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The Dubinin equation and the size of micropores in active carbons

Summary

A recently suggested relation between the Polanyi adsorption potential and the width Z of slot-like pores, is examined from the point of view of Dubinin's theory for the filling of micropores. The relation involves the structural constant B which varies with Z^2.

A semi-empirical approach has recently been suggested by Timofeev[1] for the determination of pore-widths, which is based on the Polanyi adsorption potential theory[2]. We wish to comment on this approach, and to show its implications in the light of Dubinin's theory for the filling of micropores[2,3] which has superseeded the former theory.

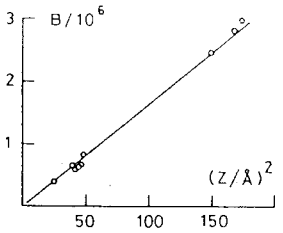
Polanyi has introduced a quantity ε, called the adsorption potential and defined by the relation

$$\varepsilon = RT \ln (P_0/P). \tag{1}$$

This is a thermodynamic potential, not to be confused with adsorption potentials arising from intermolecular forces. $-\varepsilon$ represents the change in free energy at temperature T, for the transfer of one mole of adsorbate from the liquid state (saturation pressure P_0) to the adsorbed state (pressure P and volume W). A plot of W against ε gives the so-called characteristic curve, from which a differential curve ($\Delta W/\Delta \varepsilon$ against ε) can be obtained. This is a potential distribution curve with a maximum at $\varepsilon = \varepsilon'$, for which the largest relative contribution to the filling of the pores occurs. Therefore, it is legitimate to use this particular value, ε', for investigations on the properties of the average micropores. On the basis of the values obtained from the characteristic curves of benzene adsorption on two samples of microporous carbons, Timofeev derived the expression

$$\varepsilon' = 300 / Z^{1.8} \tag{2}$$

relating ε' (in kcal/mol) to the width Z (in Å) of slot-like micropores (the derivation also includes rather crude assumptions as to the relation between Z and the diameter of the benzene molecule). The basic idea of Timofeev to use ε' is certainly valid, but more can be learnt about its theoretical implications by considering Dubinin's theory.



The Polanyi potential (1) and the volume W of (condensed) gas adsorbed by a microporous solid at T and p, are related by the equation[2,3]

$$W = W_0 \exp[-k\varepsilon^2/\beta^2] = W_0 \exp[-B(T/\beta)^2 (\log p_0/p)^2], \tag{3}$$

where W_0 is the total volume of adsorption (practically the volume of the micropores, B is the so-called structural constant which depends only on the texture of the solid, and β is a scaling factor depending on the adsorbate (affinity coefficient, equal to unity for benzene).

Equation (3) gives little direct information about the size and shape of the pores, but constant B is related to these factors. The potential distribution function and its maximum can easily be obtained from the first and second derivatives of eq. (3). The maximum is given by the condition

$$(\delta^2 W/\delta \varepsilon^2)_{\varepsilon = \varepsilon'} = 0, \tag{4}$$

which leads to the relation

$$\varepsilon' = cte \cdot \beta / B^{1/2}. \tag{5}$$

This shows that ε' is related to the structural constant B, which can be obtained easily from one isotherm only (β can be calculated[2,3]). Therefore, it is appropriate to look for a relation between B and the pore with Z, rather than between ε' and Z. Such a correlation can be found from a number of simultaneous data[4] for B and the effective pore radius R_{eff}, obtained from X-ray measurements. These data include carbons of different types (E, D, Saran), and having one or two systems of micropores (5 to 8 and 11 to 14 Å). In the case of slot-like pores, the most likely shape, R_{eff} is equal to the average pore width Z. As shown in the figure, the structural constant B is proportional to the square of the pore-width Z. This relation applies to carbons having similar W_0 values (near 0.30 and 0.15 cm³/g for the first and second pore systems respectively).

In view of eq. (5), this implies $\varepsilon' \sim 1/Z$ for adsorbates which follow the Dubinin equation. The difference with relation (2) proposed by Timofeev can be explained by the fact that this author used only two sets of experimental values for ε' and Z.

It must also be pointed out, that constant B probably depends to some extent on W_0. This can be seen from the scatter of the points in the figure, and from earlier measurements by Plavnik and Dubinin[5] on a series of carbons obtained from sucrose. More experimental data would be welcome, especially for larger pores, in order to confirm the quadratic relation between B and Z.

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