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CONTACTLESS WEIGHING UP TO HIGH PRESSURES FOR ANALYSING ADSORPTION AND DENSITY OF FLUIDS

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Abstract

Adsorption of supercritical fluids methane, nitrogen and argon by active carbons was studied up to a pressure of 500 bar. A three-parameter isothermal equation was used to represent the adsorption equilibrium. This isothermal equation is based on a physical model conception which had already been used for the modelling of adsorption processes with a pressure up to 150 bar. Beside the exact knowledge of the measurable parameters pressure, temperature and fluid composition, the density of the adsorbate are essential for the evaluation of the adsorption analysis. The fluid density can be determined either via equations of state, which is normally the most practicable and fastest way, or via lift measurements of a lowering body in the fluid based on the principle of Archimedes. This work represents and discusses the question of to what extent the fluid density determined under real conditions via equations of state, using, for example, equation of Bender, corresponds to the fluid density measured under high-pressure.

Keywords: active carbons, adsorption, high pressure, magnetic suspension balance, supercritical fluids

Introduction

Adsorption has a great significance on separation and cleaning of materials. While adsorption under low pressures has been investigated for a long time, the scientific interest in the study of adsorption under high pressures increased recently. The aim of this paper consists in thermodynamic description of excess in adsorption of gases up to pressures of 500 bar. Different carbon adsorbents have been tested to determinate the influence of the structure of pores under high pressure to obtain specific characteristics of these materials.

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Experimental

Characterization of adsorbents

Two different adsorbents were tested: activated carbon Norit R1 (Norit Co., Germany) and activated carbon SCS-3 from the Institute of Sorption and Problems of Endoecology of National Academy of Sciences of Ukraine. To compare both adsorbents the surfaces were firstly recorded by a digital scanning electron microscope DSM 940 (Zeiss Co., Germany) in different enlargements (Fig. 1). The volume of the micropores, the total volume, the internal and the BET-surfaces were determined (Table 1) by Accelerated surface area and porosimetry ACAP-2000 (Micrometrics Co., USA).

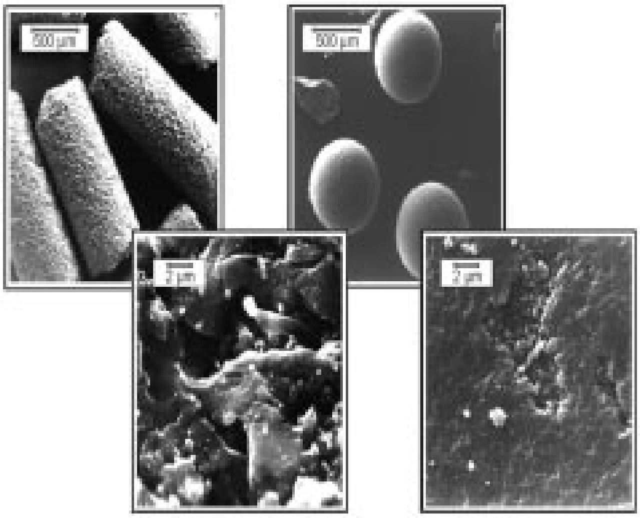

Fig. 1 Electronmicroscopic photographs of activated carbons Norit R1 (left) and SCS-3 (right) at the different enlargements

Table 1 Properties of carbon adsorbents studied

Property	Norit R1	SCS-3
BET surface/m^2 g^{-1}	1339	1094
Internal surface/m^2 g^{-1}	1307	929
Volume of micropores/cm^3 g^{-1}	0.6446	0.4382
Total pore volume/cm^3 g^{-1}	0.7074	1.0534

Magnetic suspension balance

The experimental measurements of adsorption and density were carried out with a magnetic suspension balance by Rubotherm Co. (Bochum, Germany). The balance working up to 500 bar, allows the determination of specific quantities, e.g. solubility of substances in fluids, density of fluids and adsorption behavior of fluids on adsorbents even in aggressive media without danger of pollution or destruction of the balance. In comparison to traditional balances the test substance is not directly connected with the balance, it is hanging on a so-called suspension magnet. The mass to measure is transmitted through magnetic suspension coupling from a closed and pressure-proof metal container to an external microbalance. The suspension magnet is composed of a measuring load, a sensor core and a permanent magnet. Regulation systems keep the electric magnet in free suspension and transmit the power to measure the external balance.

Results and discussion

Firstly, many experimental measurements of adsorption were carried out with pure gases argon, methane, nitrogen and carbon dioxide at 25 and 40°C at both adsorbents. Norit R1 was compared to SCS-3 higher measured values of adsorption up to ca 300 bar. It is probably caused by a larger internal surface area and a higher part of micropores. From a pressure of 300 bar onwards the adsorbent SCS-3 shows higher excess values than Norit R1. The course of the adsorption isotherms is shown for two different temperatures at Figs 2 and 3.

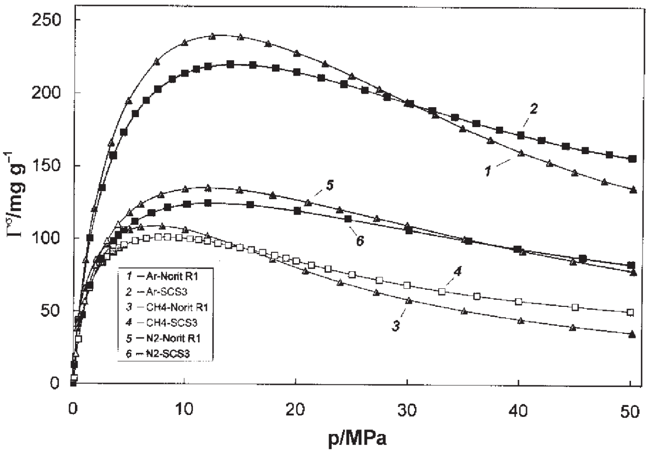

Fig. 2 Excess adsorption of Ar (1, 2), N_2 (3, 4), and CH_4 (5, 6) on Norit R1 (▲) and SCS-3 (■) activated carbons at 25°C

The Bender equation

A special thermodynamic equation of state introduced by Bender [1] mentions pressure p for pure substances as a function of temperature T and molar density ρ_m of the fluid. The equation has the form of a virial equation stopped after the sixth power. It possesses an exponential function as correction term:

$$p=R_m T\rho_m+B\rho_m^2+C\rho_m^3+D\rho_m^4+E\rho_m^5+F\rho_m^6+(G+H\rho_m^2)\rho_m^3\exp(-a_{20}\rho_m^2)$$

where R_m is the universal gas constant, B, C, D, E, F, G and H are coefficients of the equation of state, a_{20} is a non-linear parameter. The coefficients, depended only on temperature for pure substances, were calculated for the pure fluid in the following way:

$$B=a_1T-a_2-a_3/T-a_4/T^2-a_5/T^3$$

$$C=a_6T+a_7+a_8/T$$

$$D=a_9T+a_{10}$$

$$E=a_{11}T+a_{12}$$

$$F=a_{13}$$

$$G=a_{14}/T^2+a_{15}/T^3+a_{16}/T^4$$

$$H=a_{17}/T^2+a_{18}/T^3+a_{19}/T^4$$

The values of coefficients differ from substance to substance and can be determined by numeric methods through adoptions to measuring values. The Bender equation can be used for calculation of properties of mixtures by the application of laws of mixtures [2]. As a result of our extended investigations of density with pure gases by means of measuring buoyancy show that the measured values agree with the calculated densities. The results are represented in Fig. 4.

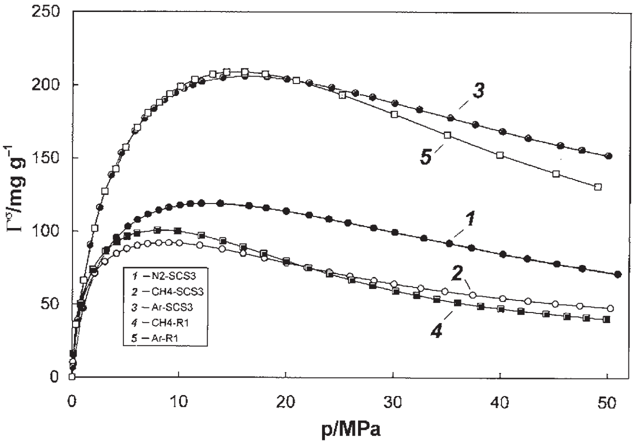

Fig. 3 Excess adsorption of Ar (1, 2), N_2 (3), and CH_4 (4, 5) on Norit R1 (■) and SCS-3 (•) activated carbons at 40°C

The three-parameter-isothermal-equation

To model the adsorption equilibrium the three parameter isothermal equation can be used as follows:

$$\Gamma^{\sigma}(p,T)=\frac{f}{f+k_0\exp\left(\frac{v_0 p}{RT}\right)}I_0$$

where $\Gamma^{\sigma}(p,T)$ is specific mass excess related to the mass of adsorbent (mg g^{-1}), f is fugacity (MPa), k_0 is Henry-coefficient (MPa), v_0 is partial molar volume (cm^3 mol^{-1}), p is pressure (MPa), T is temperature (K), R is gas constant (cm^3 MPa mol^{-1} K^{-1}), I_0 is maximum load (mg g^{-1}). This equation of isotherms is based on a physical model image [3]. Up to now this isothermal equation was only applied for pressures up to 150 bar. The application of the isothermal equation up to 500 bar shows differences between measured values and calculated results (Fig. 5). The deviation differs from gas to gas. The solution of this problem is probably the necessary modification of the isothermal equation by introducing an additional correction term.

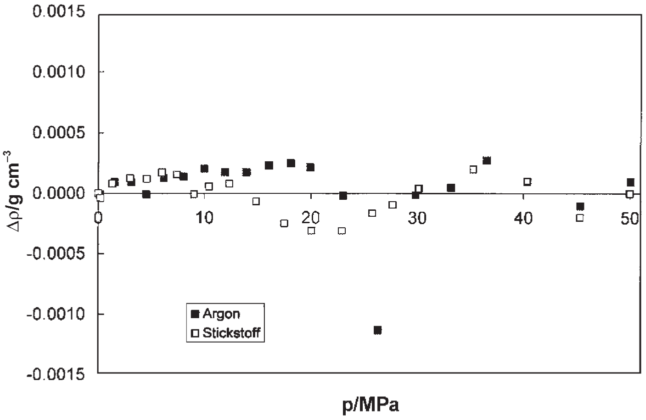

Fig. 4 Density deviations of the experimental values from values calculated from Bender equation

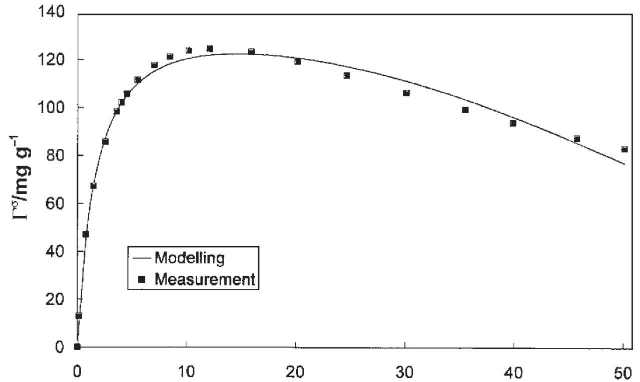

Fig. 5 Modelling of the excess adsorption of nitrogen on activated carbon SCS-3

Conclusions

In the course of this study thermodynamic consistent sets of data of adsorption equilibria were measured and analysed very precisely by use of a magnetic suspension balance up to pressures of 500 bar. Gravimetric measurements of adsorption with pure gases argon, methane, nitrogen and carbon dioxide were carried out at 25 and 40°C on two different adsorbents. The activated carbons were characterized with regard to their volume of pores and their internal surface area. The modelling of the measured values of adsorption was made by including the three parameter isothermal equation.

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