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ON THE CORRELATION BETWEEN MICROPORE DISTRIBUTION OBTAINED FROM MOLECULAR PROBES AND FROM HIGH RESOLUTION ELECTRON MICROSCOPY

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Abstract—By using immersion calorimetry with liquids of various molecular dimensions, the distributions of the micropore sizes have been obtained for a number of active carbons, for the range 0.3 to 0.75 nm. These carbons have also been examined by high-resolution electron microscopy, the results from both techniques being displayed in the form of histograms. The agreement between the two methods appears to be good and provides possible evidence of the reduced interaction radius of adsorbed molecules and of exfoliation.

Key Words—Active carbon, micropore size distribution, immersion calorimetry, high-resolution electron microscopy.

1. INTRODUCTION

The adsorption capacity of active carbon has made it an extremely important material. It had early laboratory applications in the production of high vacuum[1]. Industrially, the first applications of the substance were more concerned with its behavior towards liquids rather than gases, the purification and decolourization of sugar requiring vast quantities of carbon[2]. Much was learned about the technology of gas adsorptive carbon during World War I[3], where the utilization of toxic gas made such a study essential for the production of efficient filters in gas masks.

Today, such applications as air purification[4], volatile solvent recovery[5], deodorisation[6], and treatment of drinking water[7] still make active carbon an important material, as do its uses in the chemical industry as a catalyst and catalyst support[8,9].

In these and all of the other diverse uses of active carbons, it is its high adsorption capacity that makes it useful. This property is a result of the porous nature of the material.

Pores in carbon are generally divided into three groups by size. According to I.U.P.A.C.[10], pores should be classified by their width (i.e., the diameter of a cylindrical pore or the width of a slit pore). Pores of widths exceeding about 50 nm are called macropores, those with widths between 2 nm and 50 nm are known as mesopores, and those of widths not exceeding 2 nm are called micropores.

Micropores comprise of all pores of molecular dimensions in which volume filling of pores occurs (TVFM of Dubinin[11]) rather than capillary condensation. These pores, although smallest in size, constitute the largest part of the internal surface of a carbon and are, therefore, the pores in which most adsorption occurs. In fact, for a typical active carbon, the micropores constitute at least 90% of the apparent surface area.

The traditional theory of Brunauer, Emmett, and Teller[12] is generally used to describe isotherms that are of type 2 in the BDDT classification[13] (i.e., adsorption on nonporous solids). This treatment is also efficient in the examination of mesoporous solids or for characterizing the mesoporous contribution of a microporous solid. The model does however, have drawbacks, namely its assumption that the adsorption sites are energetically identical and its neglect of lateral interactions between neighbouring molecules. It also gives unrealistically high results when applied to some microporous solids.

When dealing with micropores, the term surface area loses its meaning and these pores are generally dealt with in a different manner. The basis of the theory of gas and vapour adsorption by microporous carbons are the Polanyi potential theories[14,15]. Adapting these theories leads to the equation of Dubinin and Astakhov[11].

$$W = W_0 \exp[-(A/\beta E_0)^n]$$

W is the volume of the adsorbate condensed in the micropores at temperature T and relative pressure p/p_0; W_0 is the total volume of the micropores accessible to the adsorbate. $A = RT \ln (p_0/p)$, and n, β, and E_0 are specific parameters of the system under investigation. Analysis of numerous adsorption experiments have shown that the parameter n, is for the most part equal to 2 for active carbons[16,17], which resulted in the equation of Dubinin and Radushkevich.

$$W = W_0 \exp[-B(T/\beta)^2 \log^2(p_0/p)]$$

The parameter B has been shown[18,19] to be related to an average dimension, $\overline{R}_g$ the mean square gyration radius of the micropores obtained from small-angle X-ray diffraction. An alternative empirical relationship has also been suggested by Dubinin and Stoeckli[20], which relates the half width of slit shaped pores X to the characteristic energy E_0. This value of X can also be used[21] to calculate the geometric surface area S_{mi} of active carbons.

Another approach to studying microporosity is by using immersion calorimetry. Using the Dubinin–Radushkevich equation as a basis and assuming the external surface area to be negligible, it can be shown[22], that the enthalpy of immersion of a microporous carbon into an organic liquid is

$$-\Delta H_i\ (J/g) = \beta E_0 W_0 (1 + \alpha T)\sqrt{\pi}/2V_m \quad (1)$$

where H_i is the enthalpy of immersion and α and V_m are the thermal expansion coefficient and the molar volume of the liquid filling the micropore system, respectively.

$$W(L) = -\Delta H_i/(\beta E_0 (1 + \alpha T)\sqrt{\pi}/2V_m) \quad (2)$$

$W(L)$ being the micropore volume filled by a liquid of molecular dimension L.

In order to calculate the micropore size distribution, eqn (2) is used for a series of molecular probes in the range 0.3 to 0.75 nm. Using a value of E_0 obtained from adsorption experiments with a small molecule, this equation can be used to calculate $W(L)$ for immersion into each of the liquids. A histogram of dW/dL can then be constructed to show the distribution of the micropores in the sample.

There are other techniques unrelated to adsorption, which can be used to study porous carbons, namely small-angle X-ray diffraction and electron microscopy. Using combinations of small-angle X-ray diffraction, molecular probes, and adsorption analysis, consistency between the results has been shown for certain carbons[24,25]. Electron microscopy was initially used in the study of chrysotile asbestos fiber to produce a correlation between the pore sizes resulting from it and those determined from gas adsorption data[26–28]. However, the pores involved here were relatively large (2–6 nm). When carbon was studied, initial attention was paid to the meso- and macropores only[29], as observation of micropores was limited by the resolution of the microscopes. The imaging of individual graphite layers[30] led to some microporous structure becoming apparent. With improved instrumentation and a clearer understanding of microscopical techniques, it was possible to study the structure of microporous samples [31–33] by high-resolution electron microscopy (HREM) and make direct measurements of micropore sizes.

As an alternative to HREM, it is also possible to utilize the dark field technique of Oberlin *et al.*[34], whereby well-defined information is obtained on d_{002}, the spacing between the aromatic sheets of carbonaceous material.

The aim of the present work is to use some of the previously mentioned techniques, especially HREM and immersion calorimetry, to study the microporous structure of active carbons.

The immersion calorimetry is a macrotechnique from which the average pore size distribution can be deduced. In comparison, HREM reveals the structure of individual pores but, of course, is less statistically representative. The comparison of these two techniques used on the same carbons should show complementary information on the micropore structure as well as a commentary on the two techniques.

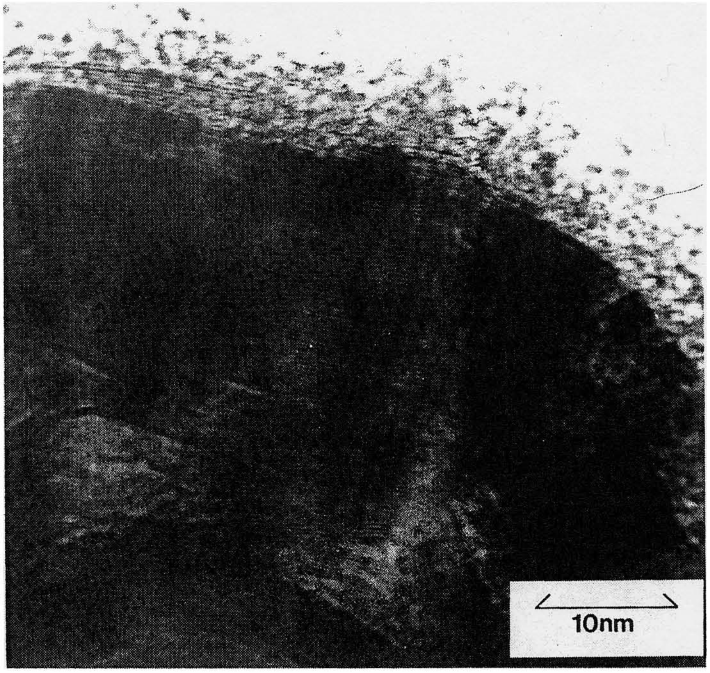
2. EXPERIMENTAL

Studies were carried out on a series of carbons produced from a commercial carbon, "Carbo-grill," denoted CEP-0 for the purpose of experiments. CEP-0 is a soft-wood carbon of very low ash content with a helium density of only 2.00 g/cm and an external surface area of around 30 m^2/g. This precursor was crushed and sieved until it consisted of particles of between 0.6 and 1.02 nm, then carbonized under nitrogen at 850°C for 1 h. It was next activated at 850°C with carbon dioxide in a fluidized bed reactor for varying amounts of time. The resulting series of carbons were known as CEP 18, 35, and 49, the number illustrating the degree of burnoff (i.e., the percentage weight decrease of the material during activation) of the sample.

These samples were characterized by Kraehenbuehl *et al.*[23] and Ballerini[35] using standard gravimetric and volumetric equipment: immersions into various organic liquids were carried out in a calorimeter of the Calvet type.

The CEP series was also examined by means of a JEOL 1200EX transmission electron microscope, the specimens being finely ground and dusted onto electron microscope grids coated with holey carbon film. Areas of the sample protruding over the holes were examined in order to obtain better resolution. A focal series, taken at defocus values of 70 to 100 nm underfocus, was obtained to allow for variations in specimen height, the best micrograph then being selected from these. The micrographs were also examined with an optical diffractometer to search for the presence of astigmatism or drift and also to show any strong periodicity that may be present.

On examining the micrographs using a hand lens, the pores were measured at the thin edge of wedge-shaped particles. In these preliminary studies, approximately 100 pores were measured for each of the samples. These results were obtained from various different areas of the sample.



3. RESULTS AND DISCUSSION

Examination of the micrographs shows the CEP series to be structurally heterogeneous. A comparison of Figs. 1 and 2 (both of CEP 18) expresses this clearly. Figure 1 shows a carbon that appears to have an almost graphitic lattice structure, these lattices occurring in bands of various thickness. However, in Fig. 2, the same carbon has a grainy, ribbonlike appearance with no apparent lattice structure. In Fig. 3, another structure intermediate between those of Figs. 1 and 2 can be seen. As well as the features already mentioned, it contains areas of short-range order with both single-layer planes and groups of

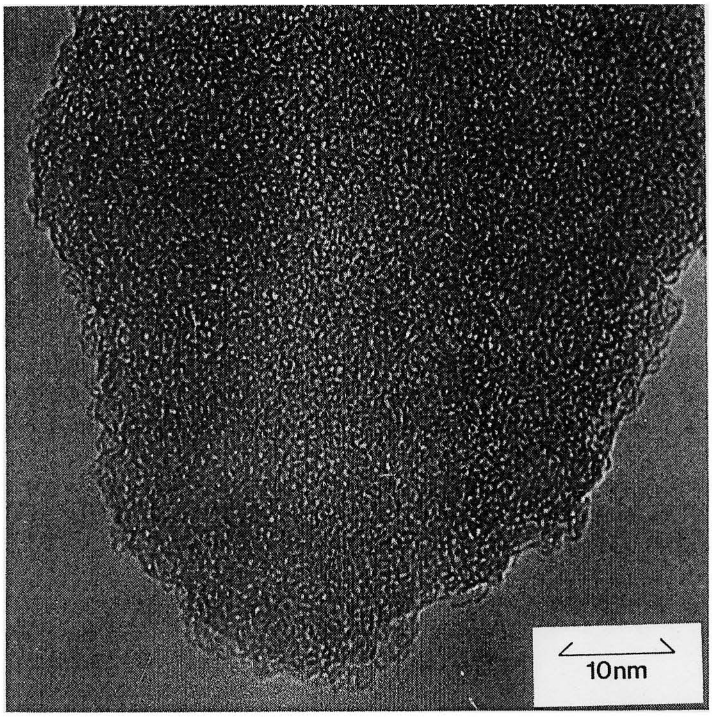


Fig. 2. Micrograph of CEP 18 showing grainy appearance.

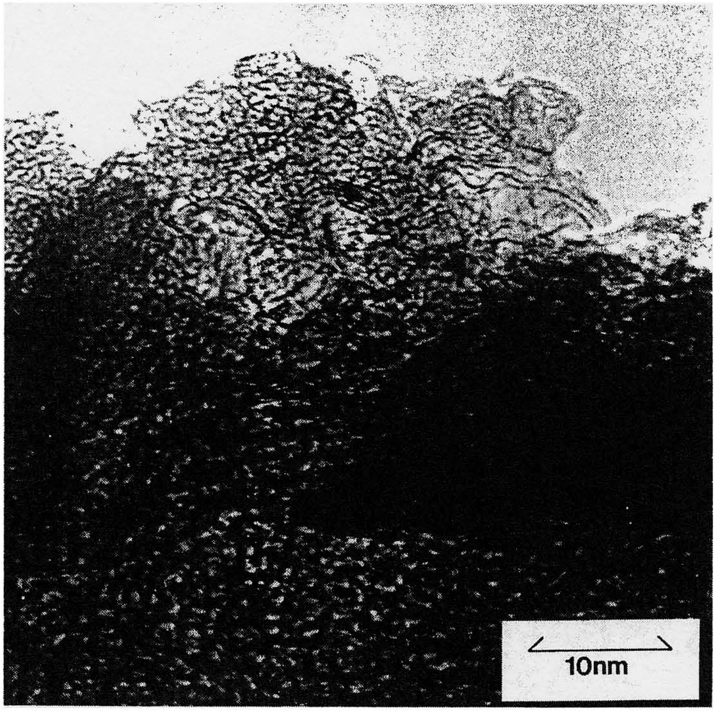


Fig. 3. Micrograph of CEP 18 showing areas of short-range order.

about two to five lattice fringes. Similar features were also observed for the other two carbons in the series. This heterogeneity is not unexpected for carbons from a wood source.

Figure 4 is a micrograph of carbon CEP 49. On micrographs such as this, the pore widths were measured. As to the shape of the pores, they appear to be channels running into the sample. Their length and shape varies greatly, as would be expected from the visibility criteria discussed previously[31]. The twisting of a pore would alter the contrast of its walls. However, some qualitative assessment of pore shape can be obtained. Some are short slits whereas others continue for considerable distances within the sample. Many branches are also apparent in some of the pores. Another feature observed in these micrographs is the presence of "cavities" formed where a number of pores exit the sample in close proximity to each other.

These values obtained for the pore sizes using HREM cannot be compared directly with those deduced from immersion calorimetry as the two techniques do not measure exactly the same quantity. Immersion calorimetry—as with all adsorption methods— measures the accessible space inside a pore; electron microscopy, on the other hand, measures the internuclear distance between two carbon sheets. In consequence, an adjustment must be made to the HREM results by subtracting the atomic diameter of carbon from them if they are to agree with immersion studies.

Unfortunately, the situation is not quite this simple because atomic radius is a variable quantity and the heat of adsorption of a gas in a pore implies that there is some interaction between the surface and adsorbate. The normal nonbonded (Van der Waals) radius of carbon is 0.17 nm, although small variations on this occur (e.g., in a hexagonal, close-packed environment such as graphite the dimension is 0.168 nm and in aromatic hydrocarbons such as perylene it is 0.174 nm). However, Everett and Powl[36] calculated that the radius should be approximately 0.1 nm. Variations occur with pore diameter and longer-range effects, depending on whether the carbon layer is isolated or surrounded by a graphitic matrix. These variations are small, however, and therefore 2 × 0.1 nm has been subtracted from the pore diameters obtained from HREM.

A comparison of the results derived from the techniques may be seen, displayed for convenience, in the form of superimposed histograms (Figs. 5–7). There is a very good agreement for CEP 18 and 35, the two carbons of lower burnoff (Figs. 5 and 6, respectively) seeming to indicate the validity of the Everett–Powl treatment, although the precise figure of 0.2 nm is unlikely to be accurate for all situations and some contraction of the gas molecule radius might be expected. Had the Van der Waals value 0.34 nm been subtracted from CEP 18 rather than the value 0.2 nm, then only about 25% of the pores would have been over 0.41 nm (i.e., large enough to accommodate a benzene molecule). This would mean that this small percentage of the pores accounts for a pore volume of 0.223 cm^3/g. The pores in the resulting narrow size distribution would also have to swell to almost twice their size to allow the adsorp-

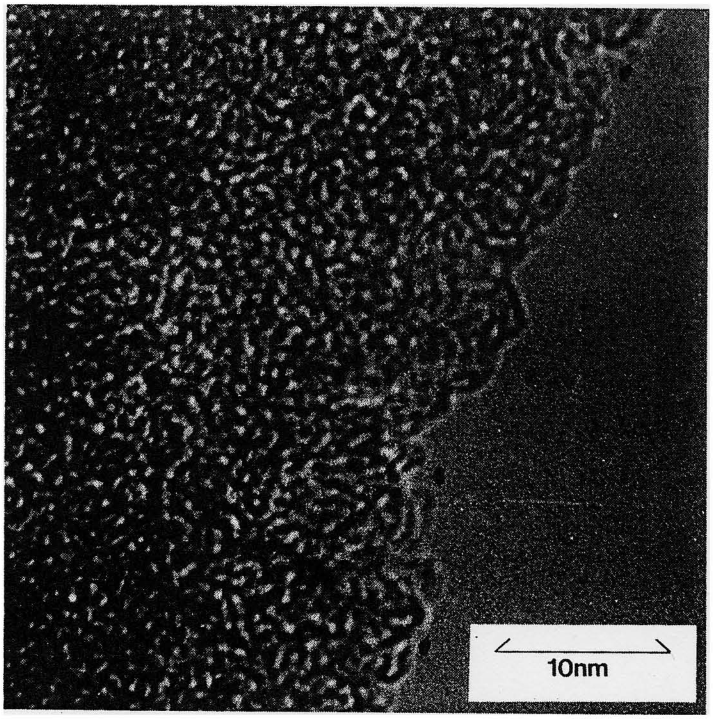


Fig. 4. Micrograph of CEP 49, the arrows indicating the presence of micropores.

tion of the larger probes such as α-pinene, into which they were immersed.

In the case of the higher burnoff carbon, CEP 49 (Fig. 7) the agreement is less good. Both techniques do show a large single peak rather than the broad distribution of the previous samples; however, that found by HREM is displaced to a lower value than that obtained from immersion calorimetry.

A possible explanation for this may be that the layer planes exfoliate in the presence of a gas or liquid and collapse under vacuum—as exists in the electron microscope. The ability to do this depends very much on the extent of a layer. As the CEP 49 is of higher burnoff than the other two samples, it would be expected that it would possess longer more flexible layer planes that would undergo exfoliation more easily. This would explain why deviations are observed for CEP 49 but not for the lower burnoff carbons CEP 18 and 35.

In conclusion, this work shows a reasonable agree-

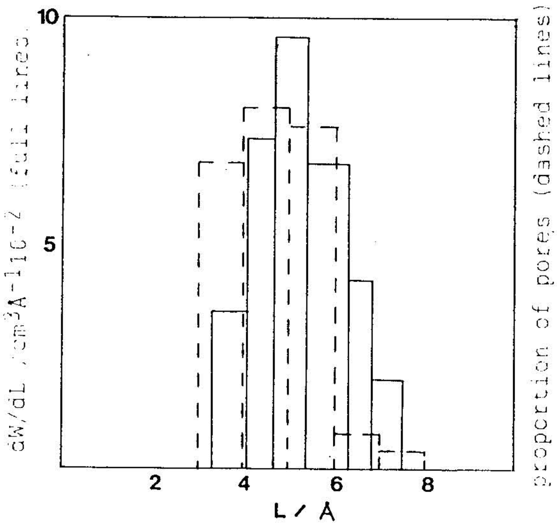


Fig. 5. Micropore size distribution of CEP 18 from immersion and HREM studies (solid and dashed lines, respectively).

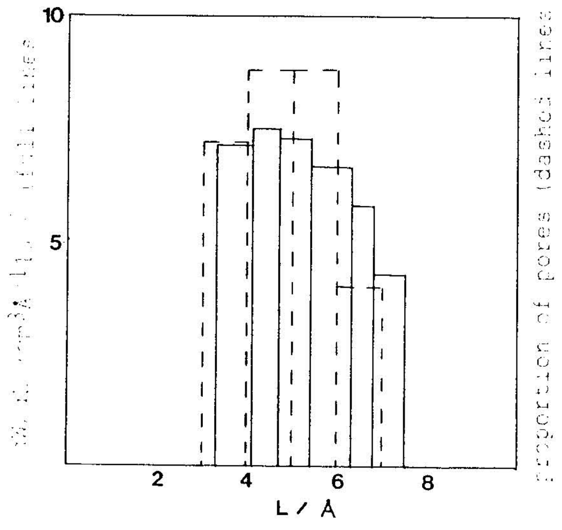


Fig. 6. Micropore size distribution of CEP 35 from immersion and HREM studies (solid and dashed lines, respectively).

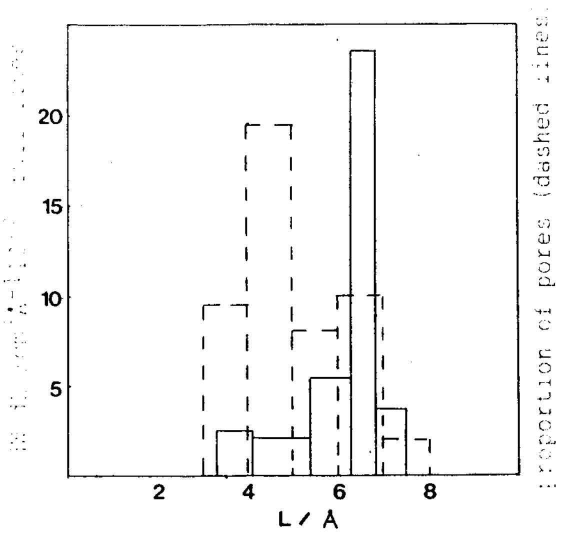


Fig. 7. Micropore size distribution of CEP 49 from immersion and HREM studies (solid and dashed lines, respectively).

ment between pore sizes deduced from immersion calorimetry and those measured from high-resolution electron micrographs. It also considers the definition of a pore and provides direct evidence for the reduced interaction radius of an adsorbed molecule. In the carbons studied there was not conclusive evidence of exfoliation, but the use of these two techniques in conjunction could be a sensitive test of this phenomenon.

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