Studies on Pore Systems in Catalysts

VII. Description of the Pore Dimensions of Carbon Blacks by the *t* Method

J. H. DE BOER, B. G. LINSEN,* TH. VAN DER PLAS,† AND G. J. ZONDERVAN†

From the Department of Chemical Technology, Technological University of Delft, The Netherlands

A description of the pore dimensions has been obtained for a group of carbon blacks by means of the universal *t* curve as given in Parts I and VI in this series. An important quantity of very narrow pores has been ascertained. The surface area of the wide pores was equal to the geometrical surface.

1. INTRODUCTION

Methods for obtaining information on the sizes, shapes, and distribution of the pores of microporous materials have been developed in preceding papers of this series (*1-5*). More particularly it was shown that the *t* curve, as derived from measurements on well-selected samples of alumina, seems to be applicable to other materials and even to graphitized carbon blacks (*5*).

In the present paper this method will be applied to a few carbon blacks. The occurrence of very narrow pores, about 10Å wide (or even less) in a number of carbon products has been presumed for a long time. Evidence has come from the adsorption of water (*6*), molecular sieve properties (*7*), and consideration of isotherms of low-temperature nitrogen adsorption (*8*).

The chemical properties of the carbon blacks used in this investigation have been investigated with the result that unexpected discrepancies were noted between the results of methods used to determine oxygen-containing functional groups on the surface (*9*). The results of the present investigation supply the data necessary for a discussion of the possibility of explaining these discrepancies

* Unilever Research Laboratory, Vlaardingen, The Netherlands.

† Euratom—R.C.N.—K.E.M.A. Reactor Development Group, Arnhem, The Netherlands.

by steric hindrance in the narrow pores. Such a discussion, however, is outside the scope of this publication.

The examples presented here may serve to illustrate the application of the *t* method to the study of the texture of carbonaceous materials. It should be noted that the pores are considered to be slitlike, an assumption that seems reasonable for the carbon blacks.

2 EXPERIMENTAL

The carbon blacks used were standard commercial products manufactured by G. L. Cabot Co., Boston, U.S.A. They are known by the names Carbolac 1, Mogul A, Spheron 6, and Elf 5 and are all of the acidic channel black type. The product indicated by Mau 4 was prepared from Mogul A by autoclaving with water at 250°C in a hydrogen atmosphere.

Since it was intended to measure the carbons with chemisorbed oxygen on the surface, the temperature of degassing was chosen low, 120°C, while the time of degassing was about 4 hr.

The isotherms for the adsorption and desorption of nitrogen were determined using the micro-BET-apparatus described in Part I of this series (*1*). The adsorption equilibrium is rapidly reached with the micro-apparatus but about a quarter of an hour was necessary for establishing equilibrium

on the desorption branch. This time, however, is much smaller than that required when a conventional BET apparatus is used.

3. RESULTS AND DISCUSSION

Parts of the adsorption isotherms are given in Fig. 1. Hysteresis in the adsorption–desorption isotherms was only found at high relative pressures $(p/p_0 > 0.8)$. Low-temperature nitrogen isotherms have already been reported for most of the carbons in the literature (10).

The BET plots calculated from the isotherms were good straight lines between

TABLE 1
DATA CALCULATED FROM THE BET PLOTS

Sample	p/p_0 at which the monolayer is formed	C value	V_m (ml/g STP)	$S_{BET} =$ 4.371 $\times V_m$ (m²/g)
Carbolac 1	0.050	532	208	911
Spheron 6	0.085	131	24.0	105
Elf 5	0.080	199	28.3	124
Mogul A	0.030	3926	65.0	285
Mau 4	0.025	1382	70.3	308

The experimental values of V_a (the volume of nitrogen adsorbed in cm³/g of adsorbent) which are obtained as a function of the
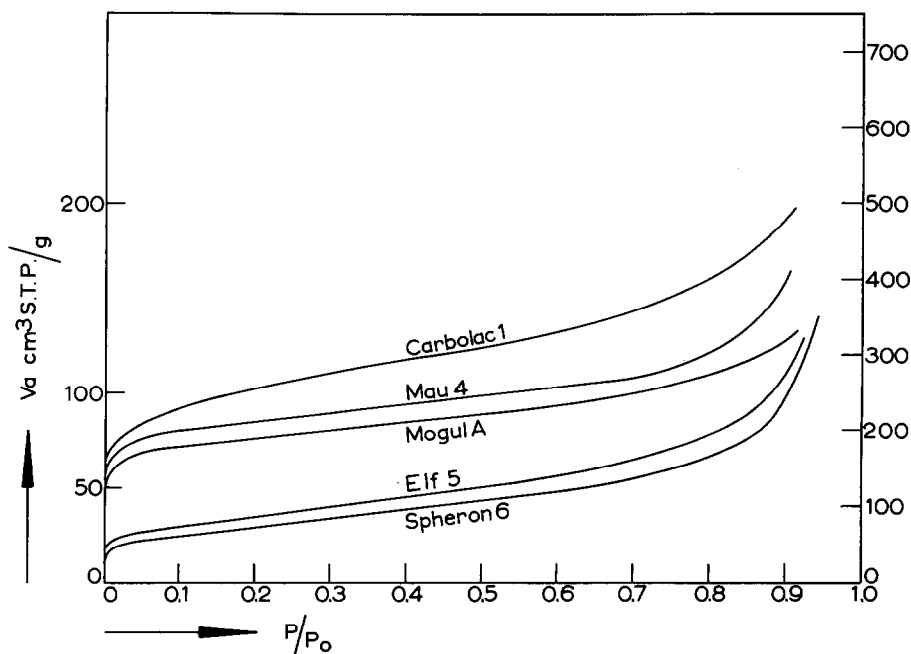

FIG. 1. Low-temperature nitrogen adsorption isotherms. Right-hand V_a scale for Carbolac 1.

relative pressures 0.05 and 0.10. From these plots it appears that the monomolecular layer for some of the samples is already formed at a very low relative pressure (Table 1, column 2). This means that high C values for the BET equation (Table 1, column 3) are found. It is seen that only for the samples Spheron 6 and Elf 5 the constant C has a normal value. The other carbons show an abnormally high C value. This indicates persorption in small pores. Abnormally high C values for carbonaceous materials have been observed earlier (8, 11).

relative pressure, p/p_0, may with the aid of the t curve given in Parts I and VI of this series (1, 5) be transformed into a function of t. By plotting then V_a for an unknown sample as a function of the experimental t, we obtain a straight line, as long as the multilayer is formed unhindered (4). This straight line goes through the origin and its slope is a measure of surface area

$$S_t = 15.47(V_a/t) \qquad (1)$$

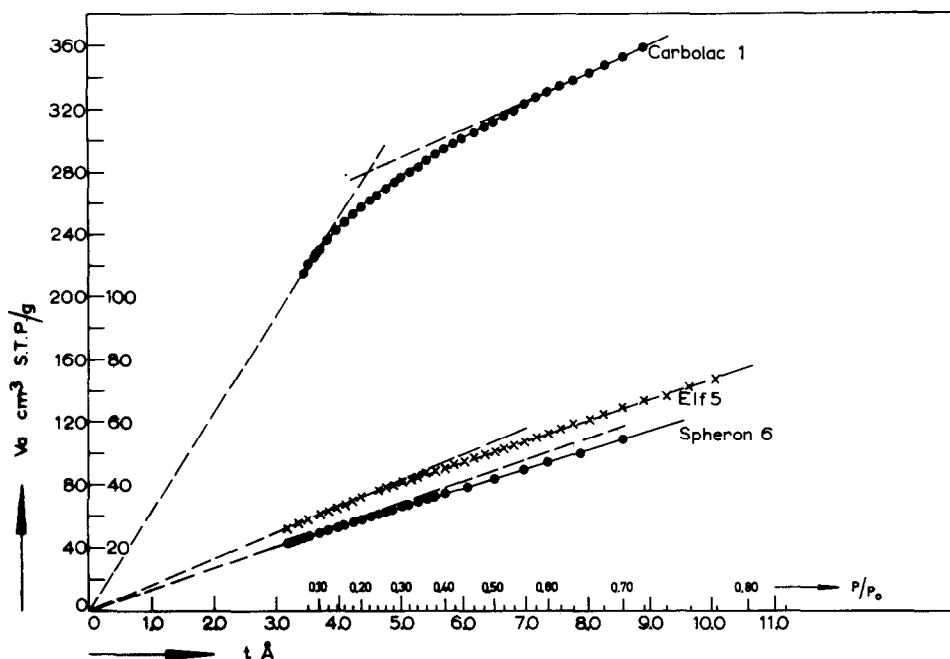Figure 2 shows the V_a–t plots for the samples Carbolac 1, Elf 5, and Spheron 6.

FIG. 2. V_a–t plots for Carbolac 1, Elf 5, and Spheron 6. Left-hand V_a scale for Carbolac 1.

The shape of the V_a–t plots suggests the presence of a group of narrow pores. For the samples Elf 5 and Spheron 6 an abrupt break between the two straight parts of the V_a–t curve occurs at $t = 4.75$ and 3.5Å, respectively. Assuming slit-shaped pores completely filled at a relative pressure for which the thickness t of the adsorbed multimolecular layer is equal to the half-width of the pores, we can calculate the volume V_n from the surface area S_n of the narrow pores and the thickness of the adsorbed layer (12, 13)

$$V_n = S_n t \qquad (2)$$

For the samples Elf 5 and Spheron 6, S_n can be calculated from the difference between the slopes of the two straight parts of their V_a–t plots.

For Carbolac 1 we are dealing with a distribution of pore dimensions; the break between the two straight parts of the V_a–t curve does not occur abruptly but via a curved line. For each point of this line the surface area that is still available is given by

$$S = 15.47(dV_a/dt) \qquad (3)$$

in which dV_a/dt is the slope of the tangent to the V_a–t curve in the considered point.

To calculate the total volume of the narrow pores, therefore, we divide the V_a–t curve for Carbolac 1 into j steps, each corresponding to an increase of $2\Delta t$ in the thickness of the multimolecular layer. At the beginning and the end of such a step we draw the tangent to the curve, determine its slope, and calculate the corresponding surface area with the aid of Eq. (3). The difference between the surface area at the beginning and that at the end of the jth step, ΔS_j, represents the surface area of the group of pores having a width between $2(t_j - \Delta t)$ and $2(t_j + \Delta t)$. If we assume that the mean width of the pores of this group is equal to $2t_j$ the volume of these pores is given by

$$\Delta V_j = t_j \Delta S_j$$

The total volume V_n of the narrow pores then is

$$V_n = \Sigma \Delta V_j = \sum_1^j t_j \Delta S_j \qquad (4)$$

The results of the calculations mentioned above are given in Table 2. The information contained in this table can be summarized

Sample	S_t (m²/g)	S_n (m²/g)	S_w (m²/g)	S_{em} (m²/g)	V_n (cm³/g)	Pore width of narrow pores (Å)
Carbolac 1	972	692	280	264	0.0362	7–15
Spheron 6	106	12	94	106	0.004	7
Elf 5	127	24	103	104	0.011	9.5
Mogul A	334	{ — 50	72	82	{ — 0.038	{ <7 15
Mau 4	353	{ — 100	94	—	{ — 0.043	{ <7 7.5–9.5
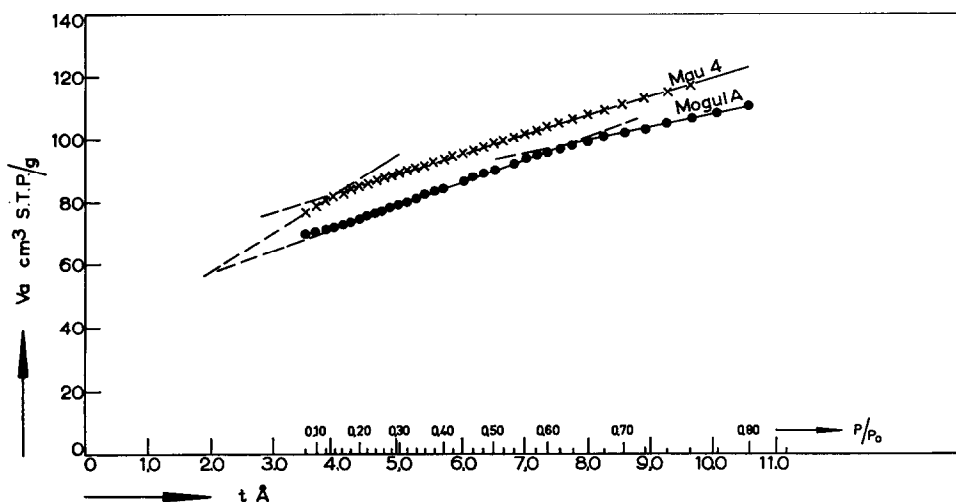
FIG. 3. V_a-t plots for Mogul A and Mau 4.

by saying that only small pores are present, namely a group of pores with a width varying from 7 up to 15Å for Carbolac 1, a group of pores with a width of 7Å for Spheron 6, and a group of pores with a width of 9.5Å for Elf 5.

From the slope of the second straight part of the V_a-t we can calculate the remaining surface area of the wide pores (indicated as S_w in Table 2). This value can be compared with the geometrical surface calculated from the measurement of particle diameters with the electron microscope (S_{em}). The electron microscope data are taken from the literature (14). As it appears from Table 2, the agreement between S_w and S_{em} is extremely good, suggesting that the remaining surface area represents only the external surface of the small particles.

For the Mogul A and Mau 4 preparations, it is noticed that the V_a-t plots for these carbons do not pass through the origin (Fig. 3). This arises because the t method cannot be used below the value $t = 3.5$Å and hence no further quantitative information is possible. It is clear, however, that the behavior shown should be explained by the presence of a group of pores with a width smaller than $2t = 7$Å.

By drawing a straight line through the origin and the point on the V_a-t plot with the lowest value of t the minimum surface that follows from the plots can be calculated. This surface, given in Table 2, is larger than the BET surface by about 20% for these samples.

When the pores have a width of about 4Å, the adsorbed molecules of nitrogen will be

attracted by both opposite walls of the pores; a strong persorption occurs, indicated by a very high C value for the BET equation. The actual specific surface is then much higher than the calculated one; adsorption on such a surface, however, also occupies part of the opposite surface of the pore.

The presence of an important quantity of very small pores with a width $< 7\text{Å}$ can only be ascertained qualitatively for the carbons Mogul A and Mau 4. Beside this group of very small pores, however, the surface area (S_n) and the volume (V_n) of a group of pores with a width varying from 7.5 up to 9.5Å for Mau 4 and of a group of pores with a width of 15Å for Mogul A can be calculated with the methods given above. The results of the calculations are given in Table 2.

The remaining surface area of wide pores (S_w) of these samples can be calculated too. For Mogul A it could be compared with the geometrical surface S_{em}. The agreement is good (Table 2), suggesting again that this remaining surface area represents only the external surface of the small particles.

GENERAL CONCLUSION

As a general conclusion it might be stated that a quantitative description of the pore dimensions has been obtained for a group of carbon blacks—Carbolac 1, Spheron 6, and Elf 5—by means of the universal t curve as given in Parts 1 and VI in this series. For two other carbons Mogul A and Mau 4 the presence of an important quantity of very narrow pores with a width $< 7\text{Å}$ has been ascertained qualitatively, whereas the surface area and volume of the pores with a width $> 7\text{Å}$ have been calculated quantitatively.

A special feature is the very narrow size distribution of the pores. It is remarkable that the dimensions found are an integral multiple of the thickness of a graphite layer $(\sim 3.4\text{Å})$.

REFERENCES

1. LIPPENS, B. C., LINSEN, B. G., AND DE BOER, J. H., J. Catalysis 3, 32 (1964).
2. DE BOER, J. H., AND LIPPENS, B. C., J. Catalysis 3, 38 (1964).
3. LIPPENS, B. C., AND DE BOER, J. H., J. Catalysis 3, 44 (1964).
4. LIPPENS, B. C., AND DE BOER, J. H., J. Catalysis 4, 319 (1965).
5. DE BOER, J. H., LINSEN, B. G., AND OSINGA, TH. J., J. Catalysis 4, 643 (1965) (preceding paper).
6. PIERCE, C., SMITH, R. N., WILEY, J. W., AND CORDES, H., J. Am. Chem. Soc. 73, 4551 (1951).
7. BOND, R. L., AND SPENCER, D. H. T., Proc. Conf. Carbon, 3rd, Buffalo, 1957, p. 357 (1959).
8. CROCKER, G. R., LASSOW, R. D., AND LYON, L. L., Proc. Conf. Carbon, 5th, Univ. Park, Penna., 1961 1, 103 (1962).
9. DE BRUIN, W. J., AND VAN DER PLAS, TH., Rev. Gén. Caoutchouc 41, 453 (1964).
10. ANDERSON, R. B., AND EMMETT, P. H., J. Phys. Chem. 56, 756 (1952); VOET, A., Rubber World, 139, 63, 232 (1958); WALKER, P. L., JR., AND KOTLENSKY, W. V., Can. J. Chem. 40, 184 (1962).
11. VOET, A., WHITTEN, W. N., JR., AND BOND, F. G., Proc. Conf. Carbon, 5th, Univ. Park, Penna., 1961 1, 110 (1962).
12. LIPPENS, B. C., thesis, Technological Univ. of Delft, 1961.
13. LINSEN, B. G., thesis, Technological Univ. of Delft, 1964.
14. "Cabot Carbons under the Electron Microscope." Cabot Corp., 1953.