

**Comment on a recent paper on micropore analysis by Spitzer, Biba and Kadlec**

A paper has recently been published in this journal by Spitzer *et al.*[1], on the pore structure analysis of active carbons. In our opinion, this paper calls for certain comments with respect to the working hypotheses of the authors.

The first point concerns the relation between  $\epsilon$ , the potential arising from intermolecular forces, and the thermodynamic potential  $\Delta G = RT \ln(P/P_0)$ ,

$$\epsilon = RT \ln(P_0/P). \quad (1)$$

From a thermodynamic treatment of the Dubinin-Radushkevich (D-R) isotherm, combined with the basic assumptions of the theory of micropore filling[2], the following relation can be derived

$$q^{\text{net}} = RT \ln(P_0/P) + \alpha \cdot T \cdot 2.30 \cdot R \cdot \beta/2B^{1/2} \times [\ln(W_0/W)]^{-1/2} \quad (2)$$

where  $P_0/P$  and  $W_0/W$  are related through the D-R equation.  $q^{\text{net}}$ , the net heat of adsorption, is the difference between the isosteric heat of adsorption in the micropores and the enthalpy of condensation of the pure adsorptive.

When typical values of  $T$ ,  $B$ ,  $\alpha$  and  $\beta$  are used, it can be shown that the last term of eqn (2) becomes small only at low degrees of filling  $\theta = W/W_0$  (in the case of benzene at 300°K, for example, it is still about 10% of the second term for  $\theta = 0.35$ ). This means that

$$q^{\text{net}} = RT \ln(P_0/P) \quad (3)$$

is only valid with a variable degree of approximation, and at small values of  $\theta$ .

The isosteric heat of adsorption and the enthalpy of condensation are both related to changes in potential, kinetic, vibrational and rotational energies, with respect to the gas phase. The potential energy terms are always leading in the case of adsorption by microporous carbons and of liquids at the normal boiling-point temperature. If the adsorbed state is similar to the liquid state, it follows with a good approximation that

$$q^{\text{net}} = \epsilon + \epsilon_{\text{lat}} - \epsilon_{\text{pot}}. \quad (4)$$

$\epsilon$  represents the minimum of the adsorption potential in the micropore, if the molecule can move freely, or the value of the potential at the place occupied by the molecule between its neighbours.  $\epsilon_{\text{lat}}$  is the average lateral interaction energy of the adsorbed molecules, which depends on the filling of the pore and the geometry of the packing. In micropores containing only a few molecules, this energy should only be a fraction of  $\epsilon_{\text{pot}}$ , the potential energy in the liquid. The comparison of eqns (2), (3) and (4) shows that (1) is only valid under special circumstances. Ideally, it corresponds to the case where the adsorbate can be treated as a bulk liquid, perturbed by the field of adsorption forces. This does not correspond to the early stages of micropore filling, and therefore eqn (1) is only an approximation. A general expression will be given below, (5).

The second point concerns the adsorption potential  $\epsilon$  itself, and in particular the analytical expressions chosen by the authors for cylindrical pores of radius  $r$ ,  $\epsilon = k/r^3$  and  $\epsilon = k_s/r^2$ .

The first expression, given by de Boer and Custers over forty years ago[3] is incomplete, because it does not contain the repulsive part of the potential. More recent calculations of adsorption potentials in cylindrical[4] and in slit-shaped pores[5] of molecular dimensions show that the real situation is more complicated. Like the Lennard-Jones (6-12) pair-potentials, the resulting adsorption potentials are functions of the position within the pore, of the specific interaction parameters and of the dimensions of the molecules involved. Moreover, the minimum of the potential does not necessarily coincide with the centre of the micropore[4, 5].

The expressions used by Spitzer *et al.* are therefore oversimplified, and their use with approximation (1) casts some doubts on the outcome of a treatment which is acceptable in itself.

In our opinion, it is important to realize that the D-R equation already implies a model-dependent micropore distribution, implicitly contained in eqn (5)

$$\epsilon = RT \ln(P_0/P) + \epsilon_{\text{pot}} - \epsilon_{\text{lat}} + \frac{(\alpha \cdot T \cdot 2.30 \cdot R \cdot \beta/2B^{1/2})}{[\ln(W_0/W)]^{1/2}}, \quad (5)$$

which is obtained from eqns (2) and (4).

The main difficulty of the micropore analysis remains the fact that the adsorption potential  $\epsilon$  depends on the size and the shape of the micropores, and that the potential itself is double-valued with respect to the pore dimension. One can therefore only draw semi-quantitative informations in the case of pores between 4 and 8-10 Å. For  $N_2$  at 78°K, for example, eqn (5) indicates that slit-shaped pores[5] would have widths between 5 and 8 Å if  $B = 0.60 \times 10^{-6}$ , and between 5 and 10 Å if  $B = 10 \times 10^{-6}$ .

Equation (5) can also be compared with recent results based on integral transform methods[6].

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