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The characterization of macroporous solids: An overview of the methodology

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ABSTRACT

This paper summarizes the principal aims, content and conclusions of a document recently submitted to IUPAC, as a Technical Report, by the IUPAC Working Group on "Liquid intrusion and alternative methods for the characterization of macroporous materials" and to be published in full in Pure and Applied Chemistry. The initial goal of the group was to list, examine and compare the methods presently used to characterize macroporous structures. In addition to mercury porosimetry, the most popular experimental techniques include the intrusion of various non-wetting and wetting liquids, capillary condensation, liquid permeation, imaging and image analysis. The statistical reconstruction of porous materials and the use of macroporous reference materials are also examined. A particular aim is to evaluate the status of mercury porosimetry, since the use of mercury raises a number of safety and environmental issues. The scope and limitations of each method are examined in the context of the scientific and technological requirements and the applicability of some new and unfamiliar methods is also discussed. Finally, an indication is given of the likely direction of future developments in the methodology of macropore characterization.

1. Introduction

IUPAC recommendations were issued in the past for the characterization of microporous and mesoporous materials (pore width <2 nm and between 2 and 50 nm, respectively) [1,2] but not yet for macroporous materials (pore width >50 nm), for which for many years mercury porosimetry was considered as a fully satisfactory method. Since the use of mercury raises a health issue, there is now some reluctance to use this method provided that a replacement method can be found. It was therefore decided to set up a new IUPAC Working Group with the following aims: (i) to evaluate all possible replacement methods, (ii) to assess the dangers associated with mercury porosimetry, (iii) to reach practical conclusions and (iv) to present these conclusions and recommendations in the form of IUPAC technical report, which will be published in full in Pure and Applied Chemistry.

The methods of characterization which we shall examine and compare can be listed into four main families, after the basic phenomena on which they rely, namely:

(a) *Liquid intrusion–extrusion*, either for non-wetting systems (like mercury with most materials) or also, as we shall see, for wetting systems.
(b) *Liquid permeametry*.
(c) *Phase change in a confined medium*, either a vapor–liquid phase change, (capillary condensation), or a liquid–solid phase change, like in thermoporometry or cryoporometry.
(d) *Imaging*, either with a physical method of visualization, like any type of optical or electron microscopy, or like NMR imaging or X-ray tomography, or with a method of statistical reconstruction which can be useful to process the data obtained by any other method.

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Now, since the calibration and comparison of all the above methods require the use of well-defined *macroporous reference materials*, we shall also consider their availability.

2. Methods based on intrusion–extrusion of liquids

2.1. Non-wetting systems

2.1.1. Mercury intrusion–extrusion

Mercury intrusion–extrusion, commonly carried out up to a pressure of 400 MPa, allows one in principle to assess pore-sizes from 0.003 μm up to ca 400 μm. The equipment is available on the market and the method is well understood and well documented [3–6] (cf Fig. 1).

This method has two main limitations, namely (i) the already mentioned environmental and health issue and (ii) the possibility that the porous structure is irreversibly modified under the high pressures used.

2.1.2. Other liquid metals?

The simplest change to address the health issue would be to replace mercury by another, safer, liquid metal. A few possible replacements are given in the following list:

- Gallium: it melts around 30 °C and, because of its much lower vapor pressure, is much safer than mercury. But, it unfortunately wets many oxides.
- Indium: the melting temperature of the pure metal is too high for practical use (156 °C).
- Galinstan® (Gallium, Indium and Tin) is liquid at room temperature, since it melts at −19 °C, but it unfortunately wets many materials.
- Wood's metal (Bismuth, Lead, Tin and Cadmium) melts at 70 °C, which could be acceptable if the lead and cadmium vaporized at that temperature were not harmful.
- Field's metal (eutectic of Bismuth, Indium and Tin) melts at 62 °C but is unfortunately a wetting liquid.

The conclusion is therefore that there is neither a pure metal nor an alloy able to play the part of mercury in porosimetry.

2.1.3. Water intrusion–extrusion in hydrophobic materials

Water intrusion–extrusion in hydrophobic silicas, zeolites or carbons was primarily studied in view of energy storage [7] but was also successfully compared with other methods of pore-size determination [8] in the range of mesopores (2–50 nm). There is no technical difficulty to extend this approach to the macropore range, but in practice the method is somewhat laborious, due to the need for special sample preparation (grafting of hydrophobic functions) in order to get a hydrophobic surface with a known contact angle with water.

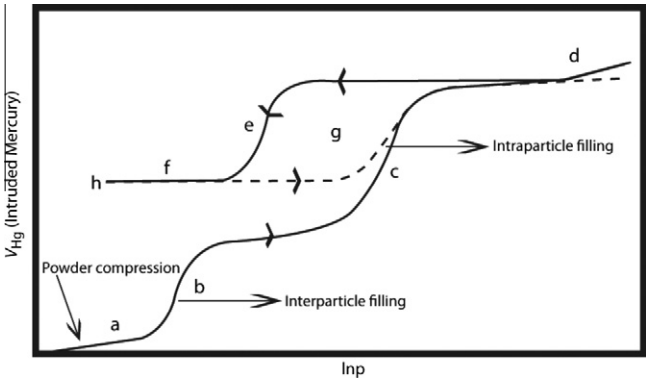

Fig. 1. Typical mercury intrusion–extrusion curve, showing here, successively, powder compression (a), interparticle filling (b), intraparticle filling (c) and partial evacuation (e) showing a mercury entrapment (h) which does not change with further intrusion–extrusion cycles (g, e, f).

2.2. In wetting systems: wetting liquid porosimetry

Wetting-liquid porosimetry [9] is the reverse of mercury porosimetry: as shown in Fig. 2, the liquid which initially completely wets the sample is pushed down through the sample and through the underlying membrane by an overpressure of air.

A flexible tube allows the extruded liquid to enter a beaker located on a balance and to be weighed. The air pressure and the corresponding mass of liquid extruded are continuously recorded. Application of the Young–Laplace equation ($r = 2\gamma\cos\theta/\Delta p$) allows the assessment of pore-sizes from 10 to 100 μm with air overpressures in the range from 200 to 15 mbar. Any wetting liquid can, in principle, be used: water, water solution, organics.

Now, a prerequisite is that the receding contact angle θ should be known. Also, the method is limited to a minimum pore-size of ca 10 μm.

3. Liquid permeametry

Fig. 3 schematically represents the principle of liquid permeametry, which requires pumping through the sample a known liquid flow, while measuring the corresponding pressure drop.

It provides a simple and fast method to estimate the hydraulic radius in the 0.1–1000 μm range [10,11] and it is of great interest whenever the macroporous solid is to be used in a liquid flow, as in chromatography.

Perhaps because of its simplicity, there is no standard equipment available. Great care is required in packing of the sample in order to avoid "leaks" or preferential paths and in the interpretation of the data (selection of the most adequate theoretical approach [12]). One should also keep in mind that this method provides a hydraulic radius (not a pore-size distribution) which tends to shift towards the broadest pore sizes.

4. Phase change

4.1. Capillary condensation

4.1.1. Contact porosimetry

This method relies on the comparison of capillary condensation on the test sample and on a reference porous sample with which it is in close contact [13]. It is assumed that, if the wetting angle is the same, pores of a given size are simultaneously evacuated from the sample and the reference. For convenience, the wetting angle is preferred to be 0, which is obtained with a good wetting liquid like, octane, decane and sometimes water. In principle, the equilibrium

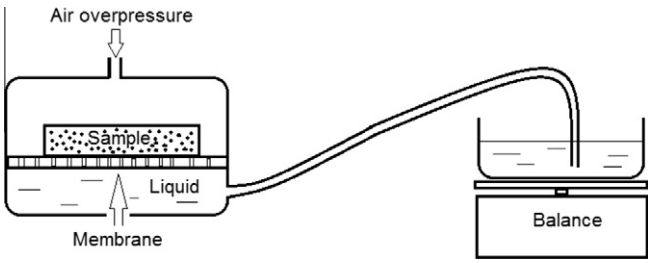

Fig. 2. Principle of wetting-liquid porosimetry, after [9].

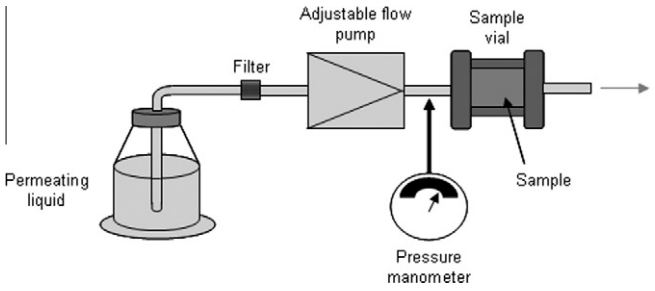

Fig. 3. Set-up of liquid permeametry.

between the two bodies (sample and reference) could be reached through the vapor phase but it would require much longer times than through the liquid phase, which requires a close contact.

The experiment is carried out as follows:

- A sample disc and two porous reference discs (one for each side of the sample disc) are dried, weighed, wetted, stacked and then introduced in the conditioning chamber shown in Fig. 4.
- When capillary equilibrium is reached, the stack is dismantled, the discs are weighed in an appropriate atmosphere (to avoid any further change in the equilibrium).
- The disks are stacked again, their liquid content is decreased (by evacuation or by heating), a new equilibrium is reached, the stack is dismantled and the disks are weighed again: the first point of the pore-size distribution curve can then be derived (the pore-size is provided by the reference whose behavior is known, whereas the pore-volume is derived from the weight change of the sample).

With an appropriate set of porous references, this method allows the assessment of pore sizes between 10 nm and 100 μm, i.e. it provides an interesting complement to wetting liquid porosimetry which, as we saw in Section 2.2, does not allow pores smaller than 10 μm to be assessed.

The method requires a demanding manual procedure, which can be replaced by an automatic manipulator.

4.1.2. Water-desorption calorimetry

The aim of this method is to determine and interpret the water desorption isotherm (along the usual Barrett, Joyner and Halenda lines) in the region of relative pressures containing the information relative to macropores, i.e. above $p/p^0 = 0.99$. This requires a very high temperature stability and homogeneity throughout the sample, together with an accurate determination of p/p^0 and measurement of the amount desorbed [14].

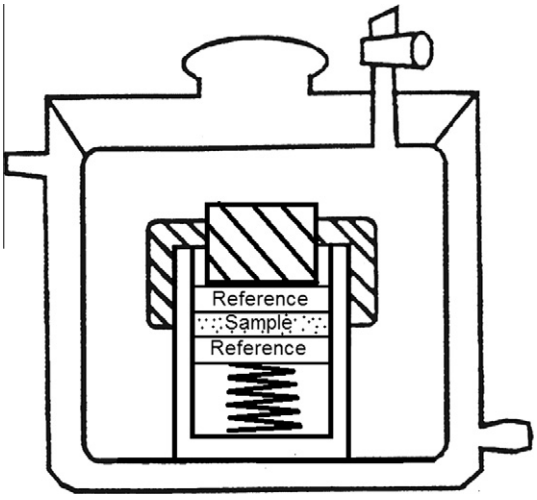

Fig. 4. Clamping device for 3 discs (sample in the middle, reference above and beneath), with its surrounding conditioning chamber, after [13].

These requirements are achieved with a set-up represented in Fig. 5. It makes use of a Tian–Calvet microcalorimeter which simultaneously provides high temperature stability (to within 10^{-5} K) and a continuous record of the amount desorbed from the endothermic signal due to water evaporation. Moreover, a reference cell with pure water is also located within the calorimeter, at that same temperature, which allows an accurate determination (by means of a differential pressure sensor) to be made of the difference between p^0 (above pure water) and p (above the sample).

The method allows pores in the 50 nm–10 μm range to be assessed.

However, it requires special care and sufficient time (typically, 1–3 days) to reach the desired quasi-equilibrium conditions throughout the pressure region of interest. During that time, the experiment is fully automated.

4.2. Freezing–melting

The method relies on the observation, confirmed by simulation, that generally, in a confined medium, the freezing and melting points are depressed. This temperature depression is easy to detect for mesopores, where it can be as high as 100 K but it is much smaller for macropores. The melting point depression is related to the pore width (through an equation analogous to the Kelvin equation) whereas the amount melting is related to the pore volume. The phase change (freezing or melting) and the amount undergoing this change can be detected and determined, as seen hereafter, either by DSC or by NMR. In spite of the theoretical background available to explain the shift of the melting or freezing temperature, both methods require calibration with well-characterized porous reference materials.

4.2.1. Freezing–melting detected by DSC: thermoporometry

Differential Scanning Calorimetry (DSC) is a simple, sensitive and quantitative means to detect freezing or melting. When used for pore-size analysis the custom is to call it "thermoporometry" [15]. With water or hexane it simply requires a cooling unit in addition to the standard DSC equipment. Fig. 6 shows a trace recorded for a macroporous sample. The broader the pores, the slower must be the cooling and heating rates: here, with a pore-width around 90 nm, these rates were set at 2×10^{-2} K min^{-1}. From left to right, one can successively see an endothermal peak (downwards) corresponding to the melting of the water filling the macropores (the heating is stopped just below 0 °C), then, during cooling, the corresponding freezing (exothermal peak) and, during the final heating ramp, the endothermal peak already seen

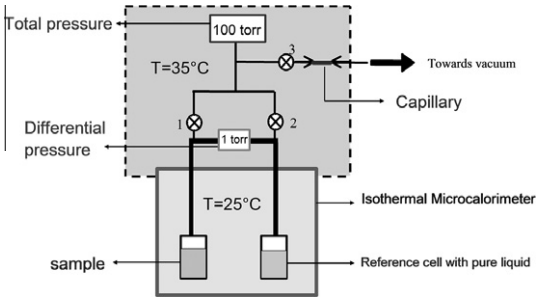

Fig. 5. Principle of a set-up for water-desorption calorimetry.

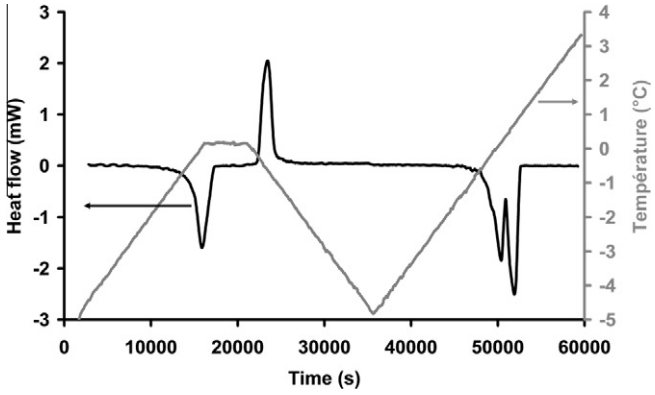

Fig. 6. DSC trace of a thermoporometry experiment (water in macroporous glass), after [16].

but now overlapping with the melting peak of the bulk water coming out of the pores (which melts exactly at 0 °C).

4.2.2. Freezing–melting detected by NMR: cryoporometry

With the spin-echo method, NMR clearly discriminates between the liquid and solid contributions to the signal amplitude and allows quantitative determination [17]. The method requires of course the same range of temperature and the same slow cooling or heating rates as thermoporometry, since the physical phenomenon observed is the same. The method was applied to detect pore widths from 10 nm up to 1 μm with octamethylcyclotetrasiloxane [18].

5. Imaging

5.1. Magnetic resonance imaging

Proton NMR is here carried out with a wetting probe fluid in pores (water, hydrocarbon) [19]. Pores of a width above 10 μm are directly visualized. Smaller pores can be assessed but requires chemically homogeneous samples (pure silica, pure alumina, etc.) and NMR contrast methods (relaxation time or pulsed-field gradient techniques).

5.2. Computerized X-ray tomography

In computerized X-ray tomography, a rotating chamber allows the sample to be viewed from different angles. The intensity of the X-ray beam is recorded and the image reconstruction is accomplished. To be detected, pore widths should be at least 100 nm if a synchrotron source is used and 1 μm if a desktop apparatus is used [20]. Smaller pores can be detected by increasing the contrast with help of a liquid filling the pores, such as mercury or di-iodomethane.

5.3. Electron microscopy

5.3.1. Electron tomography

This technique is similar to computerized X-ray tomography (cf Section 5.2), with a rotating chamber allowing the sample to be viewed from different angles. Now, the X-ray beam is replaced by an electron beam.

5.3.2. Dual-beam electron microscopy

Two beams are used here, namely (i) an ion beam (typically, gallium) to ablate the surface and (ii) an electron beam to obtain the image. This image, obtained for different depths, is used for a reconstruction of a 3-D representation of the void spaces.

A drawback of these two microscopic methods is in their application to heterogeneous samples: the samples are indeed too small (1 μm sample size for 2 nm resolution) to provide a representative sampling, which may lead to an astronomical number of experiments!

5.4. Statistical reconstruction of porous materials

One should recognize that the representations used at present to derive pore-size distribution are generally over-simplified: single pore shape, either cylindrical, or slit-shaped, or in the form of voids between close-packed spheres. It is expected that the statistical reconstruction of porous media should provide results closer to reality than our simplified models. The corresponding section of the IUPAC document therefore provides a "Toolbox for modeling" (with basic principles of stereology [21]) and then examines some ways of modeling, such as trying to mimic the chemical process involved in the formation of the porous material, to reconstruct the material from structural information, or the use of simulated annealing [22]. The section ends by stressing the interest of fractal geometry applied to porous networks [23,24].

6. Macroporous reference materials

As already mentioned, macroporous reference materials (macroporous RMs) are required to calibrate, check and compare the various characterization methods which have been listed. Their certification is not trivial since they must be (i) prepared with the desired pore-size, then (ii) homogenized and (iii) checked for their long-term stability, before they are certified by a well-documented method, with a well-defined procedure, under a recognized authority. In the case of macroporous materials, the method selected for the certification is of course the most widely used, i.e. mercury porosimetry.

About 10 macroporous RMs are now available worldwide, under several trademarks, like BAM (from the German Federal Institute for Materials Research and Testing in Berlin, Germany), ERM® (from the European Community in Geel, Belgium), and SRM® (from the National Institute for Standards and Technology (NIST), in Washington, USA).

7. How to replace or use mercury porosimetry?

Each of the ca 10 methods examined above has its merits, depending especially (i) on the destination of the material and (ii) on the equipment available on-site (for instance NMR, DSC, Electron Microscopy, or the simple apparatus for permeametry).

Some methods are able to provide a realistic pore-size distribution in the macropore range: this is the case for wetting liquid porosimetry, contact porosimetry, water desorption calorimetry, thermoporometry. The two latter still require development to extend their range towards larger pores and to shorten, if possible, the duration of an experiment. Nevertheless, at present there is no other method than mercury porosimetry which can provide in, say, 2–3 h, comparable information over so broad a pore range. We must conclude that to abandon mercury porosimetry would mean a serious loss in the efficiency of research or the routine work on macroporous materials.

Now, if mercury porosimetry is still to be used, are there any means to make it as innocuous as possible? The answer is definitely "yes", provided mercury is clearly considered as a chemical which should be used under strict rules. These rules are simple and mainly involve the systematic use of:

- Protective clothing and gloves.
- A spill tray.
- Mercury containers securely capped or sealed.

- A well-ventilated area to handle mercury.
- A fume hood to clean sample cells.
- A special room, if at all possible, for the mercury porosimeter, with «Tacky Mat» to clean shoe soles.

In addition, one should never override or disable any of the safety devices provided with the equipment (e.g. mercury vapor traps).

Finally, It is not only from an environmental standpoint that it is important to stress that used mercury should be recycled. It can be sent to an appropriate institution or company which specializes in the recycling of mercury. Re-distilled (i.e. triple distilled) mercury can be used again in mercury porosimetry applications.

8. Conclusions

The final conclusions of our Working Group are, first, that we must *stress the importance of developing alternative methods to mercury porosimetry and of extending* the range of application, ease of handling and experimental rapidity of *the methods already existing* today.

However, at least for the time being, there is still no well-established alternative to mercury porosimetry for the characterization of macropores up to 400 μm width.

Hence *it would be wise to treat mercury as a dangerous chemical and to insist on the application of the well-known safety rules.*

Although the application of such rules is common among chemists, it may be a problem in communities less accustomed to handle chemicals and who should therefore receive a special warning and instruction. Then, it is possible to properly control the safe application of mercury porosimetry.

Acknowledgements

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