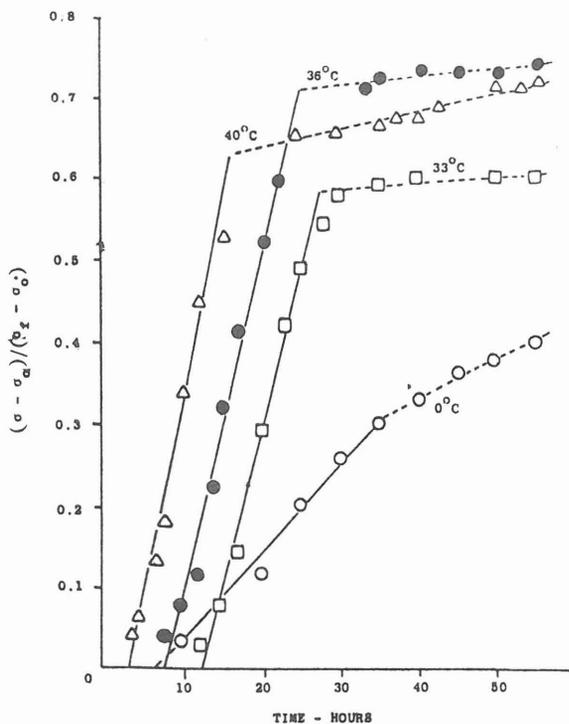
Fig. 3a shows the increase in the conductance with time for the downward flow. It can be seen that the increase occurred almost instantaneously as the surface of the conductor came into contact with water. The rate of increase was found to be faster as the temperature was raised. Similarly the maximum in the conductivity was higher at a higher temperature. Plots of sorption fraction, $(\sigma - \sigma_o) / (\sigma_f - \sigma_o)$ against time, of immersion t , were made and are given in Fig. 3b. Two intersecting straight lines were obtained for each temperature indicating two different flow mechanisms. The first portion occurred up to

sorption fraction of about 0.6 for higher temperature measurements within the first thirty minutes. A deviation was found for working temperature of 0°C. Estimations of the average pore radius have been made and are given in Table 1.

Fig. 4a shows the increase in the conductance of the sample with time of immersion for the capillary rise of water into the pores. All the curves are sigmoid, similar to the results given earlier (Badri *et al.*, 1984, 1985).



(a) Plot of conductance against time, *t*, at various temperatures



(b) Plot of $(\sigma - \sigma_0) / (\sigma_f - \sigma_0)$ against time, *t*.

Fig. 3: Conductance measurement of carbon for downward flow of water

Plots of $\ln[(\sigma_f - \sigma_0) / (\sigma_f - \sigma)] - (\sigma - \sigma_0) / (\sigma_f - \sigma)$ against time of immersion are given in Fig. 4b. An excellent fit is observed up to 0.9 sorption fraction. Calculation of the average radius yielded values given in Table 2.

Fig. 5a shows the increase in the conductance for the case of horizontal flow of water into the same pores. The shape of each curve is

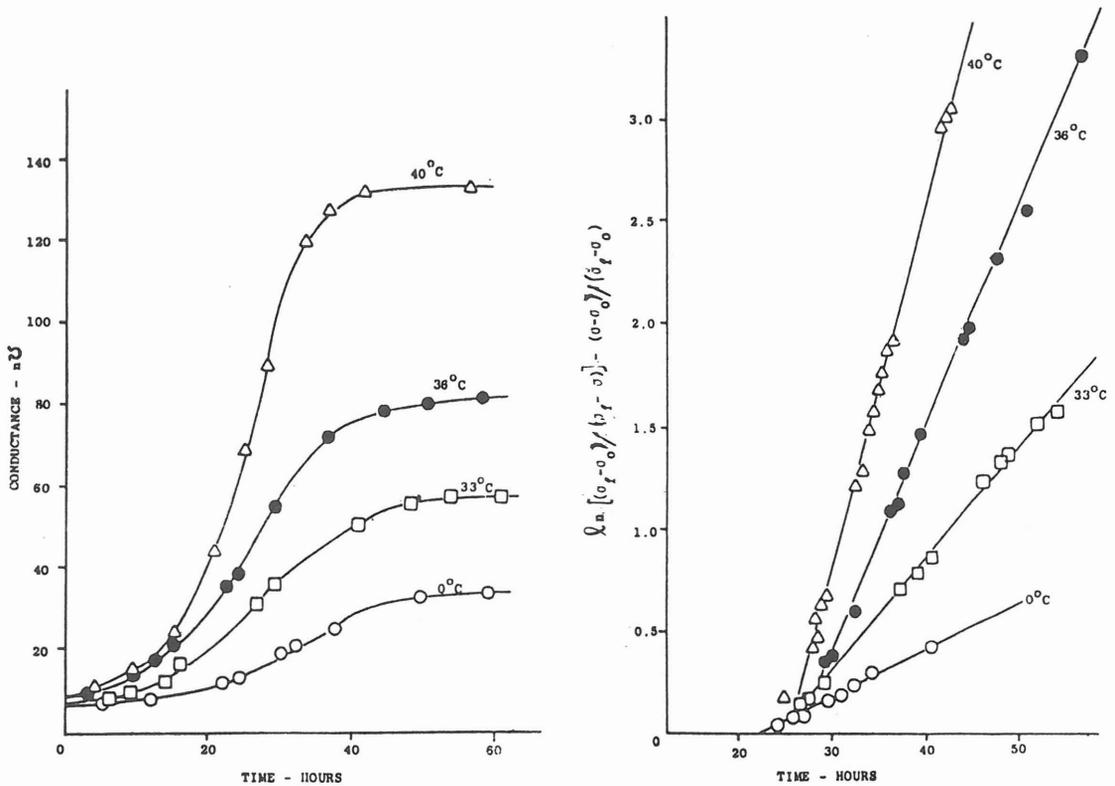
almost similar to the corresponding one found for the upward flow at a given temperature. Since all measurements were done on the same conductor, the maximum conductance at a particular temperature was the same for each flow direction.

A plot of the square of sorption fraction as a function of time is given in Fig. 5b. A good fit is

TABLE 1
Average radius of the pores from equation (13)

Temperature °C	Slope 10^{-4} /s	$\rho_{H_2O}^*$ g/cm ³	$\eta_{H_2O}^*$ 10^{-2} g/cm s	Total Radius Å
0	1.5698	0.9998	1.787	18013
33	3.9785	0.9947	0.7491	18613
36	5.0900	0.9937	0.7052	20438
40	6.8885	0.9922	0.6529	22894

*CRC Handbook of Chemistry and Physics, 1970.



(a) Plot of conductance against time, t, at various temperatures

(b) Plot of $\frac{\rho_n [(q_f - q_0) / (q_f - \sigma)] - (q - q_0) / (q - \sigma_0)}$ against time, t.

Fig. 4: Conductance measurement of carbon for upward flow of water.

observed for about 0.8 sorption fraction. The average radius calculated from the slopes are given in Table 3.

DISCUSSION

The increase in the rate of sorption of water into the carbon parallelepiped in the order

observed should be easily explained in terms of gravity. The downward flow was fastest because gravity pulled the water down into the pores whereas the upward flow took place through capillary action against the force of gravity. In horizontal flow, gravitational force was apparently a neutral factor.

TABLE 2
Average radius of the pores from equation (6)

Temperature °C	Slope $10^{-5}/s$	$\rho_{H_2O}^*$ g/cm ³	$\eta_{H_2O}^*$ 10^{-2} g/cm. s	Radius Å
0	0.9974	0.9998	1.787	4543
33	1.2360	0.9947	0.7491	3280
36	1.9018	0.9937	0.7052	3950
40	2.3669	0.9922	0.6529	4244

*CRC Handbook of Chemistry and Physics, 1970.

ACTIVATED CARBON

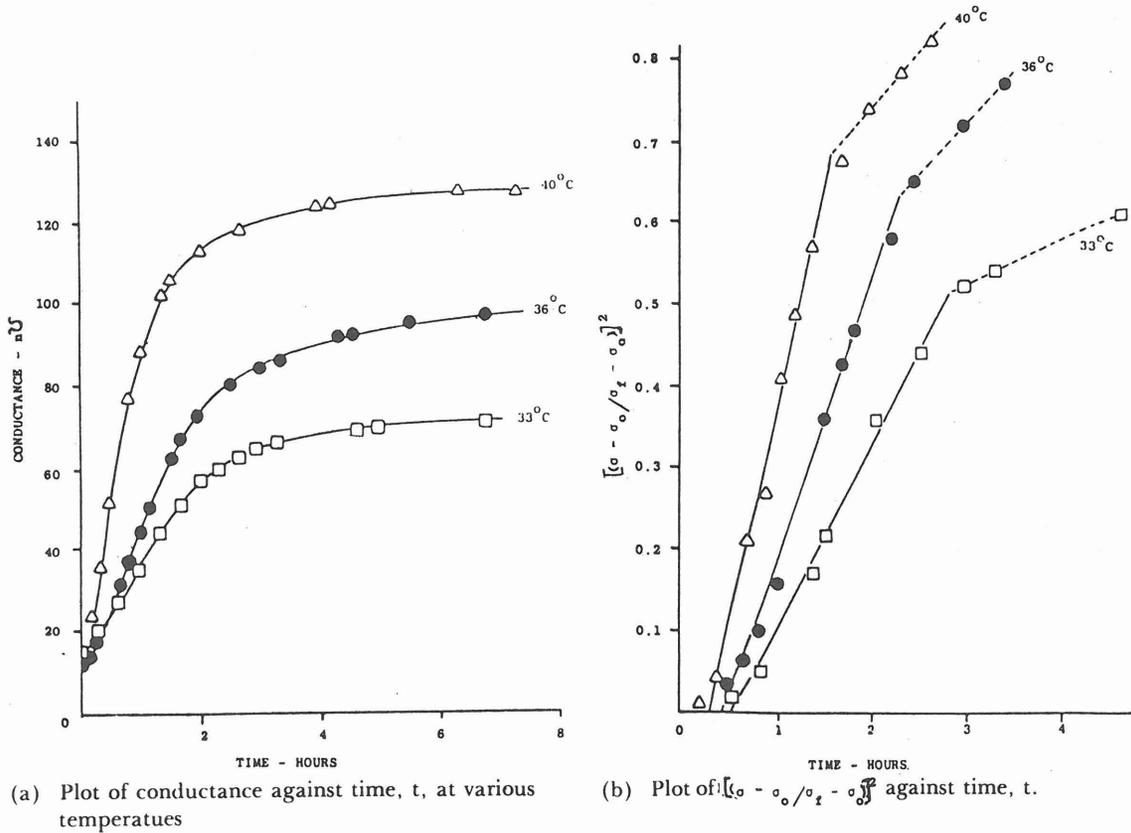


Fig. 5: Conductance measurements of carbon for horizontal flow of water.

The fact that the final conductance of the sample was the same at a particular temperature indicated that regardless of the flow direction, when the sample was fully soaked, the same pores filled with water to the same extent. The greater conductance at higher temperatures indicated more extensive filling of the pores due to lowered viscosity of water or enhanced pore-filling mechanism or simply a higher degree of

ionization of the functional groups on the wall of the pores.

A good fit of experimental results up to 0.6 of sorption fraction for the downward flow of water and higher for the other two directions to the theoretical expressions given by equations (6), (9) and (13) has lent support to the original assumption. A more complicated expression for

TABLE 3
Average radius of the pores from equation (9)

Temperature °C	Slope $10^{-5} / s$	$\gamma_{H_2O}^*$ dyne/cm	$\eta_{H_2O}^*$ $10^{-2} g/cm.s$	Radius Å
33	5.481	70.75	0.7491	4.67
36	7.635	70.25	0.7025	6.17
40	11.525	69.56	0.6529	8.70

*CRC Handbook of Chemistry and Physics, 1970

the flow rates might be necessary for a better fit because the pores in the activated carbon are not as straight as in a capillary. The bends in the pores might retard the flow of water. Furthermore the pores might be branched and interconnected or might be closed-ended. Some air could be trapped in closed-ends retarding the rate of flow which might result in an apparent reduction of pore radius.

The average pore radius calculated from the results of the three sets of experiments should have been of similar magnitude. The fact that they were not might have been due to the factors described above. One pertinent point that should be mentioned is that Bikerman (1958) had pointed out that the validity of the expressions given was limited to capillaries larger than 6 microns. Furthermore, the hydrophobicity of carbon might have further reduced the usefulness of the equations given.

However, the average values obtained from the capillary rise of water into the pores seemed to agree quite well with the values obtained earlier. The good fit of experimental results to the proposed equation (6) up to 0.9 sorption fraction has lent some support to the validity of the technique, at least for this set of experiments.

To a limited extent the large values for the average radius obtained from the experiment, on the downward flow of water could be explained. The volume V in (10) is the sum of the individual volumes of each pore, V_i , of radius r_i .

$$V = \sum_{i=1}^n V_i \quad \text{and} \quad r = \frac{\sum_{i=1}^n r_i}{n}$$

where n is the total number of pores. Therefore (13) could be written as

$$\left[\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o} \right] = \frac{\rho g}{8\eta h_f} \left[\frac{\sum_{i=1}^n r_i}{n} \right]^2 t \quad (14)$$

If x_i is the difference between the average radius \bar{r} and the individual radius r_i , then

$$\begin{aligned} r_i &= \bar{r} - x_i \\ &= \bar{r}(1 - p_i) \end{aligned} \quad (15)$$

where $p_i = x_i / \bar{r}$. Substituting (15) into (14), we get

$$\left[\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o} \right] = \frac{\rho g}{8\eta h_f} \bar{r}^2 \left[\sum_{i=1}^n (1 - p_i) \right]^2 t \quad (16)$$

For a normal distribution, the summation term would be equal to n . Thus (16) would be reduced to

$$\left[\frac{\sigma - \sigma_o}{\sigma_f - \sigma_o} \right] = \frac{\rho g}{8\eta h_f} (n\bar{r})^2 t \quad (17)$$

By comparing (17) to (13) we can see that the average radius could be obtained by dividing r by n . Thus to calculate \bar{r} we need to know the number of pores running along the conductor.

REFERENCES

- BADRI, M., K.A. CROUSE and HARUN AWANG (1984): Conductance Measurement of Water-Sorbed Activated Carbon, *Pertanika*, 7: 59 - 65.
- BIKERMAN, J.J. (1970): Physical Surfaces, New York: Academic Press Inc.
- ROSENTHAL, D. and R.M. ASIMOV. (1974): Introduction of Properties of Materials, New Delhi: East-West Press Pte. Ltd.
- UNIVERSITI PERTANIAN MALAYSIA (1983): Preparation of Activated Carbon Under Reduced Pressure, British Patent No. 2086867.
- BADRI, M., K.A. CROUSE, and HARUN AWANG (1985): The Effect of Sorbed Alkali Metal Ions on the Conductance of Activated Carbon. *Pertanika*, 8: 337 - 341.
- BIKERMAN, J.J. (1958): Surface Chemistry: Theory and Applications, New York: Academic Press Inc.

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