

HIGH-PRESSURE ADSORPTION EQUILIBRIA AND KINETICS OF GASES ON CARBONACEOUS ADSORBENTS

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Introduction

The last years in adsorption technology have seen the development of a wide range selective microporous adsorbents, both zeolites and carbon molecular sieves. Adsorption processes are now in common use for many important separations of gaseous mixtures. The proper design and optimization of such processes requires detailed knowledge of both the equilibria and kinetics of sorption. The adsorption of gases at high pressures has received limited attention in the published literature. This is surprising since most adsorptive processes operate at pressures which are substantially above atmospheric. Recently a limited number of authors have reported high pressure equilibrium adsorption data for several adsorbate/adsorbent systems and it is an almost complete absence of kinetic studies.

A volumetric type of apparatus for simultaneous equilibrium and kinetic investigations of gas adsorption at high pressures, in particular for short-time kinetic measurements, is described. A method of treatment of experimental data as well as examples of adsorption isotherms and kinetics are presented.

Experimental

Gas sorption measurements at high pressures were made using a volumetric system described before [1]. The principle of operation is to expand small doses of adsorbate gas of known volume and pressure from reservoir to sample chamber.

Kinetic measurements are also possible using presented procedure. The gas volume taken up by the sample in a given time interval can be determined from the change of pressure in system. This is done by following additional parameter - time - during adsorption studies. The pressure and the temperature inside the chamber are measured continuously and the data are collected by the computer.

Adsorption isotherms and kinetics for methane and carbon dioxide on active carbon D55/2 (Carbotech, Germany) were measured using described system.

Results and Discussion

Exemplified in Figure 1 are the adsorption isotherms of both gases at different temperatures. The ordinate of this figure represents the absolute adsorption, and the abscissa represents fugacities corresponding to the adsorption equilibrium pressure.

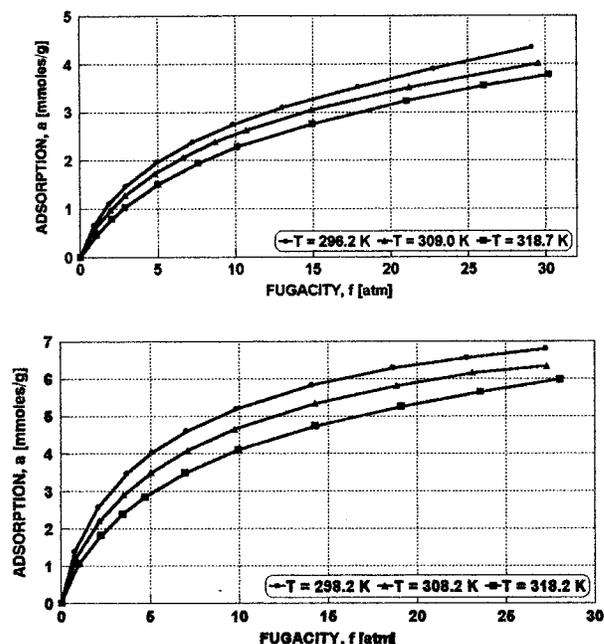


Figure 1. Adsorption isotherms of methane and carbon dioxide on active carbon D55/2

Since the conditions in this study except those of carbon dioxide were above the critical temperature, it is unlikely, that multilayer adsorption could have occurred. Some desorption isotherms were also measured and no hysteresis was observed. Experimental isotherms were interpreted by the use of the Dubinin - Radushkevich equation. All of the D-R plots show linearity which demonstrate the possibility of application of D-R equation for analysis the microporous structure of carbonaceous adsorbents because their kinetic diameter is small enough to be accessible to the micropores of smaller size.

The hypothesis that these data could be represented by the potential theory was next tested [2-4].

Some of adsorption isotherms are measured at temperatures above the critical temperatures of the adsorbates, where the concept of saturation vapor pressure is meaningless. Therefore, above the critical temperatures of adsorbates, one must estimate the "vapor" pressures at the adsorption temperatures. The difficulty of correlating data using the potential theory was overcome in the present method as follows. First, a hypothetical saturation pressure was calculated using the reduced Kirchhoff equation.

According to Dubinin the purpose of using an affinity coefficient to each adsorbate is that all characteristic curves for various adsorbates on a given adsorbent at different temperatures are superimposable on single reduced characteristic curve. In this work correlating divisor was approximated by the molar volumes of gases in adsorbed state.

Adsorption isotherms of methane, carbon dioxide and argon (77 K) were correlated by plotting the adsorbate volume vs. the reduced adsorption potential. As shown in Figure 2, a single curve correlates the isotherms for all gases. The success of this correlation justifies the selection of the molar volume of adsorbed phase as a correlating divisor.

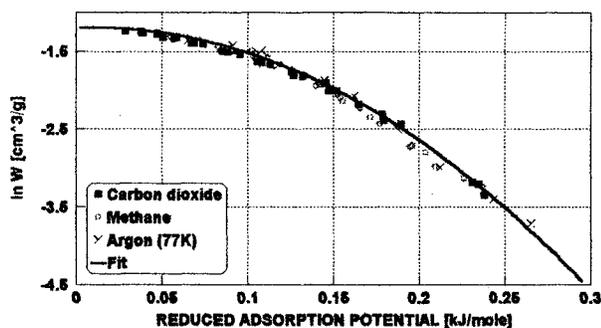


Figure 2. Generalized characteristic curve

As it mentioned above kinetic test can be realized by pressure and temperature monitoring during both runs until equilibriums were reached. A characteristic transient curves are shown in Figure 3, where the pressure and adsorption are plotted in the dimensionless form.

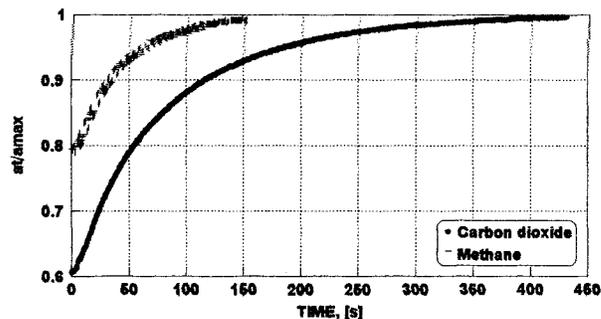
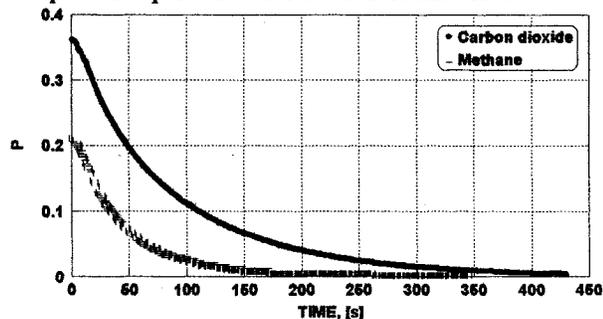


Figure 3. Pressure and adsorption transients curves and for the uptake of carbon dioxide and methane at 303K

The kinetic data are useful for analysis of pressure and temperature dependence of diffusivities, as well as modeling of separation processes of gaseous mixtures.

Conclusions

An apparatus for measuring the adsorption equilibria and kinetics of gases at high pressures is described. High pressure adsorption is of particular use for the characterization of microporous materials. Low temperature adsorption on such materials is frequently complicated by excessive equilibration times, due to activated diffusion. The use of adsorbates with small kinetic molecule diameter at temperatures above the critical temperature, help alleviate this problem.

The equilibrium, as well as, adsorption kinetic data can be directly related to gas separations to provide essential for process modeling, such as pressure swing adsorption accomplished by either selective adsorption or differences in gases diffusion rates.

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