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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 $\Delta_i H$. These molecules are adsorbed as type I isotherms, with limiting amounts N_{am}. The molar energies of transfer from the liquid to the solid, $\Delta_i H/N_{am}$, 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_{mi} and/or of the non-microporous area S_e. The specific enthalpies of immersion h_i(caffeine) $= -0.113 \pm 0.010$ J m^{-2} and h_i(phenol) $= -0.109 \pm 0.008$ J m^{-2} obtained with carbon blacks, lead to the total surface area $S_{tot} = S_{mi} + S_e$. The average width L_o of slit-shaped micropores, is given by:

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

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]

$$W = W_{ao} \exp[-(A/\beta E_o)^n] \quad (2)$$

where β is the affinity coefficient and $A = RT \ln(p_s/p)$. Following Dubinin's pioneering work [8], different empirical expressions have been suggested, for example by Stoeckli [4]

$$L_o \text{ (nm)} = 10.8/(E_o - 11.4 \text{ kJ mol}^{-1}). \quad (3)$$

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_o 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 $\Delta_i H(H_2O)/\Delta_i H(C_6H_6)$ 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

$$L_o\,(\text{nm}) = 13.7/(E_o - 9.7\ \text{kJ mol}^{-1}). \quad (4)$$

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_{mi} 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_6H_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.

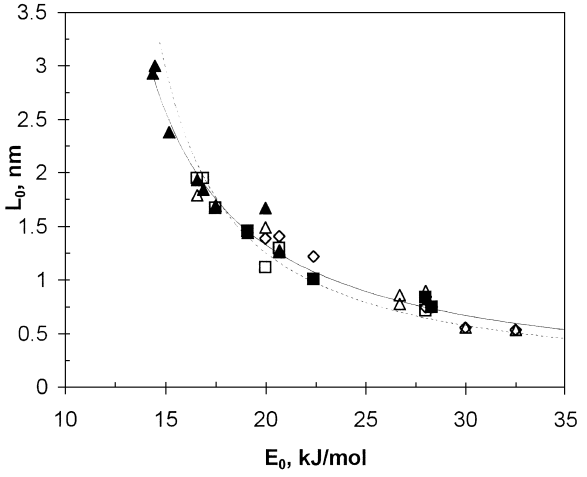

Fig. 1. Correlation between L_o and E_o, where L_o is obtained from immersion calorimetry (◇) selective adsorption of caffeine (▲) and phenol (■) from aqueous solutions, from Monte Carlo simulations of CO_2 adsorbed at 273 K (□) and from HRTEM or STM (△). The continuous and broken curves correspond, respectively, to Eqs. (4) and (3).

References

[1] Oberlin A, Terrière G, Boulmier JL. J de Microscopie 1974;21:301–8.
[2] Innes WR, Fryer J. Carbon 1989;27:71–4.
[3] Stoeckli F, Hugi-Cleary D, Centeno TA. J Eur Ceram Soc 1998;18:1177–85.
[4] Stoeckli F. In: Patrick J, editor, Porosity in carbons — characterization and applications, London: Arnold, 1995, pp. 67–92.
[5] McEnaney B, Mays T, Rodriguez-Reinoso P. Fundamental aspects of active carbons. Carbon 1998;36(10), Special issue.
[6] Stoeckli F, Guillot A, Hugi-Cleary D, Slasli AM. Carbon 2000;38:939–41.
[7] Stoeckli F, López-Ramón MV, Moreno-Castilla C. Langmuir 2001;17, in press.
[8] Dubinin MM, Plavnik GM. Carbon 1968;6:183–9.
[9] Radovic LR, Moreno-Castilla C, Rivera-Utrilla J. In: Thrower P, editor, Chemistry and physics of carbon, vol. 27, New York: Marcel Dekker, 2000, pp. 227–47.
[10] Stoeckli F, Lavanchy A. Carbon 2000;38:475–7.
[11] Guillot A, Stoeckli F. Carbon 2001;39, in press.
[12] Hugi-Cleary D, Stoeckli F. Carbon 2000;38:1309–13.