Supercritical adsorption of nitrogen on EcoSorb-activated carbon at temperatures up to 383 K and pressures up to 2 MPa

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Abstract Single adsorption isotherms and differential enthalpies of adsorption of nitrogen were measured on a microporous-activated carbon at various temperatures. A new way for calculating the differential enthalpies of adsorption is presented, and the results obtained were compared to those obtained by the isosteric method derived from the equilibrium data using the Clausius–Clapeyron equation. The measurements were made thanks to a coupled thermostated calorimetric–manometric apparatus which can be operated for pressures up to 2.5 MPa and temperatures from 303 to 423 K. This article provides experimental data which can be used for the adjustment of interaction potential in computational simulations for supercritical adsorption.

Keywords Calorimeter · Activated carbon · Supercritical condition · Nitrogen · Adsorption enthalpy · Adsorption isotherm

Introduction

The mechanism of adsorption has been studied and validated at standard conditions [1–3], as a consequence the molecular parameters used in computational simulation are adjusted closed to standard conditions. A good description of the adsorption phenomenon at supercritical condition by macroscopic model or molecular simulations requires an accurate knowledge of the differential enthalpies of adsorption and adsorption isotherms as those properties provide essential information about the energy of surface process. As a consequence, the determination of experimental adsorption isotherms and differential enthalpies of adsorption data at supercritical condition on well-characterized porous samples is necessary. In the literature adsorption isotherms data can easily be find (especially for activated carbons) [4–17] but few data are available by direct calorimetric measurement which are used to determined differential enthalpies of adsorption [18–25]. The aim of this study is to provide accurate experimental single nitrogen (N_2) adsorption data on a well-characterized activated carbon (EcoSorb) at pressure up to 2 MPa at three different temperatures (323, 353, and 383 K) thanks to a specific thermostated experimental device which can work for pressure up to 2.5 MPa and temperatures from 303 to 423 K. This experimental thermostated device is a coupled calorimetric–manometric apparatus comprising a Setaram C80 differential heat flow calorimeter coupled with a home-built manometric system which allowed determining simultaneously adsorption isotherms and differential enthalpies of adsorption. A new way for calculating the differential enthalpies of adsorption is presented, and the results are compared with those obtained by the isosteric method. The results obtained in this study can be used as accurate data for checking or adjusting the integrated potential used to characterize the gas–solid interactions in computational simulations (Density Functional Theory, Monte Carlo and Molecular Dynamics) at supercritical conditions.

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Experimental

Materials

Commercially available EcoSorb-activated carbon from Jacobi carbons was used as adsorbent material. This activated carbon was characterized with a Micromeritics ASAP 2020 System. The pore size distribution was determined by a low pressure nitrogen adsorption isotherm at 77 K (from 5×10^{-7} to 0.99 p/p_0 in relative pressure range) evaluated by the Horvath and Kawazoe (HK) model [26]. The pore size distribution function given in Fig. 1 shows that the peak pore diameter is about 4.6 Å. The specific BET surface area is 1290 ± 30 m^2 g^{-1}, and the volume of the pores is 0.6 cm^3 g^{-1}. Prior to the experiment, this activated carbon was cleaned under vacuum at 423 K during 24 h. The adsorptive gas used was nitrogen with 99.9% purity; this gas was used without any further pre-treatment.

Experimental set-up

The specific thermostated experimental device used in this study is shown in Fig. 2. The differential heat flow calorimeter is a Tian Calvet Setaram C80 model which measures the heat flux of a gas and can be operated isothermally. The inner part of the calorimeter include two calorimetric cells, one of those cells was connected to a home built manometric apparatus designed for being inserted in the upper part of the calorimeter (Fig. 2). The other calorimetric cell is connected to an empty reference cell in order to stabilize the heat flux. Thanks to the manometric heating system, the coupled apparatus works under isothermal conditions. The manometric apparatus is made of stainless steel and consists in a set-up with three parts:

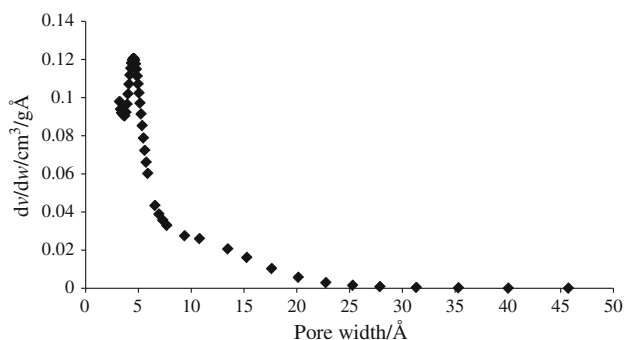– the dosing volume V_d used for stocking the gas before adsorption,

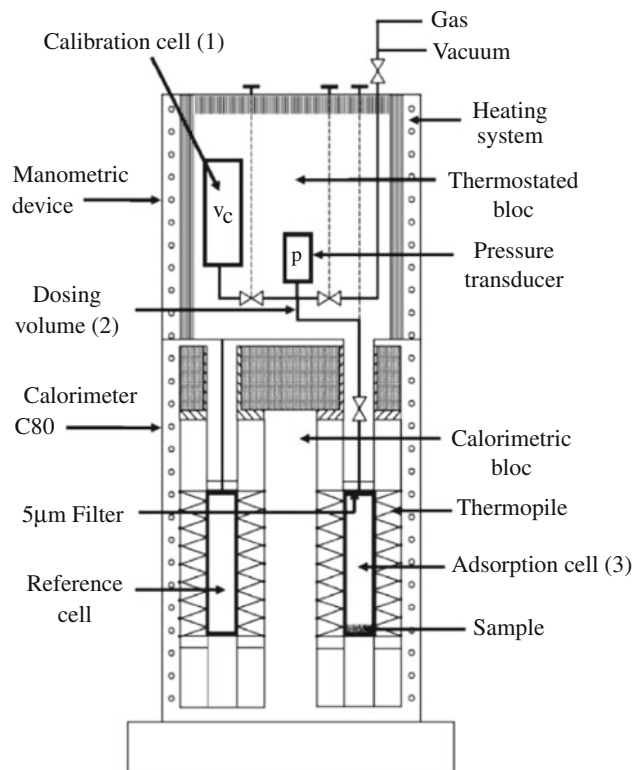Fig. 1 EcoSorb-activated carbon pore size distribution function

Fig. 2 The thermostated-coupled calorimetric–manometric apparatus

– the adsorption cell V_{ads} were the porous sample is introduced,
– the calibration cell V_c used for determining accurately the volume of V_d and V_{ads}.

This apparatus contains three valves and an accurate pressure transducer (P) type 121A from MKS Baratron. With an accuracy of 0.01% of full scale in the range from vacuum to 3.3 MPa, this pressure transducer allows an accurate measurement of the gas phase pressure in contact with the adsorbent. The separate housings of the sensor electronics unit enable the sensor to be heated to 423 K and allow the electronic units to be mounted in a convenient location. The adsorbent sample is located in the adsorption cell; this cell is closed with a 5-µm filter used in order to avoid the entrainment of little adsorbent particles and to prevent them from settling in the seating of the valves.

Methods

A mass corresponding to 1.077 g of EcoSorb-activated carbon has been introduced in the adsorption cell; the porous sample has been cleaned under vacuum at 423 K during 24 h inside the calorimeter before initializing any adsorption experiment. An accurate determination of the volume occupied by the adsorbent must be done prior to initiate the measurements, this determination is performed

by doing helium expansions from the dosing volume to the adsorption cell filled with the porous sample at pressures between 0.1 and 0.2 MPa. The resulting dead space depends on the final pressure of helium. This method has the advantage of giving a dead space volume reproducible from an adsorption experiment to another and from a laboratory to another. Helium is used for this determination because it is considered as not adsorbed [2]. Calculations were made thanks to a specific helium equation of state [27]. Next step consists in evacuate the all apparatus and settle the temperature for the study, when the temperature remain constant an amount of nitrogen is introduced in the dosing volume. When the equilibrium is reached, pressure and temperature are recorded then nitrogen is introduced in the adsorption cell. The gas must be introduced very slowly, so that the heat effect corresponding to the gas compression in the calorimeter may be calculated accurately. The calorimetric signal is continuously recorded during the complete step, the equilibrium pressure and temperature are recorded when calorimetric signals returns to baseline. The adsorption cell is then isolated by closing the valve; a new amount of nitrogen is introduced in the dosing volume and introduced in the adsorption cell when the equilibrium is reached. Those steps are repeated in order to plot the adsorption isotherms and the differential enthalpies of adsorption. In this procedure, small quantities of nitrogen are introduced at each step of the experiment. The amount of nitrogen adsorbed was calculated using the Soave–Redlich–Kwong equation of state given in Eq. 1, this equation has been chosen because it gives good results in the study pressure and temperature conditions:

$$p = \frac{RT}{v - b} - \frac{\frac{a}{\sqrt{T}}}{v(v + b)}. \tag{1}$$

It allows calculating the molar volume of the nitrogen before and after adsorption, respectively, v_1 and v_2, using the experimental conditions in which p is the pressure in Pa, T is the temperature in K, v is the molar volume of the adsorptive in $m^3 \, mol^{-1}$, R is the gas constant in $J \, mol^{-1} \, K^{-1}$.

The parameter a expresses the relation to the intermolecular interactions:

$$a = \frac{\omega_a R^2 T_c^{2.5}}{p_c}. \tag{2}$$

The parameter b is the co-volume:

$$b = \frac{\omega_b R T_c}{p_c}, \tag{3}$$

where T_c is the critical temperature of the gas in K and p_c is the critical pressure of the gas in Pa.

ω_a and ω_b are constant values and are function of the acentric factor ω:

$$\omega_a = 0.42137 e^{0.27868\omega} \tag{4}$$

$$\omega_b = 0.0855 e^{0.29161\omega} \tag{5}$$

It is then possible to calculate the molar quantity before adsorption n_1 and after adsorption n_2 in order to have the amount adsorbed n_{ads} thanks to Eqs. 6–8.

$$n_1 = \frac{V_d}{v_1} \tag{6}$$

$$n_2 = \frac{V_d + V_{ads}}{v_2} \tag{7}$$

$$n_{ads} = \frac{n_1 - n_2}{m} \tag{8}$$

where V_d is the value of the dosing volume in m^3, V_{ads} is the volume calculated by helium expansion in m^3, m is the mass of the porous sample in g, and n_{ads} is the amount adsorbed in $mol \, g^{-1}$

The data presented in this study are Gibbs (or excess) adsorption [2]. The errors estimations are about 0.6% on the determination of V_d and about 1.2% on the estimation of V_{ads}. For the molar quantity, the error estimation is about 0.5%, the error on the mass measurement has been considered as negligible, which lead to an error of 3.6% on the determination of n_{ads}.

Each introduction of gas in the adsorption cell is followed by an exothermal effect until equilibrium is reached. In this procedure, one must consider that the gas is introduced reversibly. The calorimetric adsorption cell is then considered as an open system and the calorimetric signal E (expressed in μV) recorded by the thermopiles provides the total heat Q_g resulting from two contributions: the heat of adsorption Q_{ads} and the heat dissipated by the compressed gas Q_{comp}:

$$Q_g = Q_{ads} + Q_{comp}, \tag{9}$$

where

$$Q_g = k \int E(t) dt \tag{10}$$

Q_g is the total heat measured by the thermopiles in J, Q_{ads} is the adsorption heat in J, Q_{comp} is the heat dissipated by the compressed gas in J, $E(t)$ is the calorimetric signal recorded in μV, and k is the static gain of the calorimetric detector in W $(\mu V)^{-1}$ previously measured [28].

The determination of Q_{comp} can be done thanks to the following Maxwell equation:

$$\left(\frac{\partial S}{\partial p} \right)_T = -\alpha_P V, \tag{11}$$

where α_P is the isobaric expansion coefficient defined by $1/V (\partial V/\partial T)_P$. In a mass-open type calorimeter vessel (used in this work), the quantity of heat δQ_{comp} dissipated by the
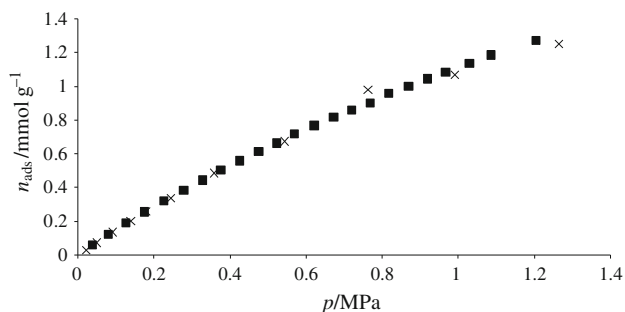
Fig. 3 Reproducibility of N$_2$ adsorption isotherms on EcoSorb-activated carbon at 323 K (*times*) Run 1; (*filled square*) Run 2

Table 1 Reproducibility of N$_2$ adsorption isotherms on EcoSorb-activated carbon at 323 K

N$_2$

$T = 323$ K

Run 1		Run 2	
n_{ads}/mmol g^{-1}	p/MPa	n_{ads}/mmol g^{-1}	p/MPa
0.029	0.02	0.064	0.04
0.073	0.05	0.127	0.08
0.136	0.09	0.193	0.13
0.203	0.14	0.259	0.17
0.258	0.18	0.324	0.23
0.337	0.24	0.387	0.28
0.486	0.36	0.446	0.33
0.674	0.54	0.506	0.38
0.979	0.76	0.561	0.43
1.068	0.99	0.615	0.47
1.250	1.26	0.665	0.52
		0.721	0.57
		0.770	0.62
		0.818	0.67
		0.860	0.72
		0.903	0.77
		0.960	0.82
		1.003	0.87
		1.045	0.92
		1.085	0.97
		1.139	1.03
		1.188	1.09
		1.272	1.20

Table 2 N$_2$ adsorption isotherms on EcoSorb-activated carbon

N$_2$

$T = 323$ K		$T = 353$ K		$T = 383$ K	
p/MPa	n_{ads}/ mmol g^{-1}	p/MPa	n_{ads}/ mmol g^{-1}	p/MPa	n_{ads}/ mmol g^{-1}
0.08	0.128	0.04	0.038	0.04	0.033
0.14	0.209	0.10	0.095	0.11	0.078
0.19	0.277	0.18	0.171	0.21	0.140
0.24	0.339	0.37	0.334	0.35	0.228
0.29	0.390	0.61	0.518	0.56	0.343
0.34	0.447	0.86	0.681	0.77	0.453
0.39	0.500	1.09	0.825	1.00	0.558
0.44	0.554	1.36	0.976	1.25	0.665
0.49	0.604	1.62	1.091	1.50	0.759
0.54	0.657	1.83	1.179	1.61	0.799
0.59	0.704	2.05	1.261	1.82	0.865
0.64	0.751			1.99	0.918
0.69	0.797				
0.74	0.842				
0.79	0.882				
0.84	0.925				
0.88	0.993				
0.94	1.023				
0.99	1.062				
1.04	1.096				
1.09	1.128				
1.15	1.171				
1.68	1.466				

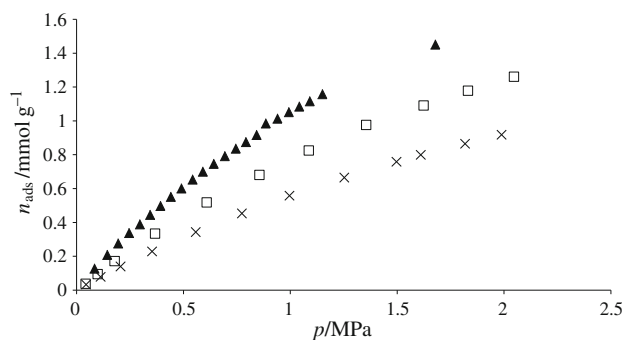**Fig. 4** N$_2$ adsorption isotherms on EcoSorb-activated carbon, (*filled triangle*) 323 K; (*open square*) 353 K; (*times*) 383 K

pressure drop dp under isothermal conditions is a sum of two opposite effects: one resulting from the gas and the other from the vessel wall [29]:

$$\delta Q_{comp} = \alpha_{SS} V_E T dp - \alpha_p V_E T dp \qquad (12)$$

where α_{ss} is the isobaric coefficient of stainless steel in K^{-1} (the material of which the adsorption cell is made), T the

temperature in K, V_E is the volume taken into account by the thermopiles deduced by helium measurement in m^3.

As small pressures steps Δp are applied in this work, the heat dissipated by the compressed gas can be expressed in the following form:

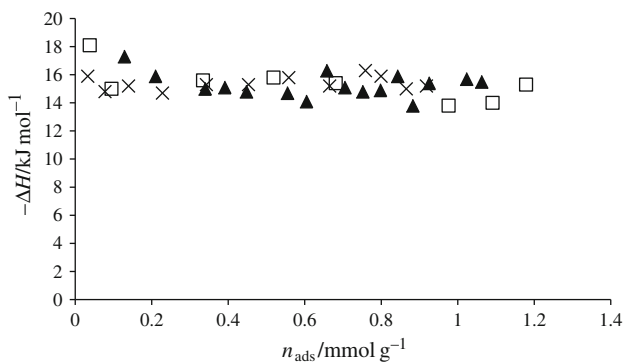$$Q_{comp} = -V_E(\alpha_P - \alpha_{ss})T\Delta p. \qquad (13)$$

Fig. 5 N$_2$ differential enthalpies of adsorption on EcoSorb-activated carbon, (*filled triangle*) 323 K; (*open square*) 353 K; (*times*) 383 K

Table 3 N$_2$ differential enthalpies of adsorption on EcoSorb-activated carbon

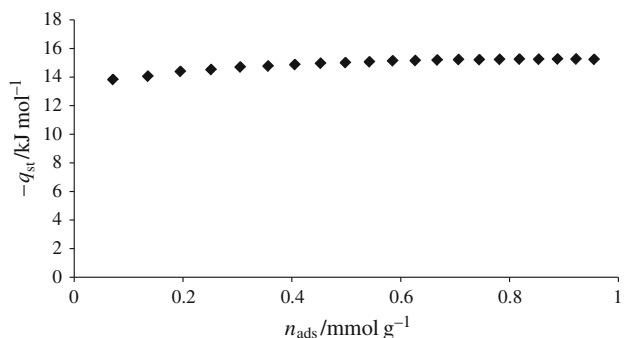| N$_2$					
$T = 323$ K		$T = 353$ K		$T = 383$ K	
$n_{ads}/$ mmol g^{-1}	$-\Delta H/$ kJ mol^{-1}	$n_{ads}/$ mmol g^{-1}	$-\Delta H/$ kJ mol^{-1}	$n_{ads}/$ mmol g^{-1}	$-\Delta H/$ kJ mol^{-1}
0.128	17.3	0.038	18.1	0.033	15.9
0.209	15.9	0.095	15	0.078	14.8
0.339	15	0.334	15.6	0.140	15.2
0.390	15.1	0.518	15.8	0.228	14.7
0.447	14.8	0.681	15.4	0.343	15.3
0.554	14.7	0.976	13.8	0.453	15.3
0.604	14.1	1.091	14	0.558	15.8
0.657	16.3	1.179	15.3	0.665	15.2
0.704	15.1			0.759	16.3
0.751	14.8			0.799	15.9
0.797	14.9			0.865	15
0.842	15.9			0.918	15.2
0.882	13.8				
0.925	15.4				
1.023	15.7				
1.062	15.5				

Fig. 6 N$_2$ differential enthalpies of adsorption by the isosteric method on EcoSorb-activated carbon

The volume taken into account by the thermopiles V_E can be deduced thanks to helium expansions from the dosing volume to the adsorption cell filled with the adsorbent. Helium is considered as not adsorbed as a consequence the calorimetric signal recorded is only due to the heat dissipated by the compressed gas into the adsorption cell. By the knowledge of the helium isobaric coefficient α_{PHe} and by calculating the integral of the calorimetric signal, it is possible to calculate V_E thanks to Eq. 14:

$$V_E = \frac{k \int E(t)\mathrm{d}t}{-(\alpha_{PHe} - \alpha_{ss})T\Delta P} \tag{14}$$

by combining Eqs. 9–14 the differential enthalpy of adsorption can be deduced thanks to Eq. 15:

$$\Delta H = \frac{Q_{ads}}{\Delta n} = \frac{k \int E(t)\mathrm{d}t + V_E(\alpha_P - \alpha_{SS})T\Delta p}{\Delta n} \tag{15}$$

where ΔH is the differential enthalpy of adsorption in J mol^{-1}, Δn is the amount of gas adsorbed between each step of the experiment in mol, and Δp is the pressure drop during adsorption experiments in Pa.

Hence the novelty in this new way of calculating the differential enthalpies of adsorption exposed here lies in the calculation of the corrective term for the compression

Table 4 N$_2$ differential enthalpies of adsorption by the isosteric method on EcoSorb-activated carbon

N$_2$	
$n_{ads}/$mmol g^{-1}	$-q_{st}/$kJ mol^{-1}
0.071	13.8
0.136	14.1
0.195	14.4
0.252	14.5
0.305	14.7
0.357	14.8
0.406	14.9
0.453	15.0
0.499	15.0
0.543	15.1
0.585	15.1
0.627	15.2
0.667	15.2
0.706	15.2
0.745	15.2
0.782	15.2
0.818	15.2
0.854	15.2
0.888	15.3
0.922	15.3
0.956	15.2

of the adsorbate and the deformation of the cell (Eq. 13). The procedure used to determine V_E leads to an uncertainty of 2% on Q_{comp}. The error associated to the total heat Q_g estimated by a test of reproducibility is about 1%. The error in the determination of Q_{ads} results from two additive causes of error in the successive determinations of Q_g and Q_{comp}. Combining errors on both Q_{ads} and n_{ads}, the error on the differential enthalpy of adsorption ΔH is 4%.

In order to make some comparison with the method exposed for calculating the adsorption enthalpies, we have also calculated the differential enthalpies of adsorption by using the isosteric method. In this case, the differential enthalpies of adsorption are noted q_{st} and are calculated thanks to the Clausius–Clapeyron equation (16) using experimental adsorption isothermal data at 323 and 383 K. For more details on this method, one can refer to the following references [2, 13, 30–33].

$$q_{st} = R \left(\frac{\partial \ln(p)}{\partial(1/T)} \right)_{n_{ads}}. \tag{16}$$

Results and conclusions

Two independent sets of measurements (Run 1 and Run 2) at $T = 323$ K represented in Fig. 3 were performed to confirm the reproducibility of the adsorption isotherms. The porous sample has been outgases at 423 K during 24 h between the two sets of measurements. The experimental data are given in Table 1, the average deviation between the two sets of measurement was less than 2%. We can notice that there is no effect of accumulation which show that the outgassing made in this study is supposed to be enough to empty the micropores. Experimental data for nitrogen adsorption isotherms at 323, 353, and 383 K on EcoSorb-activated carbons are listed in Table 2. The results, shown in Fig. 4, agree with the expected tendency: a decrease of the adsorbed quantity when the temperature increases. Figure 4 shows an expected type I tendency among the IUPAC classification. The differential enthalpies of adsorption are presented in Fig. 5, the data are reported in Table 3. As we can see the differential enthalpies of adsorption are independent of the temperature, in agreement with the micropore filling of homogenous adsorbents [34–36]. The differential enthalpy of adsorption of nitrogen on this activated carbon is about 15.3 kJ mol^{-1}. The differential enthalpies of adsorption obtain by the isosteric method are given in Fig. 6, and the data in Table 4 are about 14.9 kJ mol^{-1}. Those results reveal good agreement between the two methods; however, the calorimetric methods are more accurate because they are made on direct measurement [2, 18, 22]. The

adsorption of nitrogen was studied on a characterized microporous-activated carbon (EcoSorb), a new procedure for determining the differential enthalpies of adsorption is also presented. The adsorption data obtained by the coupled apparatus used in this study allowed to characterize porous adsorbent and can be used for adjusting the interaction potential in computational simulations for supercritical adsorption.

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