Published in Carbon 28, issue 6, 907-909, 1990
which should be used for any reference to this work

On the assessment of microporosity in active carbons, a comparison of theoretical and experimental data

Key Words - Micropore distributions, heterogeneous active carbons

We have recently shown [1] that the overall adsorption isotherm (1), given below, provides a good description of the micropore distribution of active carbons. This is in agreement with adsorption and immersion experiments carried out with vapours and liquids whose molecular dimensions vary between 0.35 and 0.8 nm [2]. Owing to the fact that most industrial active carbons are heterogeneous and have a substantial fraction of micropores in the range of 1 - 2 nm, direct experimental evidence for the validity of the model has so far only been provided for the initial part of the distribution ($L < 0.8$ nm). Indirect evidence is provided by the agreement between the calculated micropore surface area and the value obtained by the selective adsorption of caffeine from aqueous solutions [3]. However, further experimental data is needed to provide reliable standards for routine work [4] and for the use of eqn (1), to derive micropore distributions from isotherms. In the present note, we illustrate this point and we show how the range of molecularsieve experiments can be extended to approximately 1.5 nm, by using a variety of liquids with nearly spherical molecules.

It is now established that micropore systems corresponding to a linear Dubinin - Radushkevich plot are not as homogeneous as thought previously [4,5]. Consequently, we suggested the use of an integral transform with a core equation of the Dubinin Astakhov type with $n = 3$, instead of $n = 2$ as used by Jaroniec and Choma [6]. The resulting overall isotherm is

$$\theta(A) = \left(\frac{a}{a + \left(A/\beta K_o\right)^3} \right)^{\nu} \qquad (1)$$

with the underlying normalized distribution of the micropore-width L,

$$f(L) = 3 \cdot L^{(3\nu-1)} \cdot a^{\nu} \cdot \exp\left[-aL^3\right] / \Gamma(\nu) \qquad (2)$$

$A = RT \ln (P_o/P)$; β is the so-called affinity coefficient of the adsorbate; a, ν and K_o are adjustable parameters, where K_o is related to E_o and to the average pore-width of the system through $L = K_o/E_o$.

As shown earlier [1], eqns (1) and (2) lead to a good description of the micropore distributions for carbons following the Dubinin - Radushkevich equation. On the basis of independent determinations involving molecularsieve effects (described previously [1,2] and in the present work) and/or the surface area of the ideally slit-shaped micropores (SAXS and the selective adsorption of caffeine from aqueous solutions [1,3]), the following relations can now be used in the range $0.4 < L < 2$ nm,

$$E_o \text{ (kJ/mol)} = (10.8/L) + 11.4 \qquad (3)$$

$$K \text{ (nm} \cdot \text{kJ/mol)} = 10.8 - 11.4 \cdot L \qquad (4)$$

E_o being the value derived from the DR eqn. It also follows that $K(\text{nm}\cdot\text{kJ/mol}) = 10.8 + 123.1/(E_o + 11.4)$.

Eqns. (3) and (4) can replace earlier and more complicated correlations [7]. As pointed out in ref. [1], it is assumed that in eqn (1) K_o is constant for a given system of micropores and it corresponds to the *average* pore-width L, related to E_o of the DR adsorption isotherm.

We used a variety of liquids with nearly spherical molecules (see table 1), whose average critical dimension L can be estimated from molecular models and consequently a wider range of microporosity can now be investigated experimentally by immersion calorimetry. However, it is important to stress that the critical dimension L may not reflect the exact pore-width, since L corresponds to the average dimension of the molecule (Van der Waals diameters) obtained by minimizing its energy. Moreover, it is assumed that the density in the adsorbed state is equal to that of the pure liquid. Systematic errors may therefore be introduced in the assessment of micropore sizes.

The experiments were performed with three industrial active carbons and one microporous carbon black. Their main characteristics are given in table 2. Figs. 1-4 show the good agreement which can be obtained between the experimental distribution (histograms) and the distribution (curves) recalculated from extended adsorption data for C_6H_6 and N_2O near 293 K, by using eqns (1) and (2). This means that reliable information on the micropore distribution of typical active carbons can be obtained by either technique, but the external surface area S_e has to be considered in the calorimetric approach [2]. The fundamental relation used here is

$$\Delta h_i \text{ (J/g)} = \beta E_o W_o (1 + \alpha T) \sqrt{\pi} / 2V_m + h_i S_e \qquad (5)$$

Strickly speaking, in the case of bulky molecules E_o should be replaced by an effective value E'_o, smaller than E_o and corresponding to the larger pore sizes seen by these molecules, as implied by eqn (3).

Table 1

List of Recommend liquids to be used as molecular probes in immersion calorimetry. L represents the estimated critical dimension and h_i is the specific enthalpy of wetting of the external surface (see ref. [2,4])

Liquid	L [nm]	α [$10^{-3}K^{-1}$]	β	$-h_i$ [J/m^2]	Vm [cm^3/mol]
Methylene Chloride	0.33	1.34	0.66	0.152	64.02
Benzene	0.41	1.24	1.00	0.114	88.91
Cyclohexane	0.54	0.96	1.04	0.101	108.10
Carbon Tetrachloride	0.63	1.22	1.05	0.115	96.50
1,5,9-cyclododecatriene	0.76	0.76	1.90	0.103	182.02
α-Pinene	0.68/0.80	1.02	1.70	0.110	158.75
Perchlorocyclopentadiene	0.75/0.88	1.17	1.91	0.110	159.30
Tetrabutyl Urea	0.93	0.85	3.50	0.118	282.34
Tetraisopropyl Ortho Titanate	1.05	2.23	3.31	0.205	294.57
Tetrabutyl Ortho Titanate monomer	1.30	0.52	3.83	0.167	340.36
Tri-2, 4 xylylphosphate	1.50	0.66	4.05	0.160	360.04

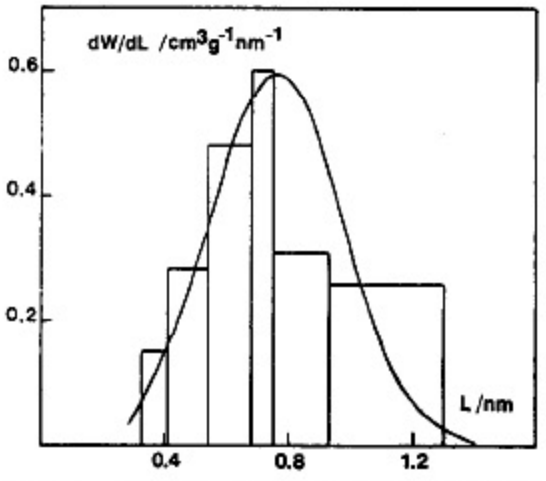

Figure 1. Carbon CAF-A (41.5% burn-off in H_2O at 850°C)

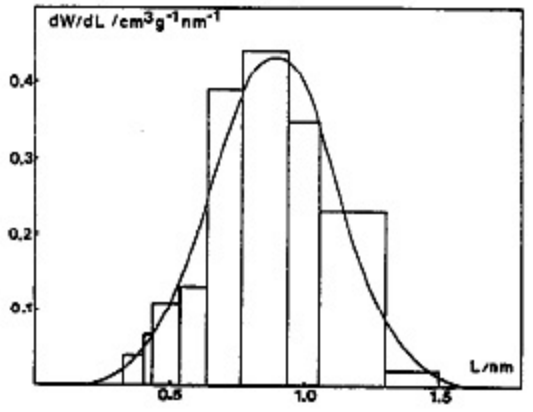

Figure 2. Carbon CM

However, as suggested by model calculation, this correction is not very important as far as the *differential* curve $\Delta W/\Delta L$ is concerned; in the case of carbon U-103 for example (see figure 4), for the largest molecular probe used (L > 1.5 nm) E'_o should be near 17.5 kJ/mol, against 20.6 kJ/mol for a molecule like benzene, which sees the entire micropore system (Table 1). The effect on the real height of the last block of the histogram (1.3 - 1.5 nm) is not very large since E'_o is effectively 18 kJ/mol for the preceeding molecule, seeing L > 1.3 nm. It appears that from a practical point of view a satisfactory histogram can be obtained from eqn (5) by using the same value of E_o = 20.6 kJ/mol with all liquids. Formally, the histogram can be refined, but it must be pointed out that the accuracy of the techniques described here is limited by the uncertainties in the molecular dimensions and in the independent assessments of the micropore surface areas, used to establish the basic correlation between E_o and L. The uncertainty in the micropore distribution may therefore be as high as 10 percent or more, but a reasonable characterization of typical active carbons is now possible

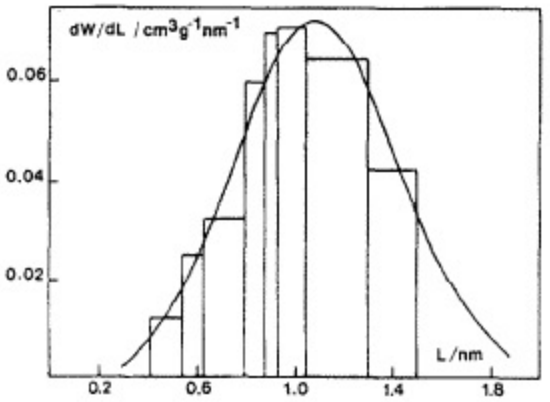

Figure 3. Microporous carbon black XC-72

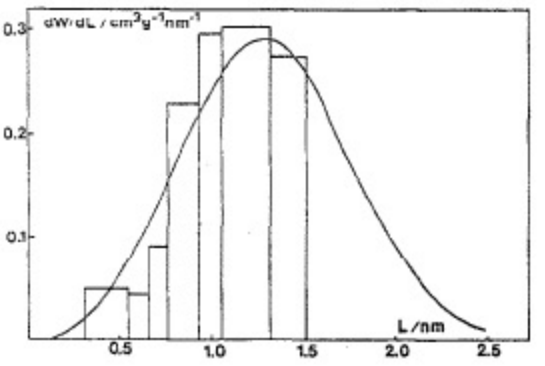

Figure 4. Carbon U-103

Table 2

Main characteristics of the carbons shown in figs 1-4, derived from adsorption and immersion experiments. The surface of the micropores S_{mi} has been calculated from the distribution (2), by assuming slit-shaped pores

Carbon	E_o [KJ/mol]	W [cm^3/g]	S_{ext} [m^2/g]	L [nm]	S_{mi} [m^2/g]
CAF-A-41.5	27.5	0.316	102.0	0.64	884.0
CM	26.2	0.252	28.0	0.75	608.0
XC-72	22.0	0.059	107.0	1.02	120.0
U-103	20.6	0.330	60.0	1.18	575.0

by two different techniques. The only restriction observed so far seems to be in the case of very strongly activated carbons, showing yet unexplained deviations in calorimetry and possibly due to deformations in the micropore structure, caused by the liquids [8], or by changes in the geometry of these pores which are not necessarily slit-shaped.

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