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On the theoretical foundation of the Dubinin–Astakhov equation

The theory for the volume filling of micropores (TVFM)[1] is based on the equation of Dubinin and Astakhov,

$$W = W_0 \exp\{-(A/\beta E_0)^n\} \qquad (1)$$

which relates the free energy of adsorption $A = RT \ln(p_s/p)$, to the degree of filling $\theta = W/W_0$. Although there exists now sufficient experimental evidence to establish clearly the validity of TVFM, no description has been proposed yet, as to the derivation of eqn (1) from molecular properties at the gas-solid interface. We wish to outline an approach which should provide useful and complementary information on the basis of Dubinin's theory.

A convenient starting point is the method of integral transforms, relating an overall isotherm θ_t to a local isotherm θ_l and a distribution of adsorption energies $\chi(\epsilon)$

$$\theta_t(T;p) = \int_{\epsilon_0}^{\infty} \theta_l(T;p;\epsilon)\chi(\epsilon)\,\mathrm{d}\epsilon \qquad (2)$$

ϵ is > 0, by convention, and it corresponds to the local minimum of the adsorption potential resulting from intermolecular forces.

Cerofolini[2-3] showed that eqn (2) reduces to

$$\theta_t(T;p) = \int_{\epsilon_0}^{\infty} \chi_c(\epsilon)\,\mathrm{d}\epsilon \qquad (3)$$

or

$$\chi_c(\epsilon) = -\partial\theta_t/\partial\epsilon, \qquad (4)$$

if a variational technique called the condensation approximation (CA)[4] is applied to the local isotherm. Following Ref. [3], model calculations show that $\chi_c(\epsilon)$ is slightly broader than the effective distribution $\chi(\epsilon)$ of eqn (2) in the present context.

If θ_l is the Langmuir isotherm, an overall isotherm of the Dubinin–Radushkevich–Kaganer type

$$\theta_t = \exp\{-B(RT \ln p_m/p)^2\}, \qquad (5)$$

corresponds to the energy distribution

$$\chi_c(\epsilon) = 2B(\epsilon - \epsilon_0)\exp\{-B(\epsilon - \epsilon_0)^2\} \qquad (6)$$

where, as a consequence of CA,

$$\epsilon - \epsilon_0 = RT \ln(p_m/p). \qquad (7)$$

The condensation pressure p_m corresponds to the sites of minimum adsorption energy ϵ_0. The meaning of p_m and empirical relations for its calculation have been discussed for adsorption by heterogeneous open surfaces[3]. With the following assumptions:

(1) the overall adsorption isotherm is the D–A eqn (1),

(2) the local isotherm in the micropores is of the Langmuir type (lateral interactions neglected, as a first approximation),

(3) $p_m = p_s$, as implied by eqn (1), and

(4) for carbons ϵ_0 is close to the adsorption energy on the open surface[5], the limit of large micropores[6, 7],

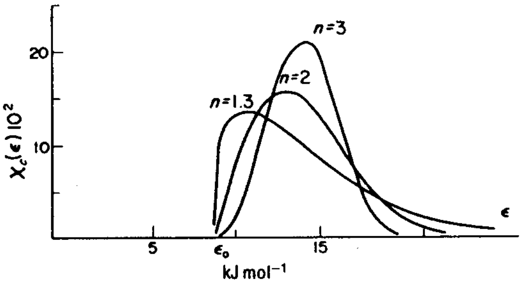

Fig. 1. Typical distributions $\chi_c(\epsilon)$ from eqn (8) calculated for argon ($\beta = 0.31$ and $\epsilon_0 = 8.9$ kJ/mole) with $E_0 = 17.45$ kJ/mole.

the generalization of the CA method leads to the following approximate energy distributions associated with the D–A eqn (1),

$$\chi_c(\epsilon) = n\frac{(\epsilon - \epsilon_0)^{n-1}}{(\beta E_0)^n}\exp\{-[(\epsilon - \epsilon_0)/\beta E_0]^n\}. \qquad (8)$$

As illustrated by Fig. 1, these distributions (and consequently the true ones) become sharper as n increases, which implies an increase in homogeneity of the micropore system for similar values of E_0. This is in agreement with the observation that $n > 4$ for zeolites[1], between 2 and 3 for homogeneous carbons[1, 8, 9], and smaller than 2 for heterogeneous active carbons[8, 10, 11]. In the case of carbons, the models proposed by Stoeckli[6] and by Everett and Powl[7] can in principle be applied to the distributions $\chi_c(\epsilon)$ or $\chi(\epsilon)$ for small molecules, in order to obtain approximate pore-width distributions. In the present context, the equation proposed by Stoeckli[10] for adsorption by heterogeneous carbons also appears to be compatible with the DA eqn (1), as established empirically[8, 12]. Stoeckli's approach corresponds effectively to the generation of the broader distributions $\chi(\epsilon)$ with $n < 2$ by a weighted sum of relatively narrow distributions with $n = 2$ and variable parameters E_0. Its main advantage is the direct physical meaning attached to E_0[8, 10].

A detailed study will be presented later.

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REFERENCES

1. M. M. Dubinin, *Surface and Membrane Science* (Edited by D. A. Cadenhead), Vol. 9, pp. 1–70. Academic Press, New York (1975).
2. G. F. Cerofolini, *Surface Sci.* **24**, 2391 (1971).
3. G. F. Cerofolini, *Thin Solid Films* **23**, 129 (1974).
4. L. B. Harris, *Surface Sci.* **10**, 128 (1968).
5. D. H. Everett, *Surface Area Determination* (Bristol Symposium (1969). Butterworth, London (1970).
6. H. F. Stoeckli, *Helv. Chim. Acta* **57**, 2195 (1975).

7. D. H. Everett and J. C. Powl, *J. C. S. Faraday I* **1976**, 619 (1976).
8. M. M. Dubinin and H. F. Stoeckli, *J. Colloid Interface Sci.* **75**, 34 (1980).
9. G. Finger and M. Bülow, *Carbon* **17**, 87 (1979).
10. U. Huber, H. F. Stoeckli and J. Ph. Houriet, *J. Colloid Interface Sci.* **67**, 195 (1978).
11. A. Janosi and H. F. Stoeckli, *Carbon* **17**, 465 (1979).
12. M. M. Dubinin, *Carbon* **17**, 505 (1980).