

# ASSESSMENT OF VALIDITY OF HORVATH-KAWAZOE METHOD FOR MICROPORE ANALYSIS ON THE BASIS OF ADSORPTION ISOTHERMS OBTAINED FROM DENSITY FUNCTIONAL THEORY

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## Introduction

Recently, a significant effort has been made in order to develop new nanoporous materials for applications in catalysis, separation of mixtures and purification of gases and liquids. In order to successfully synthesize and apply novel nanoporous solids, their surface and structural properties need to be thoroughly characterized. The pore size distribution (PSD) appears to be especially useful information about nanoporous materials. The PSD is usually obtained from gas adsorption measurements. Although methods to calculate mesopore size distributions (mesopores are pores of the width between 2 and 50 nm) are currently quite well established, the assessment of micropore size distributions (micropores have widths below 2 nm) still poses some difficulties. Horvath and Kawazoe (1) proposed a simple method of micropore analysis. The HK method and its various modifications (2) have been extensively used in studies of such nanoporous materials, as active carbons and zeolites (see (2) and references therein). However, it was realized that assumptions used in the HK method, such as the condensation approximation, are questionable and inevitably lead to inaccuracy in micropore size distribution calculations (3, 4).

In the current study, the validity of the Horvath-Kawazoe method of micropore analysis is examined using model nitrogen adsorption isotherms calculated by means of nonlocal density functional theory (5).

## Methods

In the current work, the formulation of the HK method (1) in terms of the adsorption potential distribution is used (6). In the realm of the condensation approximation (CA), the pore size distribution  $J(x) = dV/dx$  (where  $x$  is the pore width, i. e. the distance between pore walls and  $V$  is the pore volume) can be expressed as a function of the adsorption potential distribution  $X(A)$ :

$$J(x) = \frac{dV}{dx} = \left( \frac{dV}{dA} \right) \left( \frac{dA}{dx} \right) = -X(A) \left( \frac{dA}{dx} \right)$$

The adsorption potential  $A$  is defined as:  $A = RT \ln(p_0/p)$ , where  $R$  is the universal gas constant,  $T$  is temperature,  $p$  is equilibrium gas pressure and  $p_0$  is the saturation pressure. The adsorption potential distribution  $X(A)$  is defined as:  $X(A) = -dv(A)/dA$ , where  $v(A)$  is the amount adsorbed as a function of the adsorption potential  $A$ . Under the condensation approximation, the volume of pores  $V$  already filled at a given pressure is equal to the adsorbed amount  $v$  expressed as a volume of liquid adsorbate. Therefore,  $X(A) = -dV/dA$ .

The above equation for the pore size distribution  $J(x)$  requires the knowledge of the adsorption potential (for which pores of the size  $x$  are filled) as a function of the pore size  $x$  in order to obtain the derivative  $dA/dx$ . For graphite slitlike pores, the following expression was found (6):

$$\frac{dA}{dx} = \frac{C_1}{x-d_a} \left( \frac{3C_2}{(x+\delta)^4} - \frac{9C_3}{(x+\delta)^{10}} \right) - \frac{C_1}{(x-d_a)^2} \left( \frac{C_3}{(x+\delta)^9} - \frac{C_2}{(x+\delta)^3} + C_4 \right)$$

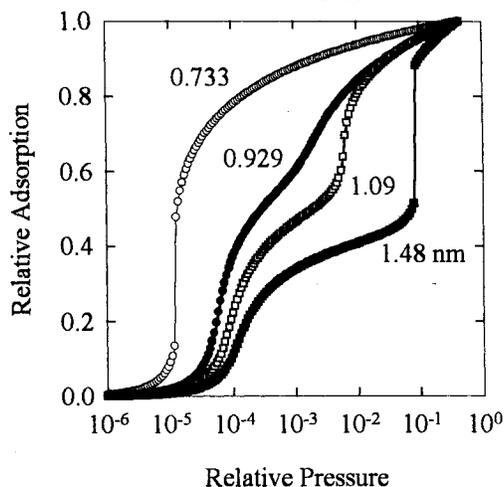
where  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are constants characteristic for a given adsorbent-adsorbate system,  $d_a$  is the diameter of the adsorbate molecule and  $\delta$  is equal to  $(d_A - d_a)/2$ , where  $d_A$  is the diameter of the adsorbent atom. For nitrogen adsorption in slitlike graphitic micropores, the constants assume the following values:  $C_1 = 39.6003 \text{ kJ}^* \text{ nm/mol}$ ,  $C_2 = 1.8942 * 10^{-3} \text{ nm}^3$ ,  $C_3 = 2.7048 * 10^{-7} \text{ nm}^9$ ,  $C_4 = 0.05012$ ,  $d_a = 0.30 \text{ nm}$  and  $\delta = 0.02 \text{ nm}$ .

Composite adsorption isotherms used to test the Horvath-Kawazoe method were obtained from model nitrogen adsorption isotherms for homogeneous graphite slitlike pores by imposing desired pore size distributions.

## Results and Discussion

Shown in Figure 1 are selected model adsorption

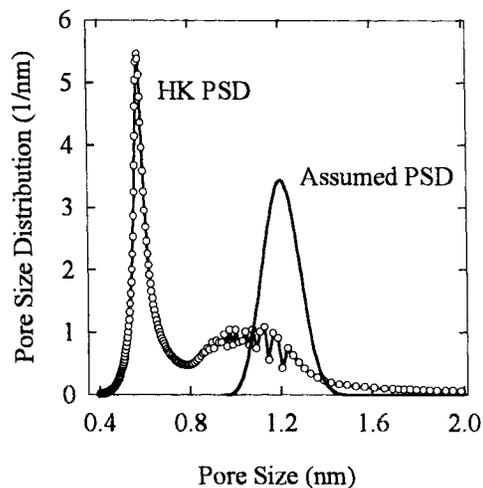
isotherms calculated using nonlocal density functional theory. One can notice that the isotherm curves for pores below ca. 0.9 nm exhibit single micropore filling steps. However, the adsorption isotherms for pores wider than ca. 0.9 nm feature two steps: a step arising from a monolayer formation on the pore walls and a step of nitrogen condensation between the already formed monolayers. It needs to be noted that the pressure, for which the monolayer formation takes place does not change significantly with the pore size increase and assumes the value of about  $10^{-4} p/p_0$ .



**Figure 1.** Model adsorption isotherms.

The essence of the Horvath-Kawazoe method is to attribute the increase in the amount adsorbed at a given pressure to the filling of pores of the size corresponding to the given pressure. The correspondence is established using the equations introduced above. It occurs that the pressure of the monolayer buildup corresponds to the pore size of about 0.6 nm. Therefore, the HK method attributes the monolayer formation on the surface of an adsorbent to the presence of 0.6 nm micropores indicating microporosity even for nonporous adsorbents. In the case of microporous adsorbents with wider micropores (above ca. 0.9 nm) and/or well developed external surface area, there arises a problem of separating contributions related to the actual microporosity and the monolayer formation. For illustrative purposes, composite isotherms were generated using isotherms for homogeneous slit-like pores with gamma distributions of pore sizes. As can be seen in Figure 2, when the HK method is applied for a composite isotherm (obtained assuming pore size distribution maximum at 1.2 nm), a bimodal distribution of pore sizes was produced. One peak indicates the presence of 0.6 nm micropores and is artificial in nature, since it resulted from the monolayer buildup, as discussed above. The other peak reproduces the assumed pore size distribution but is somewhat misplaced and broadened. A proper choice of parameters in equations used in the HK method may allow to significantly improve a reproducibility of the position and width of actual

pore size distributions. However, the presence of artificial peak corresponding to the monolayer formation results from the assumption underlying the HK method (i. e. the condensation approximation) and therefore cannot be eliminated simply by an adjustment of parameters used in the method.



**Figure 2.** Comparison of the assumed pore size distribution with the PSD calculated using the Horvath-Kawazoe method.

## Conclusions

In the case of nitrogen adsorption in slitlike graphite pores at 77 K, the Horvath-Kawazoe method attributes the monolayer formation on pore walls to the presence of nonexisting 0.6 nm micropores. Therefore, the method is expected to give wrong results (artificial peaks and improper values of pore volumes) for samples possessing significant amount of pores wider than ca. 0.9 nm and therefore its validity is restricted to samples with narrow micropores (width below 0.9 nm). The conclusions of the current study are likely to be qualitatively correct for application of the HK method for various adsorbents and pore geometries.

## References

1. Horvath, G. and Kawazoe, K., *J. Chem. Eng. Jpn.*, 1983, 16, 470.
2. Cheng, L. S. and Yang, R. T., *Chem. Eng. Sci.*, 1994, 49, 2599.
3. Kaminsky, R. D., Maglara, E. and Conner, W. C., *Langmuir*, 1994, 10, 1556.
4. Kruk, M., Jaroniec, M. and Choma, J., *Adsorption*, 1997, 3, 209.
5. Olivier, J. P., *J. Porous Mater.*, 1995, 2, 9.
6. Jaroniec, M., Gadkaree, K. P. and Choma, J., *Colloids and Surfaces*, 1996, 118, 203.