March, 1980] © *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **53**, 835—836 (1980) 835

On the Choice of Adsorptives for the Application of a Modified Dubinin-Radushkevich Equation

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(Received June 9, 1979)

Synopsis. It is shown that great care has to be taken in the choice of the adsorptives for the assessment of microporosity and its heterogeneity. Methanol, for which selective interactions may occur, is not a suitable adsorptive to be used in the framework of the generalized Dubinin-Radushkevich equation proposed by Stoeckli.

A paper has been published recently in this Journal by Tsunoda,[1] on the application of a modified Dubinin-Radushkevich equation to adsorption on active carbons with heterogeneous micropore systems. It is based on a generalization of the Dubinin-Radushkevich equation, originally proposed by Stoeckli,[2] and fully investigated by Stoeckli *et al.* in a recent paper.[3]

On the basis of experimental evidence from the adsorption of simple gases on various active carbons, we showed that the following equation could be used

$$W = W_0 \exp\{-B_0 y\}\cdot\exp\{y^2\Delta^2/2\}\cdot[1-\mathrm{erf}(x)]/2 \qquad (1)$$

where

$$y=(T/\beta)^2 \log^2(p_0/p) \text{ and } x=(y-B_0/\Delta^2)\,\Delta/\sqrt{2}.$$

W_0 is the total volume of the micropores, and W represents the volume filled at (T, p).

Equation 1 is based on the idea of a Gaussian distribution of the micropore volume W with the structural constant B,

$$f(B)=[W_0/\Delta(2\pi)^{1/2}]\exp\{-(B-B_0)^2/2\Delta^2\} \qquad (2)$$

combined with the original equation of Dubinin and Radushkevich,[4]

$$W = W_0 \exp\{-B(T/\beta)^2 \log^2(p_0/p)\}. \qquad (3)$$

The quantity Δ, a measure of the spread of B around B_0, is related to the heterogeneity of the micropore system under investigation. This is a direct consequence of the empirical relation which exists between B and the gyration radius R_g of the micropores, derived from the scattering of X-rays at small angles.[5]

The so-called affinity coefficient, β, is a characteristic of the adsorptive. It is calculated[4] from the ratios of the parachores, benzene being the reference vapor with $\beta=1$. With the use of β, the isotherms of different gases on a given microporous carbon can be reduced to a single isotherm. As shown by Stoeckli *et al.*[3] this is also the case for the generalized equation (Eq. 1), when a number of non-specific adsorptives are used. (A representation of $\ln(W)$ *versus* y yields a single curve for heterogeneous carbons). Typical values of B_0 and Δ, obtained from our experimental data,[3] are shown in Table 1.

Table 1. Parameters of Eq. 1 for various carbons

Carbon	Origin	$\dfrac{W_0}{\mathrm{cm^3\,g^{-1}}}$	$\dfrac{B_0}{10^{-6}\,\mathrm{K^{-2}}}$	$\dfrac{\Delta}{10^{-6}\,\mathrm{K^{-2}}}$
U-02	Mineral	0.43	0.92	0.21
F-02	Vegetable	0.64	1.03	0.29
F-85	Vegetable	0.75	0.98	0.35
Carbosieve	Polymer	0.51	0.57	—
AC-400 (7)	Mineral	0.42	0.73	0.21
AC-900 (7)	Mineral	0.43	0.72	0.28

The smaller values of B_0 correspond to narrow systems of micropores, where the spread Δ is also reduced or equal to zero (molecular-sieves). The recent work of Tsunoda is essentially an extension of a generalized equation (Eq. 1), taking into account possibility of a non-negligeable fraction of the Gaussian distribution (Eq. 2) existing in the region of $B<0$, which is physically unrealistic.

Although this possibility is mathematically conceivable, our extended investigations have not revealed it so far. The typical values of B_0 and Δ given in the table correspond to negligeable contributions from the region $B<0$, since B_0 is close to 3Δ. Even for $B_0=2\Delta$, this contribution would only represent 2% of the total area of the normalized Gaussian (Eq. 2).

Relatively larger values were reported by Tsunoda[1] for the spread Δ, which may justify the use of his modification of Eq. 1. However, a closer examination reveals that his approach is based on the adsorption of methanol alone, and at a single temperature (30 °C). As found in our own investigation, methanol is not a suitable adsorptive. The main reason, as in the case of water, is the possibility of selective interactions with chemical groups on the surface of the carbon.

The isotherms may often be ill-defined, or of type III or V, not described by Eqs. 1 or 3. Therefore, they show a deviation from linearity in the classical Dubinin-Radushkevich plot of $\ln(W)$ *versus* $\log^2(p_0/p)$, reflecting specific differences in the mode of adsorption. This is fundamental difference with the usual collection of molecules without specific interactions, to which the theory of micropore filling essentially applies.

In the case of carbon U-02, well characterized by N_2, Xe, SF_6, N_2O, C_6H_6, and CCl_4, one finds the average values of Table 1.

The adsorption of methanol at 230 K, on the other hand, interpreted through Eq. 1, leads to $B_0=1.71\times10^{-6}\,\mathrm{K^{-2}}$ and $\Delta=0.54\times10^{-6}\,\mathrm{K^{-2}}$, using the value $\beta(CH_3OH)=0.40$. The difference with the results from the other gases is evident, and it is also found that the ratio Δ/B_0 is larger for methanol. The results of a single gas like methanol, are therefore not necessarily representative for a range of adsorptives. This suggests that great care has to be taken in the choice of adsorptives for the assessment of microporosity.

We also would like to point out, that in the case of Tsunoda's modification of Eq. 1, the quantity B_0 is no longer comparable with ours, or with the structural constant B of the D-R equation (Eq. 3). This is due to the fact that the affinity coefficient β has been omitted, implying that methanol is now the reference vapor.

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