

MICROCALORIMETRIC METHODS FOR STUDYING VAPOUR ADSORPTION AND WETTING OF POWDERS

*R. Denoyel**, *I. Beurroies* and *D. Vincent*

Madirel, Unité mixte CNRS-Université de Provence, 26 rue du 141 RIA, 13003 Marseille, France

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Abstract

The interaction of a powder with vapours or their wettability by liquids are involved in many industrial processes and then needs to be studied by simple and reproducible methods. Two microcalorimetric methods, one for the simultaneous measurement of adsorption isotherm and enthalpy and the other for the determination of wetting or immersion energy, are described. A few examples are given for the adsorption and wetting of powders by water and organic vapours.

Keywords: adsorption, measurements of adsorption isotherm, measurements of enthalpy, microcalorimetric methods, wetting

Introduction

In many industrial processes, the use of powders or porous solids is a determining step. This leads to wettability, dispersability, or storage problems, which are directly linked to the divided state of the solid. The characterisation of divided solids is then of first importance both at the textural and chemical point of view. The textural properties include the morphology of particles, their surface area and the pore size distribution. The surface chemistry must be considered from the chemical nature of surface functions (which can be assessed by spectroscopic methods) but also from their surface density and accessibility which influence directly the surface wettability. It may then be interesting to define global parameters, like surface energy, whose value is supposed to allow the prediction of the solid wettability. Experimental methods based on adsorption or wetting are then useful both for the characterisation of divided solids and the direct study of industrial processes.

Two simple experiments are proposed here for studying the interaction of vapours or liquids with solids. The first one was developed to determine both the adsorption isotherm and the adsorption enthalpy of condensable vapours onto solids. In that aim, a new volumetric apparatus and an isothermal microcalorimeter were coupled. The second one allows the immersion energy of a solid in a liquid to be deter-

* Author for correspondence: E-mail: r.denoyel@ctm.cnrs-mrs.fr

mined even in the case of a non-wetting liquid/solid system by using a pressure and volume controlled experiment.

Vapour adsorption

Experimental method

The most suited method to determine the adsorption isotherm of vapour onto powders is the gravimetry [1], but it is difficult to couple it with a microcalorimeter. Continuous volumetric methods (notably those using a sonic nozzle) are well adapted to the adsorption of gas that are supercritical at room temperature [2]. In the case of vapours that are condensable at room temperature, point by point volumetric procedures are generally used [3, 4]. They need a good control of the temperature gradients in the system, particularly when the equilibrium pressure is close to saturation. They also need a very large dosing volume when the saturation vapour pressure is low at room temperature. All these facts lead to technical complications as well as to an increase of the experimental error that finds its origin in both the large dead volume and surface of the apparatus, onto which the adsorption may be non-negligible. These drawbacks are eliminated in the following procedure, where a syringe-pump is used to directly inject the liquid inside the calorimetric cell. A schematic representation of this apparatus is given in Fig. 1.

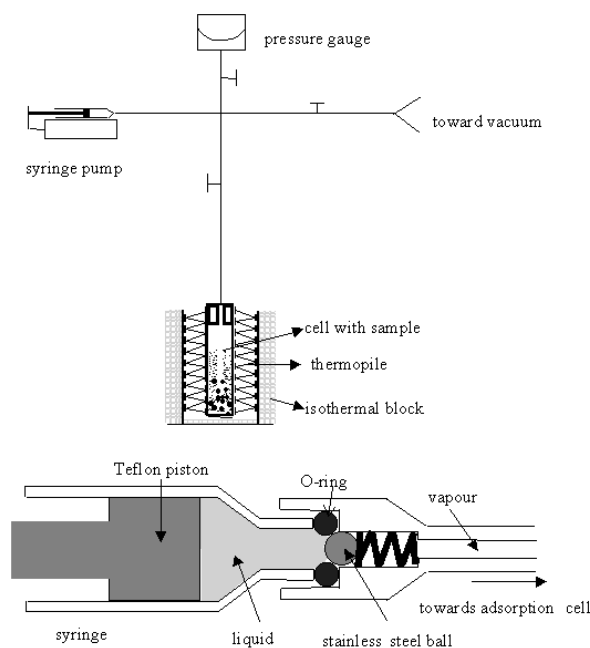


Fig. 1 Schematic representation of the vapour adsorption set-up with details of the micro check valve

After outgassing of the sample (and, if needed, a heat treatment), the cell filled with the sample is placed inside the thermopile of an isothermal Tian–Calvet type microcalorimeter and connected to the manifold. This latter include a valve linked to a vacuum pump, the syringe-pump and a valve connected to the pressure gauge (Baratron from MKS, 1 mbar or 100 mbar). In order to control the vaporisation rate of the liquid at the outlet of the syringe, a micro home-made check-valve is put between the syringe and the manifold as shown in Fig. 1. The liquid is vaporised at the check-valve outlet. The temperature at the level of the manifold is higher than that of the calorimeter. With this system, the injection of liquid can be done either continuously or stepwise. When the continuous way is carried out, the quasi-equilibrium conditions can be realised thanks to the use of micro-syringes (Microliter Syringes, manufactured by Hamilton, Bonaduz, Switzerland) having volumes in the range 5–50 μL for an overall displacement of about 60 mm. The linear speed of the syringe-pump (model Precidor 5003 manufactured by Infors, Basel, Switzerland) may be set between 0.001 and 1 mm min^{-1} , which corresponds to flow rates (in the case of water) ranging between 0.0001 and 1 mg min^{-1} . These flow rates are as low as those used in gas adsorption procedures that use a sonic nozzle [2, 5]. The constancy of the flow rate can be directly controlled from the pressure vs. time recording when the liquid is introduced into an empty cell.

Data processing

Whatever the procedure, continuous or stepwise, the vapour pressure above the sample and the heat flow are recorded as a function of time. Two types of experiments are needed: one without solid inside the cell (blank experiment) and the other with the sample. Whatever the adsorbent, only one blank experiment is needed for a given liquid or temperature. The corresponding recordings are shown in Fig. 2. Knowing the flow rate of the pump, the injected mass is directly derived from time. Also the pressure can be trans-

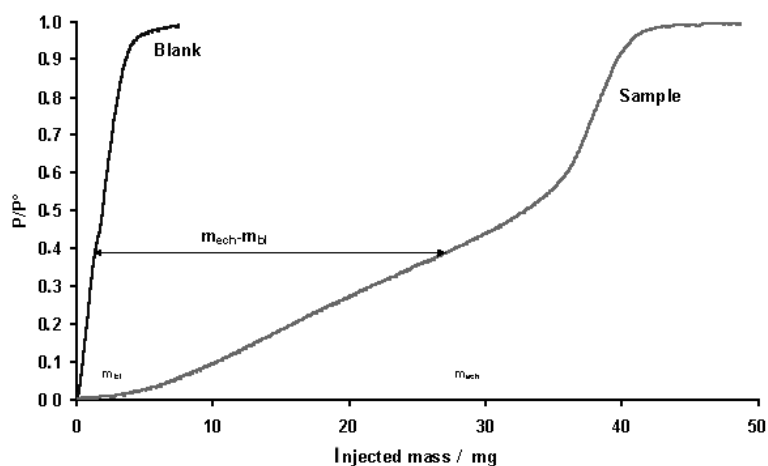


Fig. 2 Relative pressure vs. injected mass for blank and sample experiment. The sample is porous silica

formed directly in relative pressure by knowing the saturation pressure at the calorimeter temperature. This is why in the Fig. 2, the relative pressure/injected mass graphs are plotted for the experiment with the sample and the corresponding blank. These recordings show the stability of the flow rate. For both the sample and the empty cell, there is a plateau of the relative pressure at 1, indicating that there is no noticeable leak in the system and that condensation occurs at the temperature of the calorimeter. Usually, the amount adsorbed is calculated from the difference between the amount introduced and the amount staying in the gas phase. Nevertheless, in order to take into account the amount of vapour that is adsorbed on the walls of the apparatus, it is interesting to calculate the mass adsorbed at a given relative pressure, $m^a P/P^\circ$, from the difference between the mass injected for the sample experiment m_{ech} and that injected for the blank experiment m_{bl} at the same pressure (Fig. 2). This leads to the following equation:

$$m^a (P/P^\circ) m_s = [(m_{ech} - m_{bl}) + m_s P / \rho_s M R T] m_s \quad (1)$$

where m_s is the sample mass, ρ_s its density, M the adsorbate molar mass, T the temperature, R the Boltzmann constant and P° is the saturation pressure at the sample temperature. The last term of the right hand side of the equation is a correction that takes into account the dead volume change between the sample and the blank experiment: the sample indeed decreases the dead volume ($m_s P / \rho_s M R T$ is the mass of vapour which would be present at the temperature T in a volume equal to that of the sample (m_s / ρ_s)). This correction is generally negligible. The value of m_{bl} at the relative pressure P/P° is derived from the fitting of the pressure/injected mass curve of the blank experiment by an appropriate equation. A linear fitting is well suited in many cases. Nevertheless, adsorption of the vapour on the walls of the apparatus at low pressure or condensation at high pressure may need a more complicated equation. This is especially true for water that is a small molecule sensitive to any roughness at the molecular level. This is evidenced in Fig. 3, where the blank experiment

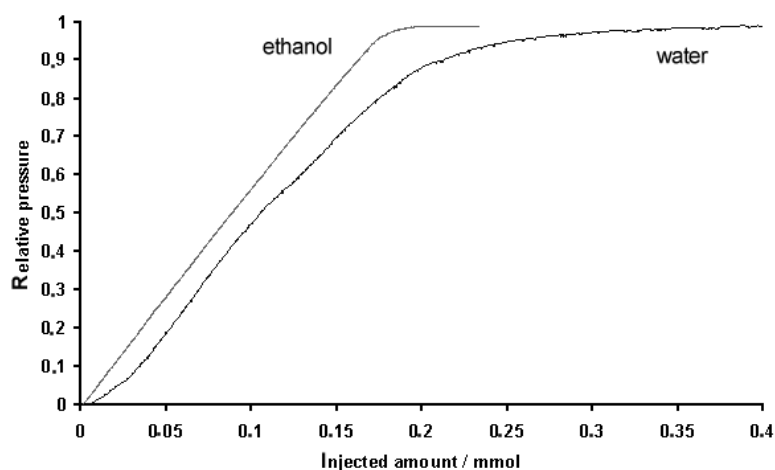


Fig. 3 Blank experiments for water and ethanol

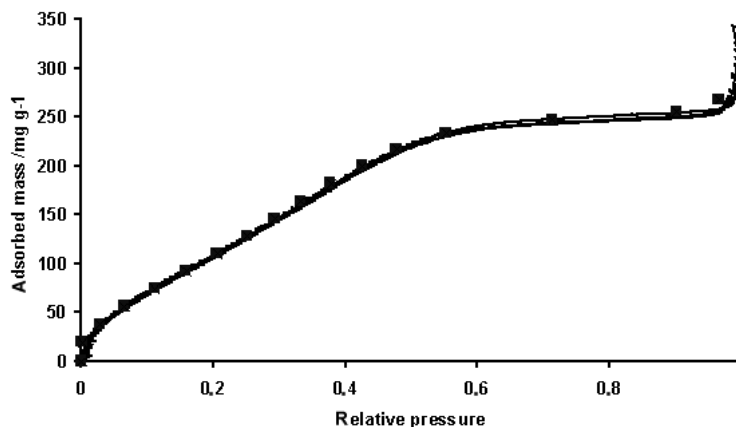


Fig. 4 Adsorption isotherm of water onto mesoporous silica. The lines (three experiments) correspond to the continuous procedure. The squares correspond to the point by point procedure

recording is shown for both water and ethanol. The low initial slope for water indicates a non-negligible adsorption on the walls of the set-up. The reference curve (i.e. blank experiment) determined by the continuous procedure can be used also for the stepwise procedure and the same equation as above is applied to calculate the adsorbed mass.

The differential or the integral adsorption enthalpies can be calculated by following procedures already established for gas adsorption [6].

Examples

In Fig. 4 are shown a set of adsorption isotherms of water onto mesoporous silica. Three continuous and one step by step experiment are plotted on the same graph, showing excellent reproducibility. For a comparison, experiments were made with this set-up and a gravimetric apparatus [1]. The agreement is better than 3% in the relative pressure range 0.05–0.95. The differences that are observed at extreme relative pressures may be due to temperature control difficulties as it was pointed out for gas adsorption gravimetry [6]. The agreement for adsorption enthalpies is also good between the continuous and the stepwise approach (Fig. 5). The continuous heat flow recording is not totally smooth, especially with water which can strongly interact with the cell itself, as it was already above. The continuous recording of the Fig. 5 is not corrected for time response of the calorimeter, then the ascending part at the beginning. The good agreement with the point by point procedure comes from the very low flow rate that is used. This experiment lasts around 20 h.

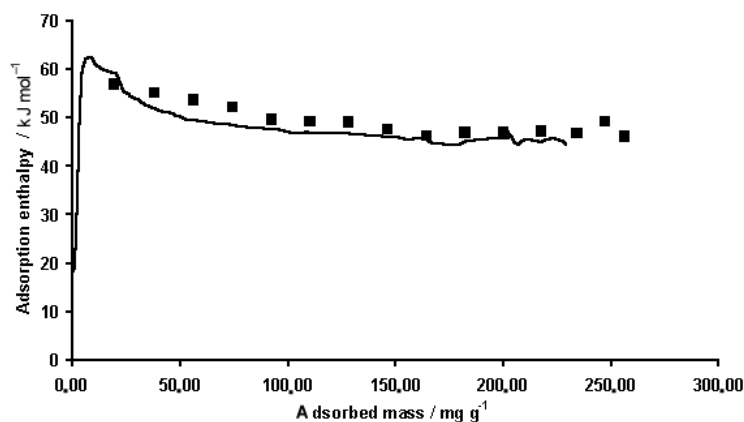


Fig. 5 Water adsorption enthalpies determined by calorimetry coupled to the adsorption isotherms of Fig. 4. The line and the squares correspond to the continuous and stepwise procedures, respectively

Immersion energy

Experimental set-up and procedure

The reproducible determination of immersion energy is usually carried out by breaking an ampoule in a calorimetric cell [6–8]. The method proposed here does not need any glass blowing and uses a set-up similar to the preceding one because a syringe pump is also used to fill the cell with the studied liquid. The syringe pump may here deliver a large volume of liquid (until 100 mL) and is able to provide a high pressure (0–700 bars) making the study of porous non-wetting systems possible. For these latter systems it is necessary to apply a pressure to force the liquid inside the pores [9]. Their characterisation needs the knowledge of both the pressure-volume intrusion-extrusion curve and the corresponding dissipated heat. A schematic representation of the system we developed is given in Fig. 6. The cell containing the sample is placed inside the thermopile of an isothermal Tian–Calvet type microcalorimeter. The cell is linked to the manifold that allows either the evacuation of the system (a mechanical pump is used to insure a primary vacuum in the manifold) or to introduce the liquid. The syringe pump (Model 100DM, manufactured by Isco, USA) allows the control of both the intruded volume and the pressure in the range 0–700 bars. Before the experiment, the pump is contacted with liquid reservoir in order to fill the cylinder of the pump and calibrate the pressure gauge at 1 bar.

In a first step, the cell is evacuated until a vacuum of about 0.01 mbar. When the immersion of a wetting solid is studied, it is possible to fix the cell (including the first valve) to an apparatus for heat treatment. When the thermal equilibrium is realised, the manifold is closed on the vacuum side and opened on the syringe pump side. There is vaporisation of the liquid at the level of the manifold and adsorption of the vapour on the sample (adsorption step). This adsorption step provides a calorimetric peak (heat flow vs. time) which corresponds to the vapour adsorption until an equilib-

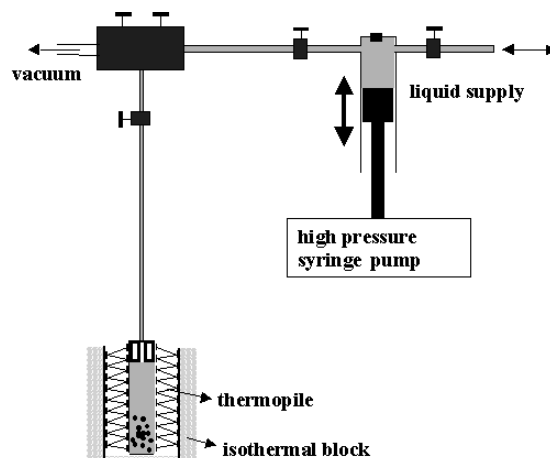


Fig. 6 Schematic representation of the microcalorimetric experimental set-up for immersion and liquid intrusion experiments

rium pressure, which is given by the saturation pressure of the liquid at the manifold temperature (which is lower than that of the calorimeter for this experiment), is reached. When the thermal equilibrium is again reached, the filling of the cell is started and continued until an equilibrium pressure of 1 bar is reached (filling step). When the solid is wettable, this step leads to the full wetting of the surface. If the solid is non-wettable by the liquid, it is then proceeded to the intrusion-extrusion steps. The liquid is introduced inside the cell by volume increments ranging between 40 and 200 μL . The experiment is fully computerised. At each step, the equilibrium pressure and the heat flow are recorded as a function of time. The next step is started only when both thermal and mechanical equilibrium are reached. Pressure and volume are indicated by the pump that have its own gauges.

Two kinds of experiment are carried out: one without the sample and the others with the sample. This allows the contributions of vaporisation and wetting of the cell walls for the adsorption and filling steps to be calculated. For the intrusion-extrusion steps, it is necessary to correct the measured heat and volume from the compressibility of the liquid in order to get only the physical pore volume that have been filled and the wetting heat. The compressibility of the solid is generally neglected. The values that are obtained after correction are characteristic of the superficial properties.

Data processing

If the immersion of a fully wettable solid is studied, only the two first steps of the experiment are realised. At each step, the heat measured with the sample experiment has to be corrected from the heat measured without sample for the same step. The heat of immersion, as classically defined [6], is the sum of the two corrected heats divided by the sample mass.

In the case of a non-wetting system, it is necessary to analyse the pressure (P), volume (V) and heat (Q) data obtained for all the intrusion-extrusion steps. In Fig. 7,

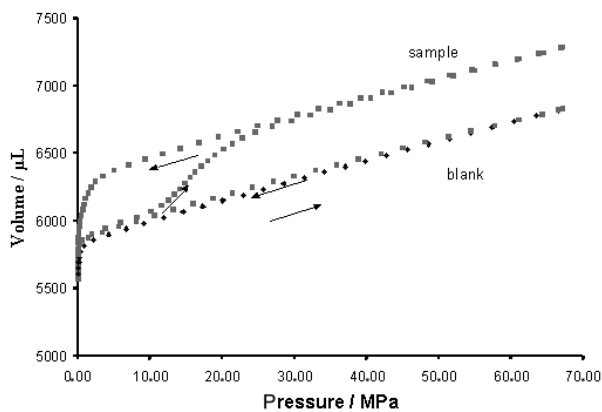


Fig. 7 Raw data for the blank experiment and the intrusion/extrusion of water in hydrophobic porous silica (pore size around 10 nm)

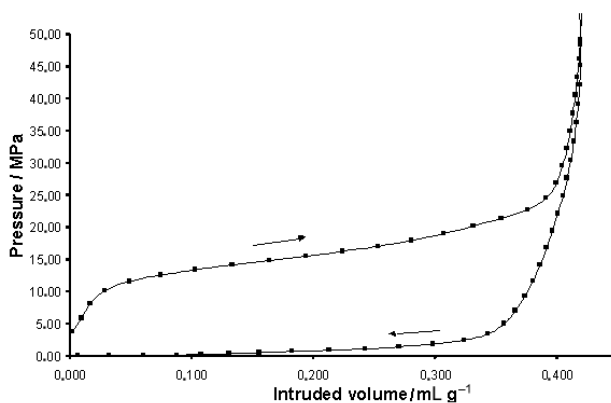


Fig. 8 Pressure vs. intruded volume of water in hydrophobic silica after correction of the data of Fig. 7 for water compressibility

the pressure/volume raw data are shown for both blank and sample experiment in the case of hydrophobic porous silica. The initial ascending part of these curves correspond to the filling of the cell until 1 bar. Each point corresponds to an equilibrium state after the introduction of one volume increment. In the case of the blank experiment, after an initial curved part, one gets a straight line whose slope depends on the liquid compressibility and system volume (including the pump cylinder). In the case of the sample, one gets a curve with hysteresis between intrusion and extrusion, which indicates the presence of pores. In order to get the data corrected from the compressibility, the volumes of the two curves (blank and sample) are simply subtracted at a given pressure. This is only possible because the same volume of liquid is used for the two types of experiment. In Fig. 8 the corrected data are shown. The processing of calorimetric data is more complex for the intrusion-extrusion steps than for the adsorption and filling steps. The heat dissipated by liquid compression is measured at

the level of the calorimetric cell, which contains an amount of liquid that varies with pressure. For each calorimetric peak, the term corresponding to the interfacial phenomenon is calculated from the following equations:

$$Q_{\text{exp}} = Q_w + Q_p \quad (2)$$

$$Q_p = h(V_{\text{cell}} - V_{\text{init}} + V_i) \cdot \rho_l \cdot \Delta P \quad (3)$$

where Q_{exp} is the experimental measured heat, Q_w the wanted interfacial contribution and Q_p the bulk liquid compression contribution; h is the thermal compressibility coefficient and ρ_l is the liquid specific density, V_{cell} is the volume of the calorimetric cell, V_{init} the initial liquid volume in the calorimetric cell after the filling step until 1 bar, V_i the intruded volume determined by the preceding P - V calculation and ΔP is the pressure variation corresponding to the analysed calorimetric peak. V_{cell} corresponds to the part of the calorimetric cell that is inside the thermopile and exchange heat with the isothermal block of the calorimeter. This volume can be determined by direct measurement by filling the calorimetric cell with water. Nevertheless, the level of the cell where there is no more heat exchange through the thermopile is not well defined. Fortunately, the value chosen for V_{cell} can be assessed in the linear part of the blank experiment. In Fig. 9 an example of corrected heat vs. intruded volume is given for the sample already analysed in Figs 7 and 8.

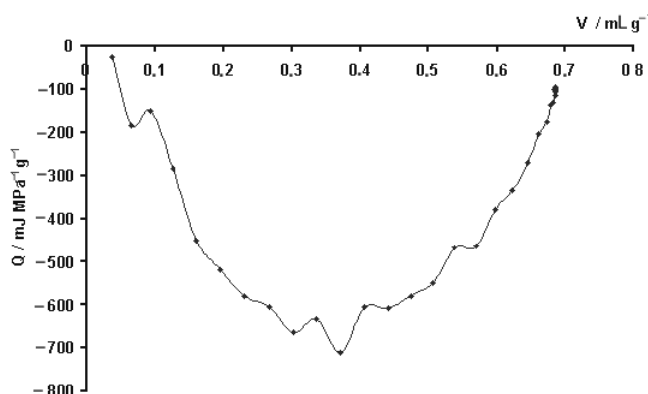


Fig. 9 Wetting heat of hydrophobic silica as a function of water intruded volume

Applications

In a recent paper [9], we have shown how this kind of experiment helps in characterising hydrophobic porous systems in terms of pore size distribution as well as homogeneity and value of contact angle. The intrusion-extrusion part is analysed for this application. In the case of wetting solids, the measured thermal effect during the second step (filling step) can be used to determine the surface area of a non-porous solid by the so-called modified Harkins and Jura method [7]. In this method the solid has to be first equilibrated with the vapour at a relative pressure corresponding to the ad-

sorption of at least two layers (P/P° ranging between 0.5 and 0.8). In the standard procedure, this is generally realised by pre-equilibration of the adsorbent with a source of water (which is at a lower temperature than that of the sample) before to seal the ampoule. This is directly realised here, because after the first adsorption step the temperature of the liquid/vapour interface in the manifold imposes the relative pressure in the system. For example, if the manifold is at 20°C (regulated room temperature) and the calorimeter at 25°C the relative pressure is 0.74, which is in the suited range. The immersion energy of the pre-covered solid, which is therefore determined here during the filling step, was shown to be proportional to the surface area of the sample with a coefficient that only depends on liquid properties (in fact a liquid/vapour interface disappears at the powder surface):

$$\Delta_{\text{imm}}U = A_s(\gamma - T(d\gamma/dT)) \quad (4)$$

where A_s is the surface area of the sample, T the temperature and γ the surface tension of the liquid.

As already underlined the sum of the corrected heats determined for the two first steps gives directly the immersion energy. The applications of the measure of immersion energy to the characterisation of divided solids have been stressed in the recent literature [6, 9–11]. Methods were developed to determine surface areas or pore size distributions in the case of microporous solids [10, 11], to study the surface energy of solids and their wettability [12–14] or to follow the surface state of a solid as a function of a given treatment [6].

References

- 1 J. Rouquerol and L. Davy, *Thermochim. Acta*, 24 (1978) 391.
- 2 J. Rouquerol, F. Rouquerol, Y. Grillet and R. J. Ward, *Characterisation of Porous Solids*, Elsevier, Amsterdam 1988, p. 67.
- 3 H. Naono and M. Hakuman, *J. Colloid and Interface Sci.*, 145 (1991) 405.
- 4 M. H. Simonot-Grange, O. Bertrand, E. Pilverdier, J. P. Bellat and C. Paulin, *J. Thermal Anal.*, 48 (1997) 741.
- 5 L. Michot, M. François and J. M. Cases, *Langmuir*, 6 (1990) 677.
- 6 F. Rouquerol, J. Rouquerol and K. Sing, in *Adsorption by Powders and Porous Solids*, Academic Press, London 1999.
- 7 S. Partyka, F. Rouquerol and J. Rouquerol, *J. Colloid Interface Sci.*, 68 (1979) 21.
- 8 D. H. Everett, A. G. Langdon and P. Maher, *J. Chem. Thermodyn.*, 16 (1984) 98.
- 9 F. Gomez, R. Denoyel and J. Rouquerol, *Langmuir*, 16 (2000) 4374.
- 10 J. Silvestre-Alberto, C. Gomez de Salazar, A. Sepulveda-Escribano and F. Rodriguez-Reinoso, *Colloids Surfaces A*, 187 (2001) 151.
- 11 R. Denoyel, F. Fernandez-Colinas, Y. Grillet and J. Rouquerol, *Langmuir*, 9 (1993) 515.
- 12 J. M. Douillard, T. Zoungrana and S. Partyka, *J. Petr. Sci. Eng.*, 14 (1995) 51.
- 13 V. Medout-Madère, *J. Colloid Interface Sci.*, 228 (2000) 437.
- 14 D. A. Spagnolo, Y. Maham and K. T. Chuang, *J. Phys. Chem.*, 100 (1996) 6626.