

## Effect of Bromine Treatment on Microporosity & Adsorption Characteristics of Some Microcrystalline Carbons

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Irreversible adsorption of bromine on carbons such as Mogul, Spheron-6, Spheron-C, sugarcane charcoal and the commercially available activated carbon results in a substantial fall in microporosity of the carbons as determined from the Dubinin plots of adsorption isotherms of carbon dioxide at 0°. There is also a considerable fall in the sorption values of water and benzene vapours as indicated by their adsorption isotherms at 35°. The pore size distribution curves, as obtained by applying Kelvin equation to the adsorption isotherms of water vapours, indicate considerable narrowing down of the capillary pores. These data support the view that irreversibly adsorbed bromine is held-up within the capillary pores of the carbons.

PURI and coworkers<sup>1</sup> while studying the adsorption of bromine on microcrystalline carbons observed that the sorption-desorption branches of the isotherms at 35° did not meet even at zero pressure because a certain amount of the adsorbed bromine could not be recovered even on evacuating the system. A major portion of the irreversibly adsorbed bromine was shown to be neither due to chemisorption nor due to intercalation between graphitic layers<sup>2,3</sup>. It was considered<sup>1</sup> to be entrapped within the narrow capillary pores of the carbons and required activation energy to diffuse out of the pores. In order to provide further support to this line of thinking, we have now estimated the microporosity as well as certain other adsorption characteristics of a few microcrystalline carbons such as Mogul, Spheron-C, Spheron-6, sugarcane charcoal and the commercially available activated carbon before and after the irreversible adsorption of bromine. The results are reported in this paper.

### Materials and Methods

Three carbon blacks (Mogul, Spheron-C and Spheron-6), a charcoal (obtained by the carbonization of cane sugar and outgassed at 600° and 900°) and a commercially available activated carbon were used in the present investigations. Adsorption of bromine on each sample was carried out at 35° up to nearly saturation vapour pressure of bromine by employing the McBain balance technique, and the system was then evacuated at the same temperature as described earlier<sup>1</sup>. The amount of bromine retained by each carbon was noted, and the values are given in Table 1. The products thus obtained are referred to as bromine-treated carbons in the text. The original carbons not exposed to bromine vapour as well as the bromine-treated carbons were examined for their microporosity by determining adsorption isotherms (at 0°) of carbon dioxide<sup>4</sup> and applying Dubinin equation<sup>5</sup>. These were also examined for adsorption of water as well as benzene vapours at 35° employing the McBain balance technique using quartz-fibre spring of sensitivity

16.8 cm/g. The amount of carbon taken for each determination was 0.25 g.

### Results and Discussion

The adsorption isotherms of carbon dioxide at 0° on Spheron-C, Mogul and sugar charcoal (degassed at 600° and 900°) before and after bromine treatment are shown in Fig. 1. There is, evidently, an appreciable fall in the sorption value at each pressure up to 170-180 torr in each case. This may be due to blocking-up of some of the pores by the irreversibly adsorbed bromine. In order to get an idea of the effect of bromine treatment on the microporosity, the data were analysed in the light of Dubinin equation (1)

$$\log V = \log V_0 - D (\log p_s/p)^2 \quad \dots(1)$$

where  $V$  = volume of carbon dioxide adsorbed at equilibrium pressure  $p$ ,  $p_s$  = saturation pressure of carbon dioxide at 0° ( $\sim 34.4$  atms),  $V_0$  = micropore capacity, and  $D = 2.303 kR^2T^2/\beta^2$  where  $\beta$  is the

TABLE 1 — BROMINE RETAINED AND ITS EFFECT ON MICROPORE CAPACITY OF VARIOUS CARBONS

Carbon	Retained bromine (g/100 g carbon)	$D \times 10^{-3}$	Micropore capacity [cc(STP)/g carbon]
MOGUL			
Original	—	14.09	72.4
Original, bromine treated	20.1	14.70	52.5
SPHERON-C			
Original	—	14.06	63.0
Original, bromine treated	20.0	14.70	30.2
SUGAR CHARCOAL			
Degassed at 600°	—	12.00	144.5
Degassed at 600°, bromine treated	64.8	20.60	87.0
Degassed at 900°	—	17.52	67.6
Degassed at 900°, bromine treated	44.5	25.00	28.2

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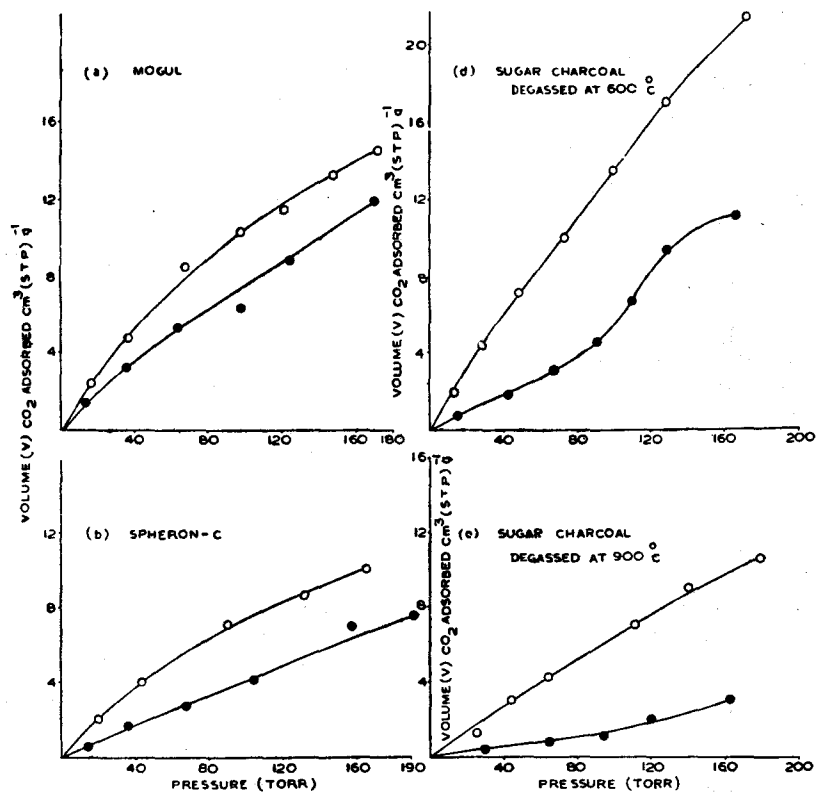


Fig. 1 — Adsorption isotherms of CO<sub>2</sub> at 0° on different carbon samples (O-O, original degassed samples; ●-● bromine-treated samples)

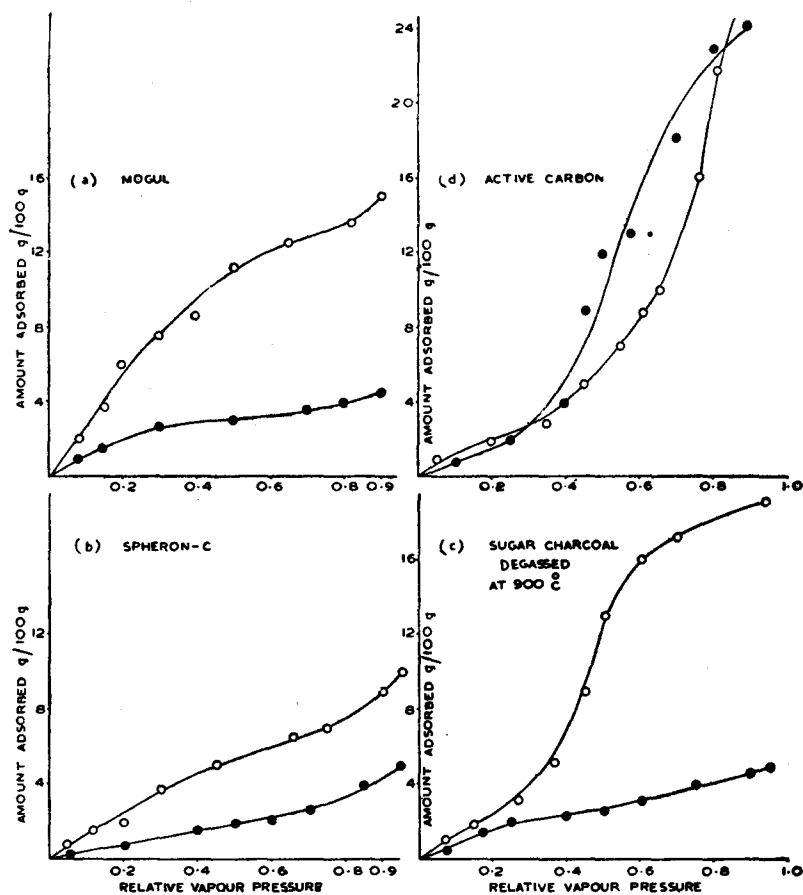


Fig. 2 — Adsorption isotherms of water at 35° on different carbon samples (O-O, original or degassed samples; ●-●, bromine-treated samples)

affinity coefficient of the adsorbate,  $k$  is a constant and  $R$  and  $T$  have their usual significance.

The plots of  $(\log p_s/p)^2$  against  $\log V$  for the various carbons before and after bromine treatment are linear. The intercept of these plots at  $(\log p_s/p)^2 = 0$  gives the value of  $V_0$  while the slope gives the value of  $D$ . These values for the various carbons are given in Table 1. It is seen that there is a substantial fall in microporosity in every case after the irreversible adsorption of bromine. The value of  $D$ , the gradient of the Dubinin plot, which is inversely proportional to  $\beta$ , rises appreciably after the adsorption of bromine. The effect is more pronounced in the case of activated charcoal as compared with carbon blacks. This indicates that the intensity of interaction of carbon dioxide with the surface falls appreciably after the fixation of bromine. This may also be due to fall in microporosity in the carbons.

The adsorption isotherms of water vapour on various carbons, before and after bromine treatment, are shown in Fig. 2. It is seen that there is a considerable fall in the sorption values at all relative vapour pressures (r.v.ps) in the case of carbon blacks (Figs. 2a and 2b) and sugar charcoal (Fig. 2c). The effect is much more in the case of sugar charcoal which may be partly due to retention of a maximum amount of bromine in this case (Table 1). The surface in all the three carbons, in any case, becomes much less hydrophilic after bromine treatment. This indicates narrowing down of the capillary pores lying within the adsorption range from the vapour

phase. The water isotherms on the activated carbon (Fig. 2d), however, gives a different picture; the sorption values, particularly between 0.25 and 0.8 r.v.p. increase after the irreversible adsorption of bromine. As is well known, activated carbon contains relatively wider pores and some of these are too wide to entrap a large amount of water vapours at lower relative vapour pressures. This is supported by the fact that activated carbon as such, before treatment with bromine, takes up much less water vapours than sugar charcoal at r.v.ps < 0.7, although it adsorbs relatively more vapours at r.v.ps > 0.7. However, after irreversible adsorption of bromine, there is a considerable rise in the sorption of water vapours by activated carbon, particularly at r.v.ps < 0.7. It appears that irreversible adsorption of bromine by the activated carbon takes place in relatively wider capillary pores thereby accentuating the proportion of pores of the size range involved in the sorption of water vapours at r.v.ps < 0.7. It is interesting to note that sorption of water vapour at 0.5, 0.6 and 0.7 r.v.ps by the activated carbon increases from 6.0, 8.5 and 12.9 mg/g to 9.8, 15.6 and 19.3 mg/g after the irreversible adsorption of bromine.

It was thought of interest to calculate the pore size distribution curves of the various carbons before and after the fixation of bromine applying the Kelvin equation (2)

$$\ln \frac{p}{p_0} = - \frac{2\gamma M}{r\rho RT} \quad \dots(2)$$

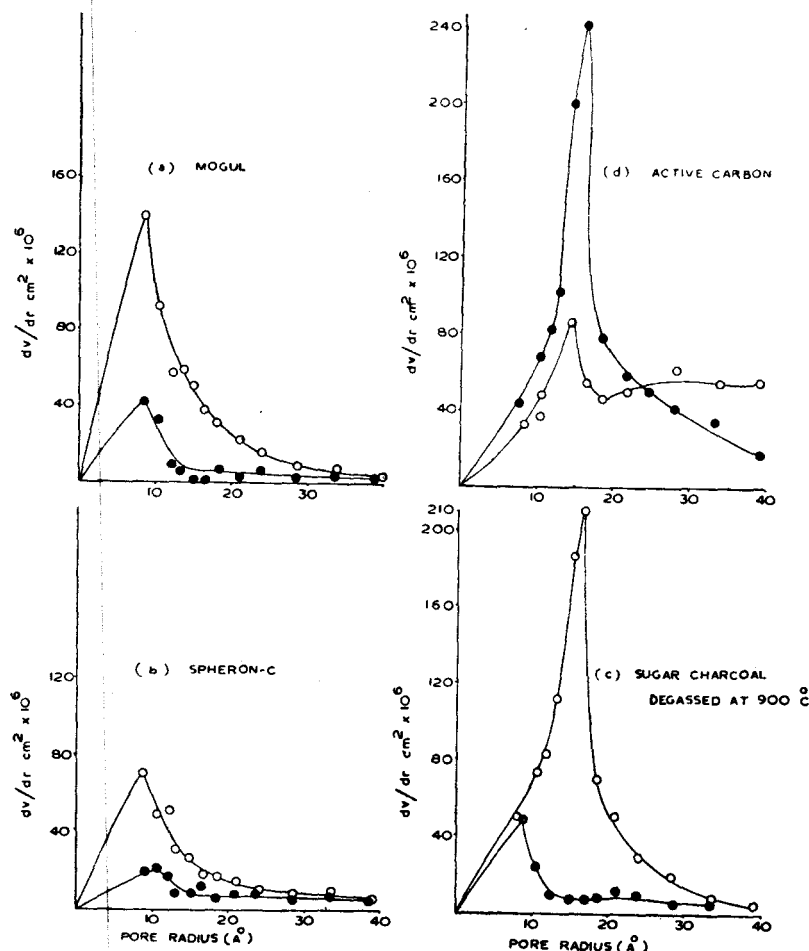


Fig. 3 — Pore size-distribution curves for water on different carbon samples at 35° (○-○, original or degassed samples; ●-●, bromine-treated samples)

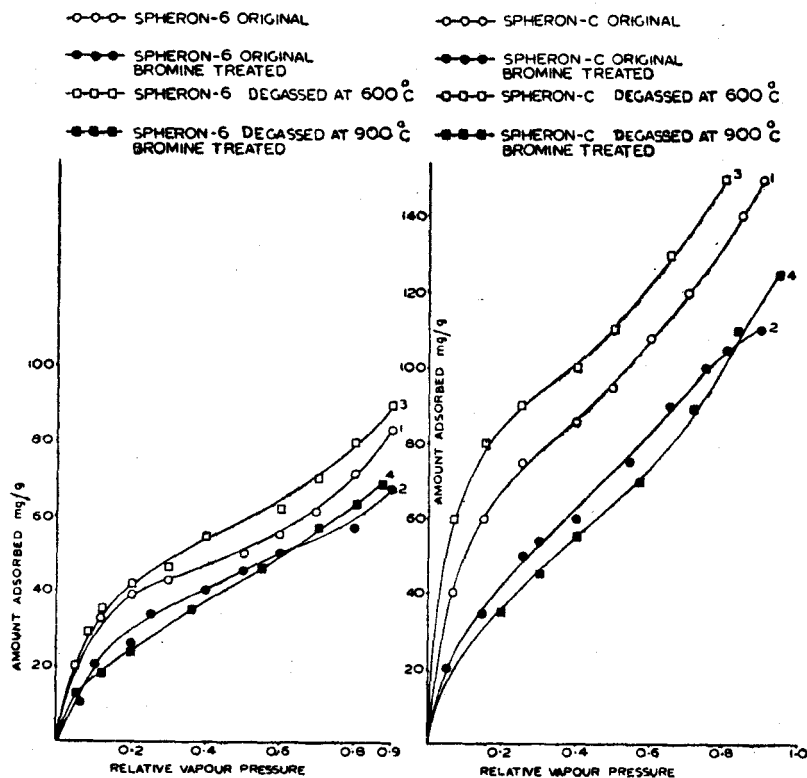


Fig. 4—Adsorption isotherms of benzene vapours at 35° on carbon blacks

where  $p/p_0$  = relative vapour pressure of the adsorbate at which adsorption occurs in a pore of radius  $r$ ,  $\gamma$  = surface tension,  $M$  = molecular weight and  $\rho$  = density of the adsorbate while  $R$  and  $T$  have their usual significance. It is assumed that the contact angle between the adsorbate and the adsorbent is zero. This may not be quite correct but Eq. (2) can be used to get comparative data, at least. The pore radius  $r$  calculated from Eq. (2) is usually referred to as Kelvin radius. It is necessary to add  $t$ , the thickness of the adsorbate film formed in the pores, to  $r$  in order to get a more relevant value of the pore radius. If water is the adsorbate, as in the present case,  $t$  may be taken as 3.2 Å (ref. 6). A correction is also necessary, particularly in early stages of the sorption as  $t$  may not have acquired the proper value. To avoid this possibility, the calculations were made from the sorption values at r.v.ps > 0.10. The error beyond this range, if any, should be negligible.

The pore size-distribution curves (Fig. 3) are the derived plots of  $dV_r/dr$  versus  $r$ . The value of  $dV_r/dr$  is evaluated by reading the slope of the curve  $V_r$  against  $r$  at suitable intervals of  $r$ . It is seen that there is a considerable fall in the volume associated with the pores of radii < 30 Å in the case of carbon blacks as well as sugar charcoal (Figs. 3a, 3b and 3c). The results are striking, particularly in the latter case. In the case of activated carbon (Fig. 3d), as expected, the volumes associated with pores of radii > 20 Å now increase while those associated with wider pores, particularly between 24 Å and 36 Å, decrease after the fixation of bromine. These results offer support to the view that irreversibly adsorbed bromine is locked up in the capillary pores of the adsorbent carbons.

Adsorption isotherms of benzene on the original as well as 600°-degassed samples of Spheron-6 and

Spheron-C are shown in Fig. 4. It is seen, as expected from previous observations<sup>7</sup>, that each carbon takes up more benzene vapours when degassed at 600°. This has been attributed to the interaction of  $\pi$ -electrons of benzene with quinonic oxygen which exists predominantly as surface complex in the carbons when degassed at 600°. This behaviour, in fact, has been taken as an indirect evidence for the presence of quinonic groups on carbon surfaces<sup>7</sup>. Significantly, the irreversible adsorption of bromine causes an appreciable fall in the sorption values of benzene in each case and the fall is much more in the case of carbons degassed at 600° as compared with the original samples. This indicates that the activity of quinonic groups in enhancing the interaction of carbons with benzene is suppressed to a large extent after the fixation of bromine. This means that surface quinonic groups are also perhaps located within the capillary pores of carbons and that fixation of bromine introduces a sort of steric effect hindering the interaction of carbons with benzene vapours, particularly at r.v.ps < 0.7.

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