MODELING OF CARBON DIOXIDE ADSORPTION IN CARBON PORES

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Introduction

Carbon dioxide adsorption in micropores of activated carbons is of considerable practical interest as a basis for controlling CO_2 emissions and pore structure characterization. At ambient temperatures the carbon dioxide molecules may penetrate into the most narrow pores of molecular sizes, which are not accessible for nitrogen molecules at cryogenic temperatures [1]. The use of carbon dioxide adsorption in activated carbons to control the CO_2 concentration in atmosphere is an important environmental technology aiming to reduce global climate changes.

Behavior of carbon dioxide molecules in active carbon micropores depends on the interplay between fluid-fluid and fluid-solid interactions. We study the properties of carbon dioxide confined in micropores by means of Grand Canonical Monte Carlo (GCMC) simulations. Different models of the adsorbate molecules are considered.

Method

The GCMC simulations [2] were used as the most convenient method for modeling adsorption in pores. The details of the method can be found elsewhere [3]. Three molecular representations of the carbon-dioxide were used, one-, two- [4], and three Lennard-Jones (LJ) center model (see Fig. 1). In the latter case permanent charges were placed on each center [5].

The interaction energy of the carbon dioxide molecules with the carbon wall were described by Steele's potential [6].

The solid-fluid collision diameters for all models were estimated by using Lorentz combination rule, while the potential well-depths of solid-fluid interactions were obtained by fitting the Henry's law region of the experimental carbon dioxide adsorption isotherm on the open surface of graphite at 273.2 K [7]. Thus, in the case of the one- and two-center carbon dioxide models one parameter had

to be adjusted, while for the three-center model two parameters representing oxygen (CO_2)-carbon and carbon (CO_2)-carbon were adjusted while keeping their ratio constant.
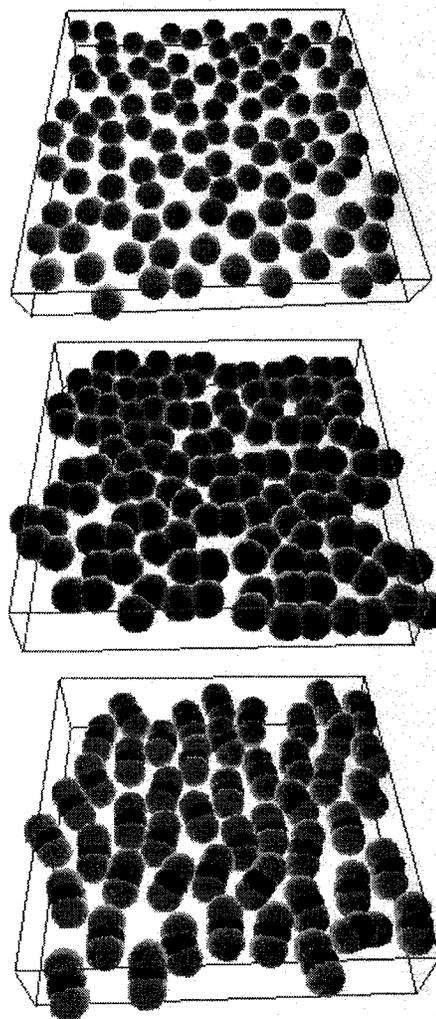

Figure 1. Snapshots of the carbon dioxide molecules in the simulation cell mimicking 0.67 nm wide slit pore, P=750 Torr, T= 273.2 K. One-, two- and three-center models are shown.

Results

The density and pore widths are reported for the space between the walls' outer carbon centers.
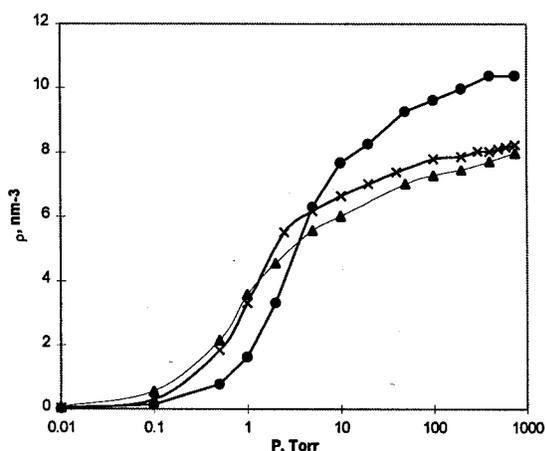

Figure 2. Carbon dioxide adsorption isotherms in the 0.667 nm wide slit pore for three adsorbate molecular models, T= 273.2 K: circles - one center; crosses - two-center; triangles - three-center models

Fig. 2 illustrates the models behavior in the very narrow pores, where only one monolayer of carbon dioxide molecules can form. In these conditions all three models show a qualitatively similar behavior. Linear two- and three center models yield quantitatively very close isotherms. These, however, differ considerably from the isotherm produced by the spherical one-center carbon dioxide model, especially at near saturation densities.
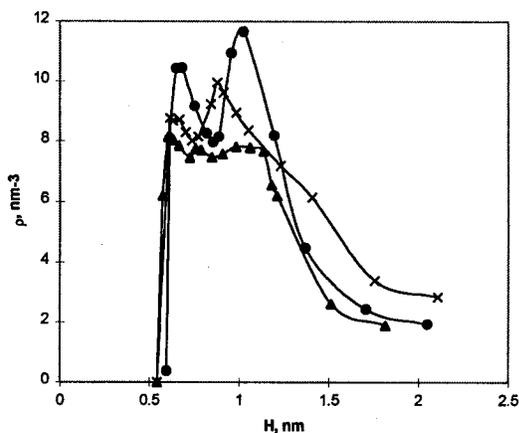

Figure 3. Carbon dioxide adsorption in the slit pore as a function of its width, P=750 Torr, T= 273.2 K. Legend as in the Fig. 3

The dependence of the adsorption capacity on the pore size at P=750 Torr and T=273.2 K shown on Fig. 3 reveals at least two peaks in the case of each model. The behavior of the one-center model is most dependent on pore size while for the three-center model it is less.

Discussion and conclusions

The GCMC simulations performed with different carbon dioxide molecular models show that the results are sensitive to the choice of the model and the parameters of center-center interactions. There exists an ambiguity in the interaction parameters recommended in literature, which increases with the complexity of the model. While applying the simulations to practical needs, it is necessary to find a reasonable compromise between the complexity of the molecular model and the number of input parameters employed. The agreement between the experimental and calculated bulk adsorbate properties and between the experimental and calculated adsorption on the open surface (within the Henry's law region) should be considered one of the most important requirements of the molecular model aiming to predict adsorption in micropores. The dependence of the adsorbate density on the micropore size has to be appreciated in phenomenological models of micropore volume filling.

Acknowledgments

References

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