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CALORIMETRIC AND GRAVIMETRIC MEASUREMENTS OF HYDROCARBON ADSORPTION ON A GRANULATED ACTIVE CARBON

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Abstract

Adsorption isotherms of *n*-butane on a granulated activated carbon were measured by two different but complementary experimental methods: calorimetry and gravimetry. Adsorption heats were determined in different ways. For the system studied, the experimental results prove that the adsorbent offers a homogeneous site distribution. Besides, there can be differences between the adsorption heat values which might come from the way they are obtained (by calculation or direct measurements).

Keywords: activated carbon, adsorption, calorimetry, gravimetry, hydrocarbon

Introduction

Due to a very large internal surface area and a microporous structure, activated carbons present high adsorptive properties. According to the type of raw material and activation mode, numerous kinds of adsorbent can be obtained. Thus, active carbons are used in various applications: water treatment [1], precious metal recovery [2], odour treatment [3], gas storage [4]... This work is particularly devoted to the removal of fuel vapours evolved from vehicle tanks. These vapours are known to be one of the main sources of urban volatile organic compound (VOC) air pollutants [5] which are harmful to human health [6]. The objective of this study consists in following the behaviour of an active carbon in contact with gaseous *n*-butane, a major compound of fuel vapours. The *n*-butane adsorption was characterised by two independent and complementary experimental methods which are commonly used for gas adsorption studies: gravimetry [7–9] and calorimetry [10–13]. We are particularly interested in studying the influence of hydrocarbon partial pressure and temperature on the adsorption dynamics (kinetic study) and on the adsorption capacity of the adsorbent (thermodynamic study). Though some kinetic results will be presented here, we shall mainly focus on the comparison between different thermodynamic results.

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Experimental

Activated carbon features and gases

Gravimetric and calorimetric adsorption studies were carried out on an activated carbon composed of cylindrical grains (5 mm high; 2 mm in diameter) produced by an extrusion process. The density, porosity and porous volume of this granulated activated carbon are respectively 1.60 g cm^{-3}, 0.65 and 1.15 cm^3 g^{-1}. Its BET specific surface area obtained from 77 K nitrogen adsorption isotherms reaches 1600 m^2 g^{-1}. The low-temperature nitrogen adsorption isotherm combined with mercury porosimetry has shown a bimodal porous distribution: micropores of half-widths less than 1.4 nm coexist with very large macropores about 20 μm wide. More information concerning the sample characterisation was given earlier [14]. Nitrogen (min. 99.995%) and *n*-butane (min. 99.5%) are provided by Air Liquide.

Adsorption of n-butane: experimental procedure

First, the *n*-butane amount adsorbed on the activated carbon was measured by using a thermobalance we adapted in order to work under dynamic conditions and get information about the solid sample temperature as described in details elsewhere [14]. Thus, such an apparatus gives simultaneously both the adsorbent mass and inner temperature measurements.

On the other hand, integral adsorption heats were determined by a Tian-Calvet differential microcalorimeter manufactured by Thermanalyse S.A. As for the gravimetric measurements, *n*-butane is diluted into nitrogen under dynamic conditions at atmospheric pressure from commercial gas-bottles using a bank of thermal flowmeters (Brooks 5850 E). The mixture flow rate has been determined so that it does not have any influence on calorimetric kinetic curves. A schematic drawing of the calorimetric experimental apparatus is shown in Fig. 1. The part of the apparatus up-

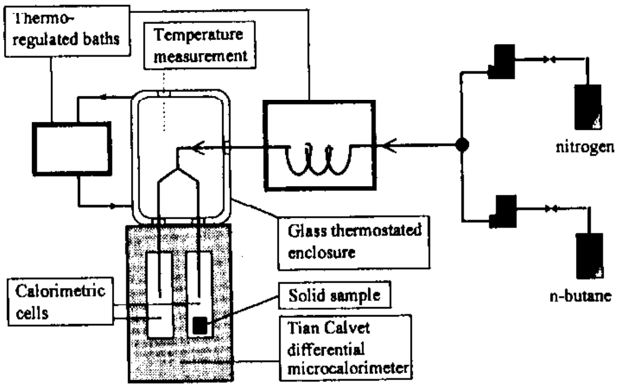

Fig. 1 Experimental apparatus for calorimetric measurements

stream from the calorimeter inlet has been found out to ensure a perfect thermal symmetry of the two gaseous streams entering the calorimeter. At the outlet of the two thermal mass flowmeters, *n*-butane and nitrogen are collected in a common pipe where they are mixed. This stainless pipe is 40 m long and is plunged into a thermoregulated bath, thus the two gases are perfectly mixed and their temperature perfectly reaches the calorimeter temperature. Then the gaseous mixture is distributed into two stainless pipes, the length and shape of which are identical. Afterwards, a glass thermostated enclosure avoids any thermal perturbation from the room when the gas runs from the thermoregulated bath to the calorimeter inlet. This glass thermostated enclosure is regulated by a second thermoregulated bath. At last, the pipes lead the gaseous mixtures into the two calorimetric cells 1 cm above the cell bottom. As a consequence, a perfect thermal symmetry is guaranteed, which is the obligatory condition to get reliable calorimetric measurements. The adsorption experiments were carried out on a single carbon grain (mass: 10.3 mg).

Gravimetric and calorimetric adsorption equilibrium were achieved at four temperatures T (25, 40, 55 and 70°C) and at six *n*-butane partial pressures P_i (0.01, 0.05, 0.10, 0.20, 0.40 and 0.80 atm).

Results

Gravimetric results

As said previously, the gravimetric apparatus we have elaborated enables simultaneous measurements of the sample mass uptake as well as the temperature variations inside a granule during the *n*-butane adsorption. A characteristic example is given in Fig. 2. Generally, the equilibrium is reached very quickly: the most encountered equilibrium times are comprised between 100 and 300 s. Furthermore, strong temperature variations have been detected inside the activated carbon extruded grains during the *n*-butane adsorption, which means that the *n*-butane adsorption on the extruded active carbon cannot be considered as an isothermal reaction. Figure 3 shows the *n*-butane adsorption isotherms.

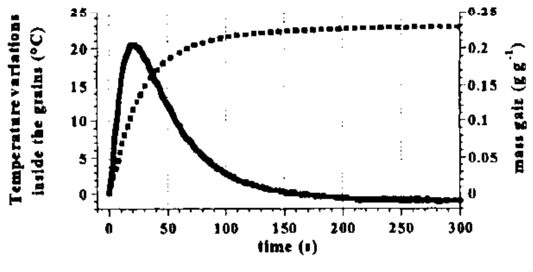

Fig. 2 Example of an uptake curve (---) with thermal effects (—) measured inside an extruded particle. P_i=0.4 atm; T=40°C

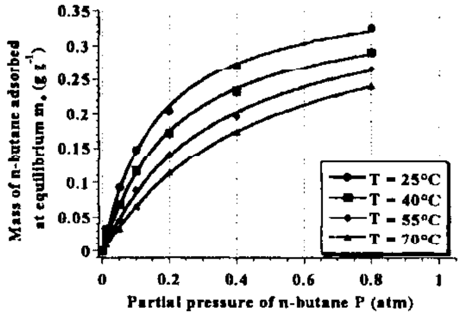

Fig. 3 Isotherms obtained from gravimetric experiments

The curve used to fit the experimental data corresponds to the Langmuir equation [15]:

$$m_c = m_{tot}\left(\frac{KP}{1+KP}\right) \tag{1}$$

where m_e is the mass of n-butane adsorbed at equilibrium per unit mass of adsorbent (g g^{-1}), m_{tot} is the total amount of n-butane which could be fixed in the whole porous system at infinite pressure (g g^{-1}), P the n-butane relative partial pressure (reference: 1 atmosphere) (dimensionless) and K the equilibrium constant (dimensionless). Therefore, the good agreement between a simple Langmuirian equation and the experimental results provides the variations of K with the temperature. The evolution of the equilibrium constant K *vs.* temperature must follow the Van't Hoff equation:

$$K = K_0\exp\left(\frac{-\Delta_a H^0}{RT}\right) \tag{2}$$

where $\Delta_a H^0$ is the standard enthalpy variation for adsorption (J mol^{-1}). When ln$K$ is plotted as a function of $1/RT$, straight lines are obtained from which $\Delta_a H^0$ can be deduced: the slope yields $\Delta_a H^0=-22.3$ kJ mol^{-1}. In addition, isosteric heats can be calculated as a function of the mass of n-butane adsorbed at equilibrium (Fig. 4) thanks to the Clausius-Clapeyron equation. For each value of m_e, the slopes of the $\ln P=f(1/T)$ lines give a value of the adsorption isosteric heat Q_{iso}. The values of Q_{iso} *vs.* m_c are nearly constant when $m_e>0.03$ g g^{-1}, around an average of $Q_{iso}=22.1$ kJ mol^{-1}. However a clear increase of Q_{iso} is observed when $m_e<0.03$ g g^{-1}. Moreover, the curve seems to decrease for higher values of m_c but this might be due to higher calculation unreliability as the concerned part of the isotherm is near the plateau.

Calorimetric results

For each n-butane partial pressure and temperature conditions, the heat flow is measured with time. Since the sample temperature and the exchanged heat are

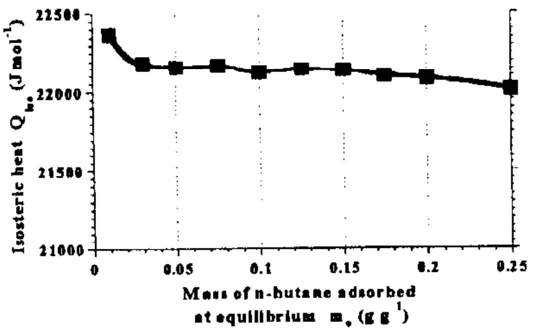

Fig. 4 Variations of the isosteric heat with m_e

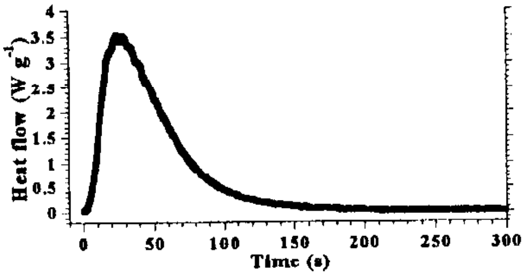

Fig. 5 Example of a calorimetric measurement of n-butane adsorption on an activated carbon extruded particle. P_i=0.4 atm; T=40°C

linked, a peak with a similar shape as the temperature peak on Fig. 2 is obtained as shown on the characteristic example in Fig. 5. One can notice that, from a kinetic point of view, the calorimetric results are very consistent with the gravimetric ones. Particularly, by comparing the three experimental curves on Figs 2 and 5 which were obtained under the same experimental conditions, one can see that the same equilibrium times are involved. The area under the heat flow peaks represents the integral heat of adsorption Q_a (J mol^{-1}). Obviously, as for the mass of n-butane measured at equilibrium by gravimetry, integral adsorption heats increase when the temperature decreases and when the hydrocarbon partial pressure increases. From the gravimetric and the calorimetric isotherms. All the curves have the same shape. On the first part of the curves, for low values of coverage, the curves are well superposed and the derivative in each point of the curve decreases with m_e. On the second part, from m_e=0.03 g g^{-1}, the curves are nearly linear with the lowest slope. Moreover the slopes of the second part of the four curves vary a little from one temperature to another. These slopes refer to an average adsorption enthalpy $\Delta_a H_{cal}$ (J mol^{-1}) and are gathered in Table 1.

Table 1 Mean adsorption enthalpy $\Delta_a H_{cal}$ for n-butane adsorption between 25 and 70°C

T/°C	25	40	55	70
$\Delta_a H_{cal}$ /kJ mol^{-1}	37.0	38.5	39.2	33.6

Discussion

The experimental results allow two types of comments. To start with, a first set of observations about the values of the several obtained adsorption heats. $|\Delta_a H_{cal}|$ and Q_{iso} are very close to each other and are moreover close to the n-butane vaporisation enthalpy (21.02 kJ mol^{-1} at 25°C). Hydrocarbon adsorption on activated carbons is a non-polar gaseous molecule adsorption on a non-polar surface, so this should not be surprising since the forces involved in this kind of adsorption are of the same type as the condensation forces. However, $\Delta_a H_{cal}$ is quite higher than $|\Delta_a H^0|$ and Q_{iso}. We believe that this shift cannot be explained by experimental errors as we tried to ensure the best experimental conditions, in particular about the gas and calorimeter temperature regulation. As far as we know, such differences have already been reported by other authors [16] in the case of another kind of fluid/solid system (namely ethanol/activated carbon) involving other kind of bindings between adsorbate and adsorbent. We propose another possible explanation. This shift may be due to the way adsorption heats are determined. As a matter of fact, $\Delta_a H_{cal}$ is obtained directly from experimental calorimetric and gravimetric isotherms whereas $\Delta_a H^0$ and Q_{iso} are calculated by equations which might not be adapted for the studied gas/solid system. In fact the Langmuirian expression is based upon the assumption of a perfect mixture of free and occupied adsorption sites. If it is not the case, excess enthalpy or exchange energy between the two kinds of sites must be considered depending on the thermodynamic models chosen to explain the non-ideality feature. Besides, a perfect homogeneous site distribution is supposed to write these equations. Which is not exactly the case and this is our second comment: both variations of Q_a and Q_{iso} with m_e (respectively Fig. 6 and Fig. 4) show that the adsorption heats are homogeneously distributed from m_e=0.03 g g^{-1}. From two information sources which are rather independent, it can be noticed that, nearly over the whole range of the surface coverage,

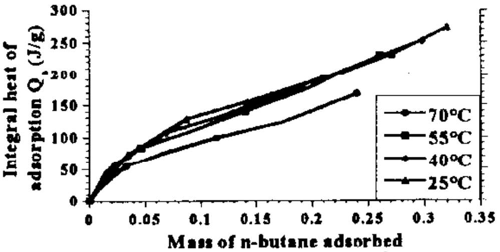

Fig. 6 Calorimetric and gravimetic isotherms between 25 and 70°C

the *n*-butane adsorption on the studied activated carbon occurs on a single type of adsorption site.

Conclusions

The *n*-butane adsorption on a granulated activated carbon was characterised by calorimetry and gravimetry. More especially, we conceived a calorimetric apparatus ensuring a perfect flow symmetry (flow rates and temperatures) at the differential calorimeter inlet. The two independent information sources show that the phenomenon nearly involves a homogeneous adsorption site distribution. However, these two experimental means provide adsorption energies which are quite different. This can be explained by the fact that some are calculated by equations which might not be adapted in this case while the other is directly measured. These conclusions are helpful for this system adsorption modelling which should predict the active carbon mass and temperature variation with time, temperature and *n*-butane partial pressure.

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