Micropore sizes in activated carbons determined from the
Dubinin–Radushkevich equation

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Microporous carbons are characterized by relatively heterogeneous pore size distributions (PSD), but their structure may be regarded as a collection of locally slit-shaped micropores [1–3]. Different techniques have been used to derive PSDs, in particular the use of molecular probes adsorbed from the vapour and the liquid phases [4] and, more recently, the analysis of adsorption data with the help of model isotherms resulting from computer simulations [5,6]. These studies provide information on the average micropore width $L_o$. Further evidence can be obtained from the adsorption of caffeine [4] and of phenol [7] from aqueous solutions and the corresponding enthalpies of immersion $\Delta H$. These molecules are adsorbed as type I isotherms, with limiting amounts $N_{\text{am}}$. The molar energies of transfer from the liquid to the solid, $\Delta H/N_{\text{am}}$, respectively $-64$ to $-66$ kJ mol$^{-1}$ (caffeine) and $-30$ to $-32$ kJ mol$^{-1}$ (phenol), are identical for non-porous and porous carbons. This suggests that the same mechanism takes place, i.e. the coating of the micropore wall area $S_{\text{m}}$ and/or of the non-microporous area $S_e$. The specific enthalpies of immersion $h_1$(caffeine) = $-0.113 \pm 0.010$ J m$^{-2}$ and $h_1$(phenol) = $-0.109 \pm 0.008$ J m$^{-2}$ obtained with carbon blacks, lead to the total surface area $S_{\text{tot}} = S_{\text{m}} + S_e$. The average width $L_o$ of slit-shaped micropores, is given by:

$$L_o (\text{nm}) = 2000 \frac{W_o (\text{cm}^3 \text{ g}^{-1})}{S_{\text{m}} (\text{m}^2 \text{ g}^{-1})}$$

(1)

$W_o$ being the volume filled. It has been shown that a correlation exists between $L_o$ and the so-called characteristic energy $E_o$ of the Dubinin–Radushkevich (DR) equation [4]

$$W = W_{\text{am}} \exp\left[-(A/\beta E_o)^n\right]$$

(2)

where $\beta$ is the affinity coefficient and $A = RT \ln(p/p_0)$.

Following Dubinin’s pioneering work [8], different empirical expressions have been suggested, for example by Stoeckli [4]

$$L_o (\text{nm}) = 10.8/(E_o - 11.4 \text{ kJ mol}^{-1}).$$

(3)

Eq. (3) provides a good estimate for $0.5 < L_o < 1.5–1.8$ nm, but inconsistencies appeared later, due to different factors. One of them is the restricted accessibility of wide pores due to gate effects (entrances being blocked by constrictions or larger pores placed behind smaller pores). This leads to apparent contradictions between the predictions based on $E_o$ and $W_{\text{am}}$ provided by small molecules, and the experimental enthalpies of immersion into bulky liquids. Gate effects may also prevent caffeine from reaching certain pores normally accessible to it. This leads to smaller areas and larger values of $L_o$. Consequently, we re-examined Eq. (3) by adding computer modelling of CO$_2$ adsorption [6] and by considering the selective adsorption of phenol [7], which can probe the same micropores as

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benzene (0.4 nm). Its adsorption depends on the oxygen content of the surface [9], but for the carbons considered here, the ratio \(\Delta H(H_2O)/\Delta H(C_6H_6)\) varies between 0.23 and 0.32. This corresponds to a relatively low oxygen content [10].

The reassessment of Eq. (3) is based on 14 microporous carbons and \(L_o\) was obtained from at least two of the following techniques: (a) immersion calorimetry into liquids of molecular dimensions up to 1.5 nm, (b) the selective adsorption of caffeine and phenol, (c) the analysis of CO\(_2\) isotherms at 273 K [11] with the help of model isotherms obtained from simulations, (d) electron microscopy and STM. The correlation shown in Fig. 1 (32 values) corresponds to the following expression for \(0.5 < L_o < 2.5 - 3.0\) nm

\[
L_o (\text{nm}) = 13.7/(E_o - 9.7 \text{kJ mol}^{-1}).
\]  

(Eqs. (4) and (3) are compatible, as their differences lie within the standard deviation \(\sigma = 0.11\) nm. Beyond 1.5–2.0 nm, the shape of the micropores may change, although slits may still be present, as indicated by STM. High values of \(L_o\) must therefore be regarded as equivalent pore-widths, relating \(W_o\) and \(S_m\) through Eq. (1). It is also interesting to note that the limiting value of 9.7 kJ mol\(^{-1}\) is close to the values of \(E_o\) derived from the DRK equation for adsorption on graphitised carbon blacks (9.8 to 10.8 kJ mol\(^{-1}\)) [12]. This provides support for expressions like Eqs. (3) and (4) and for Dubinin’s theory itself.

In conclusion, Eq. (4) can be used for the assessment of the probable micropore width \(L_o\) on the basis of the characteristic energy \(E_o\) given by the DR equation for the adsorption of small molecules such as C\(_6\)H\(_6\) and CO\(_2\). It is therefore advisable to check for the presence of constrictions by determining the enthalpy of immersion into liquids with critical diameters around 0.6–0.9 nm. Finally, one should emphasize the statistical nature of Eq. (4), reflected by \(\sigma = 0.11\) nm. This value also corresponds to the scatter observed in \(L_o\) for different techniques applied to the same carbon, which shows that the accuracy of \(L_o\) should not be overestimated.

**References**


