

UNIFIED APPROACH TO PORE SIZE CHARACTERIZATION OF ACTIVATED CARBONS AND CARBON FIBERS FROM N₂, Ar, AND CO₂ ADSORPTION ISOTHERMS

Peter I. Ravikovitch, Aleksey Vishnyakov, Ron Russo, and Alexander V. Neimark[▲]
TRI/Princeton, 601 Prospect Ave., Princeton, NJ 08542-0625

Introduction

Numerous research efforts have been focused on the development of reliable methods for pore size characterization of activated carbons by gas adsorption (see e.g. [1]). Recent advances in molecular modeling of adsorption phenomena by means of Monte Carlo simulations and Density Functional Theory calculations have led to a better understanding of specifics of interactions of adsorbed species with carbon micropores [1]. The simplest molecular models present the pore structure in activated carbons as a collection of idealized slit-shaped pores with smooth graphitic walls.

In this work we examine the consistency of the pore size distributions obtained from N₂, Ar and CO₂ adsorption isotherms using the slit-shaped model of activated carbons. We present a unified approach to pore size characterization of activated carbons based on the nonlocal density functional theory (NLDFT) and grand canonical Monte Carlo simulations (GCMC). The method is suitable for calculating pore size distributions from N₂ and Ar adsorption isotherms at 77 K, and CO₂ adsorption isotherms at 273 K measured up to 1 atm. The experimental conditions were standard for most adsorption measurements. The limits of applicability and sensitivity of the method proposed are examined.

Method

To calculate adsorption isotherms in individual pores we employed the Tarazona's version of the non-local density functional theory [2] that was used earlier for the description of N₂ [1,3,4], Ar [1,4], and CO₂ [5] adsorption in carbons and in nanoporous siliceous materials [6,7]. Parameters of the fluid-fluid interactions were chosen to reproduce the bulk liquid-gas coexistence at respective temperatures with the best possible accuracy [7].

CO₂ adsorption isotherms were also calculated by means of grand canonical Monte Carlo simulations using three-center LJ model with quadrupole, which gives a good description of the bulk thermodynamic properties of CO₂ [8].

Carbon-fluid interactions were modeled with the Steele 10-4-3 potential with the parameters validated against N₂, Ar [4], and CO₂ [9,10] experimental adsorption isotherms on Sterling graphite.

The experimental adsorption isotherms were measured with the Autosorb-1C adsorption apparatus (Quantachrome Corp., USA) equipped with a 1×10^{-4} torr pressure transducer. Corrections on the thermal transpiration effect were applied. For accurate measurements of CO₂ adsorption at 273.2 K we used an electric thermostat developed at TRI/Princeton.

The pore size distributions were calculated by considering the experimental isotherm as a linear combination of the theoretical isotherms in individual pores. This is an ill-posed problem, which was solved using Tikhonov regularization scheme [11]. A detailed description of the numerical method used is presented elsewhere [12].

Results and Discussion

In Fig. 1 we present the experimental and calculated adsorption isotherms on a sample of the CFCMS carbon fiber of low degree of activation [13]. The cumulative and differential pore volume distributions obtained from three different gases are presented in Figures 2 and 3. A good agreement between the total micropore volumes obtained from N₂, Ar and CO₂ adsorption isotherms indicates the consistency of our method. It also indicates that for this particular carbon fiber, most micropores are equally accessible to these gases.

Differential pore volume distributions show that the sample predominantly contains pores in the range 4-8 Å with more than 80% of all micropores smaller than 10 Å. Carbon dioxide adsorption at 273 K measured for up to 1 atm is effective for characterization of micropores smaller than ca. 10 Å.

It is worth noticing that the results of the three-center CO₂ model used in the GCMC agree well with the pore size distributions obtained from the NLDFT model, which also supports the consistency of our approach.

[▲] e-mail: aneimark@triprinceton.org

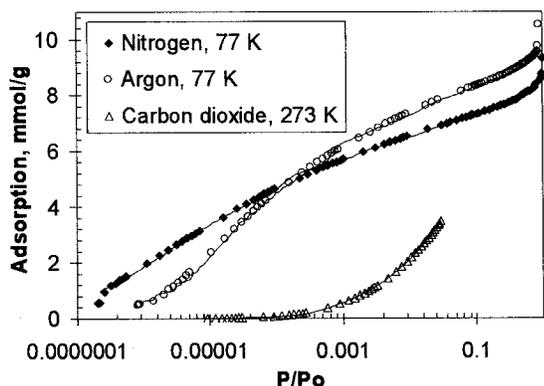


Figure 1. N₂ and Ar adsorption isotherms at 77 K, and CO₂ isotherm at 273 K on a sample of CFCMS carbon fiber. Experimental isotherms (points). Theoretical fits (lines).

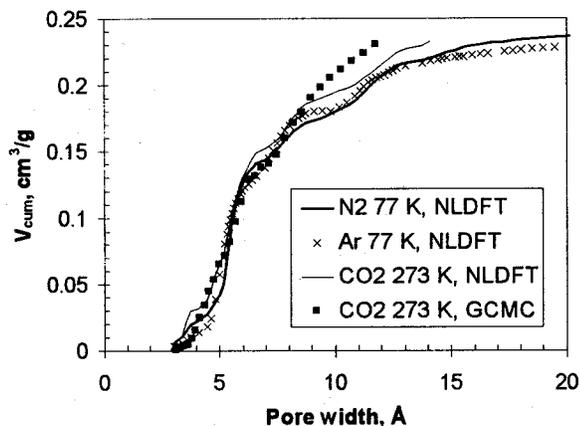


Figure 2. Cumulative pore volume distributions of the CFCMS carbon fiber calculated from N₂ and Ar adsorption isotherms at 77 K using NLDFT model, and from CO₂ adsorption isotherm at 273 K using NLDFT and three-center GCMC model.

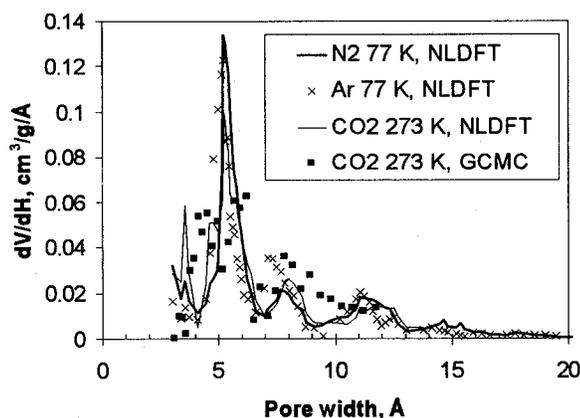


Figure 3. Pore volume distributions of the CFCMS carbon fiber. The same legend as Figure 2.

Conclusions

We conclude that the nonlocal density functional theory model gives the consistent pore size distributions for microporous activated carbon fibers. The pore size distribution obtained from the CO₂ isotherms complements those obtained from the N₂ and Ar isotherms in the range of ultramicropores. However, we believe that the Monte Carlo method may have some advantages especially for more advanced structural models beyond the slit-shaped pore geometry [1,14].

Acknowledgement

This work has been supported by the EPA grant R825959-010, and by Quantachrome Corp. We thank M.J. Mercado for the CFCMS sample.

References

1. McEnaney B, Mays TJ, Rodríguez-Reinoso F, editors. Fundamental Aspects of Active Carbons [special issue]. *Carbon* **36**, (1998).
2. Tarazona P, Marini Bettolo Marconi U, Evans R, *Mol. Phys.* **60**, 573 (1987)
3. Lastoskie C, Gubbins KE, Quirke N *J. Phys. Chem.* **97**, 4786 (1993)
4. Olivier JP, *J. Porous Mater.* **2**, 217 (1995)
5. Ravikovitch PI, Gusev VYu, Leon y Leon CA, Neimark AV. Extended abstracts, 23rd Biennial Conf. on Carbon, PennState, vol 1, 136-137 (1997)
6. Ravikovitch PI, Ó Domhnaill SC, Neimark AV, Schüth F, Unger KK. *Langmuir* **11**, 4765 (1995)
7. Neimark AV, Ravikovitch PI, Grün M, Schüth F, Unger KK. *J. Coll. Interf. Sci.* **207**, 159 (1998)
8. Harris JG, Yung KH, *J. Phys. Chem.* **99**, 12021 (1995)
9. Bottani EJ, Bakaev V, Steele WA, *Chem. Eng. Sci.* **49**, 2931 (1994)
10. Beebe RA, Kiselev AV, Kovaleva NV, Tyson RFS, Holmes JM, *Rus. J. Phys. Chem.* **38**, 372 (1964)
11. Lawson CL, Hanson RJ, Solving Least Squares Problems. SIAM. Philadelphia, 1995.
12. Ravikovitch PI, PhD thesis, Yale University, 1998.
13. Ravikovitch PI, Neimark AV, Mercado MJ, Haller GL, Paper 150g presented at the 1998 AIChE Annual Meeting, Miami Beach, FL.
14. Vishnyakov A, Piotrovskaya EM, Brodskaya EN, *Adsorption* **4**, 207 (1998)