Published in Adsorption at the Gas-Solid and Gas-Liquid Interface 201-209, 1982
which should be used for any reference to this work

RECENT DEVELOPMENTS IN THE CONTEXT OF THE DUBININ-ASTAKHOV EQUATION

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ABSTRACT

The present work deals with two important aspects of the Dubinin-Astakhov equation, the fundamental relation of the theory for the filling of micropores. First, the theoretical basis of this equation is examined in the framework of a possible model, which leads to a reasonable agreement with experimental results.

Secondly, it is shown how the D-A equation leads to an exact relation for the calculation of enthalpies of immersion of microporous carbons into organic liquids. So far, this relation has been tested with more than 35 systems (10 carbons and 8 liquids).

A SIMPLE THEORETICAL MODEL FOR THE D-A EQUATION

Adsorption of vapours and gases by microporous solids such as carbons and zeolites, is described by the equation of Dubinin and Astakhov (ref. 1)

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

where W is the volume of the adsorbate condensed in the micropores at temperature T and relative pressure p/p_0; W_0 is the total volume of the micropores, $A = \Delta G = RT\ln(p_0/p)$ and n, β and E_0 are specific parameters of the system under investigation.

The so-called affinity coefficient β is a shifting factor which depends on the adsorptive only, and by convention $\beta(C_6H_6) = 1$. As shown by Dubinin and Stoeckli (ref. 2), the characteristic energy E_0 is directly related to the inertia radius

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of the pore R_i, an average dimension involving its width and its depth,

$$R_i E_o = (14.8 \pm 0.6) \text{ nm kJ/mole} \quad (2)$$

On the other hand, the accessible width L_e of slit-shaped micropores is related to E_o through the approximate equation

$$L_e = K/E_o \quad (3)$$

Parameter K is found to vary from 18 to 25 nm kJ/mole, as L_e increases from 0.5 to 1 nm.

The exponent n is linked to the degree of heterogeneity of the micropore system, as suggested by the adsorption of various molecular probes. In the case of active carbons, the range $2 < n < 3$ corresponds to relatively homogeneous pores and of decreasing size (for a true molecular-sieve of 0.5 nm, $n = 3$). The range $1 < n < 2$, on the other hand, corresponds to heterogeneous micropore systems with dimensions above 0.7 nm approximately (ref. 1,3,4). In the case of zeolites, n is usually between 3 and 6.

The D-A eqn (1) has an empirical basis, although it is confirmed by a large number of experiments. Its drawback, from a theoretical point of view, is the fact that it contains a free energy (-A) instead of a true adsorption energy. However, as shown below, it is possible to link this equation to a simple theoretical model, which allows a formal description of its basis and of its parameters.

One can postulate that an overall isotherm $\theta_t(T;p)$ results from the combination of a local isotherm $\theta_l(T;p;\varepsilon)$ with an adsorption energy distribution $\chi(\varepsilon)$,

$$\theta_t(T;p) = \int_{\varepsilon_o}^{\varepsilon max} \theta_l(T;p;\varepsilon)\chi(\varepsilon)d\varepsilon \quad (4)$$

The limits of the energy domain, in particular the lower bound ε_o, reflect real physical properties of the system. The simplest local isotherm, valid to a good first approximation in the case of micropores, is the isotherm of Langmuir,

$$\theta_l(T;p;\varepsilon) = [1+(K/p) \exp \{-\varepsilon/RT\}]^{-1} \quad (5)$$

The adsorption energy ε is usually defined as the difference between the minimum of the gas-solid adsorption potential on the site ε^* (micropore) and the vibrational energy. In the case of micropores in carbons, ε can be identified to a first approximation with ε^* (lateral interactions and vibrational energies neglected). The lower bound ε_o can be taken as ε_g, the adsorption potential on the surface of graphitized carbons (ref. 5), which is the limit of large micropores.

As shown by Cerofolini (ref. 6), the problem of solving integral eqn (4) can be simplified by using a variational technique called the condensation approximation. Eqn (4) leads to

$$\Theta_t(T;p) = \int_{\varepsilon_o}^{\infty} \chi(\varepsilon)d\varepsilon \qquad (6)$$

or

$$\chi_c(\varepsilon) = - \delta\Theta_t/\delta\varepsilon \qquad (7)$$

The approximate energy distribution $\chi_c(\varepsilon)$ turns out to be slightly broader than the real distribution in eqn (4).

The same procedure, applied to the Dubinin-Astakhov eqn (1) as the overall adsorption isotherm, leads to the distribution (ref. 7)

$$\chi_c(\varepsilon)_{DA} = n \frac{(\varepsilon-\varepsilon_o)^{n-1}}{(\beta E_o)^n} \exp\{-[(\varepsilon-\varepsilon_o)/\beta E_o]^n\} \qquad (8)$$

This expression can be used, as a first approximation, to investigate formally the relation which exists between the parameters of the DA eqn (1) and the distribution of the micropore widths. As illustrated by fig. 1, the energy distribution (8) becomes sharper as n increases, which implies that the underlying micropore distribution becomes more homogeneous.

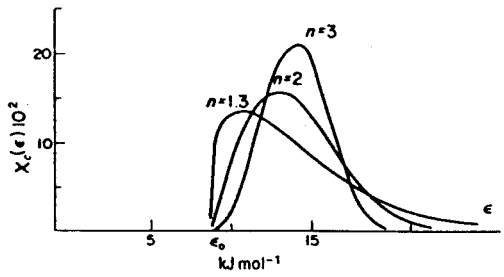

Fig. 1. Typical distribution $\chi_c(\varepsilon)$ calculated for Argon (β = 0.31, ε_o = 8.9 kJ/mole and E_o = 17.5 kJ/mole)

The case n = 2 in eqn (1) corresponds to the well-known equation of Dubinin and Radushkevich (ref. 1,2). This relation applies, with a variable degree of accuracy, to a range of typical industrial active carbons. The maximum of the distribution $\chi_c(\varepsilon)$ with n = 2 is

$$\varepsilon_{max} = \varepsilon_o + (\beta/\sqrt{2})E_o \tag{9}$$

The corresponding average energy is

$$\bar{\varepsilon} = \varepsilon_o + \beta(\sqrt{\pi}/2)E_o \tag{10}$$

It appears that ε_{max} and $\bar{\varepsilon}$ are related to the minimum adsorption energy ε_o or ε_g through βE_o. Eqn (10) is in good agreement with the empirical relation

$$\bar{\varepsilon}_{mi} - \varepsilon_g = (0.85 \pm 0.07)\beta E_o \tag{11}$$

proposed by Stoeckli and Morel (ref. 8). The quantity $\bar{\varepsilon}_{mi}$ represents the adsorption energy at low degree of micropore filling, a weighted energy, obtained from gas-solid chromatography at high temperature (ref. 9-12). Relation (11) is illustrated by fig. 2, for a range of typical active carbons.

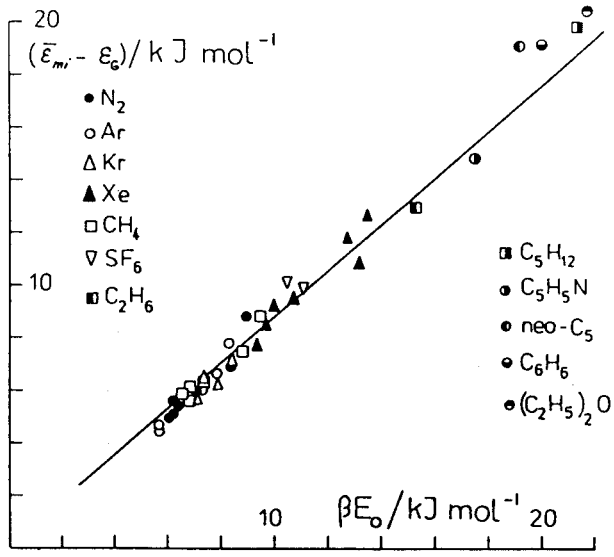

Fig. 2. Relation between the average increase in adsorption energy in the micropores, with respect to graphitized carbon black, and the characteristic energy βE_o of the Dubinin-Radushkevich equation

Theoretical models have been proposed by Everett and Powl (ref. 9) and by Stoeckli (ref. 10), relating the ratio $\varepsilon^*/\varepsilon_g$ to the width of slit-shaped micropores. The results obtained by the latter, for a (3:9) gas-solid adsorption potential, can be expressed in the analytical form

$$\varepsilon^*/\varepsilon_g = 1 + \frac{3}{2}\frac{1}{(L/Z_o-1)^3} - \frac{1}{2}\frac{1}{(L/Z_o-1)^9} \qquad (12)$$

where L is the distance between the atoms of opposed walls and Z_o corresponds to the distance of the minimum of the gas-solid potential (ref. 9,11). As shown in ref. 9, the effective pore width L_e, accessible to simple probes, is approximately 0.14 nm smaller than L in the case of the (3:9) potential.

Table 1 gives the results obtained through the combination of eqns (8) and (12), by using typical values of n and E_o, and for simple molecular probes with known parameters ε_g and Z_o (ref. 5,9,11).

TABLE 1

Values calculated for adsorption by typical carbons (E_o in kJ/mole and L in nm)
L_{max} corresponds to the maximum of the pore-width distribution

Molecule		MSC-5 n=2 E_o=35.6	MSC-5 n=3 E_o=23.9	Carbosieve n=2 E_o=24.5	AP-9 n=1.65 E_o=20.0
Benzene	L_{max}	0.68	0.70	0.73	0.80
Ar	L_{max}	0.63	0.66	0.69	0.75
Kr	L_{max}	0.65	0.68	0.71	0.78
CH_4	L_{max}	0.69	0.72	0.75	0.82
Averages					
L_{max}		0.66	0.69	0.72	0.79
L_e		0.52	0.55	0.58	0.65
$E_o.L_e$		18.5	13.2	14.2	13.0

The distribution functions for the accessible pore-widths L_e are practically of the log-normal type and they illustrate the general trend suggested by the energy distributions of fig. 1.

In the case of the theoretical system benzene/MSC-5, it is found that the pore-width distribution obtained for n = 3 is effectively contained within the range 0.48 nm < L_e < 0.58 nm, whereas it is broader for n = 2. This confirms the earlier observation of Dubinin (ref. 1), that the value n = 3 describes better adsorption by carbons with fine micropores.

As illustrated by the values of table 1 and by further calculations, the predicted values of L_e are smaller than the experimental ones for carbons with accessible pore-widths above 0.65-0.70 nm. Similar results are also obtained for the average pore widths calculated from gas-solid chromatography (ref. 9-12). This may reflect, partly at least, inadequacies in the form the traditional (3:9) and (4:10) adsorption potentials, and the simplifications implied by the condensation approximation. As a consequence, parameter $K = E_o \cdot L_e$ does not increase as fast as the experimental value.

Although the present treatment is only partly in agreement with experimental data, it has the advantage that it offers a formal explanation for the basis of the Dubinin-Astakhov equation. It follows that a clear physical meaning can be given to its parameters E_o and n, in terms of adsorption energies and of pore-widths.

THE ENTHALPIES OF IMMERSION

A further interesting feature of the Dubinin-Astakhov eqn (1) lies in the prediction of enthalpies of immersion into liquids, for which adsorption from the vapor phase is described by this relation.

As shown by Dubinin (ref. 1), the net differential heat of adsorption, usually in kJ/mole,

$$q^{net} = q^{st} - \Delta H_{vap} \tag{13}$$

can be derived exactly from eqn (1). For n = 2, corresponding to the equation of Dubinin and Radushkevich,

$$q^{net}(T;\theta) = \beta E_o \left[(\ln 1/\theta)^{1/2} + (\alpha T/2)(\ln 1/\theta)^{-1/2}\right] \tag{14}$$

where α is the expansion coefficient of the adsorbate at temperature T, and $\theta = W/W_o$.

On the other hand, for microporous solids without external surface area, the enthalpy of immersion ΔH_i is given by (ref. 13-14)

$$-\Delta H_i\ (T;p) = \int_0^1 q^{st}(T;\theta)d\theta - \Delta H_{vap}\ (T;p) \tag{15}$$

The combination of eqns (13-14), followed by integration (ref. 15) leads to (ref. 16)

$$-\Delta H_i\ (T;p) = \beta E_o(\frac{\sqrt{\pi}}{2})\ (1+\alpha T) \tag{16}$$

In this form, ΔH_i represents the filling of a volume of micropores corresponding to 1 mole of liquid. If one assumes that its molar volume in the micropores is close the value for the pure liquid, one obtains

$$-\Delta H_i\ (J/cm^3) = \beta E_o(1+\alpha T)\ \sqrt{\pi}/2V_m \tag{17}$$

This relation is also valid for heterogeneous carbons, if one uses the concept of weighted D-R equations (ref. 17).

As illustrated by fig. 3, eqn (17) has been tested so far at 34° C with a total of 35 systems, including 10 carbons and 8 liquids. The systems follow eqn (1) in the vapour phase, from which the accessible micropore volumes W_0 were derived. The experimental procedure and a discussion are given in ref. (17).

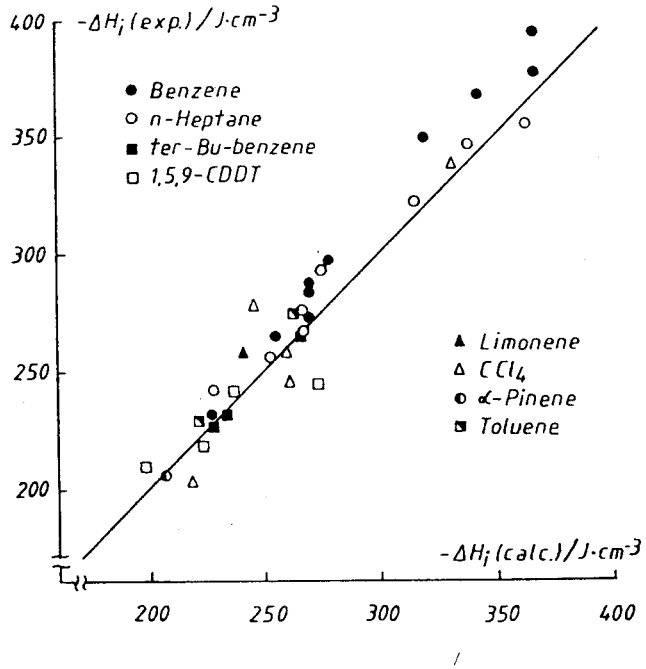

Fig. 3. Experimental and calculated enthalpies of immersion, at 34° C.
CDDT = cyclododecatriene.

Eqn (17), a direct consequence of (1), shows how the parameters of the Dubinin theory are related to the solid-liquid interaction. An important observation is the fact that the enthalpy of immersion per cm^3 of micropores is a function of the liquid, through β, and of the pore-width L through E_0. The latter property shows that it is not possible to introduce standard values relating ΔH and the micropore volume, as opposed to the case of open surfaces.

Analogues of eqn (17) can also be derived for other values of exponent n.

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