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A comparison between melting-solidification and capillary condensation hysteresis in mesoporous materials: application to the interpretation of thermoporometry data

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Abstract

A methodology based on thermoporometry is proposed to evidence the hysteresis phenomenon observed between melting and solidification of a confined fluid. This method allows plotting hysteresis loops comparable to those observed for gas adsorption–desorption. It is applied to solids with various pore structure, size or connectivity. The hysteresis loops obtained have common features with those observed for capillary condensation suggesting the same type of classification. These are interpreted by similarities between the microscopic mechanisms of displacement of a phase by another in pore systems.

Keywords: Melting-solidification; Mesoporous materials; Thermoporometry

1. Introduction

Thermoporometry is a characterisation method of porous solids that is based on the study of the melting and solidification of a fluid confined in a porous material. The main idea is to use the heat versus temperature curve determined with a differential scanning calorimeter (DSC) to calculate a pore size distribution. Because the confinement of a fluid in a porous material modifies its phase diagram [1], there is a relationship between the size of the pore and the temperature shift of the phase transition as compared with the bulk value. Moreover, the heat dissipated at the corresponding temperature is proportional to the amount of component that experiences the transition. It means that the peaks that are observed during the melting or the solidification of the confined fluid are directly related to the pore size distribution as well as to the pore organisation. Although it was introduced many years ago [2], thermoporometry has received much less attention than other methods based on capillary condensation. The main reason is that the parameters that are involved in the equations relating pore size and freezing (or melting) temperature are not as well-defined as for liquid–vapour phase changes.

From a thermodynamic analysis analogous to the derivation of the Kelvin equation for capillary condensation, it is possible to derive the following equation in the case of a cylindrical pore:

$$\frac{1}{R_p - t} = -\frac{1}{2\gamma_{sl}} \int_{T_0}^{T} \frac{\Delta H_f}{v_l T} \mathrm{d}T \qquad (1)$$

where, R_p is the pore radius, γ_{sl} the solid–liquid surface tension, ΔH_f the melting enthalpy, v_l the molar volume of the adsorbate, t is the thickness of the bound layer (assumed to be constant), T_0 is the bulk melting temperature and T that in the pore. It means that in the simplest approach the solid–liquid interfacial tension is needed but is not directly measurable contrary to the liquid–vapour interfacial tension that enters in the Kelvin equation. The knowledge of the variation of melting–freezing enthalpy with temperature in the super-cooled range is also needed but not directly measurable in a sufficiently large temperature range. Moreover, the structural state of the solid inside the pores is difficult to identify. Indeed the crystalline variety that is formed in pores may be different from that observed for the bulk transition. For example, in the case of water, cubic or hexagonal ice has been described depending on the pore size and the sample preparation conditions [3,4]. As a consequence, most

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people prefer to use gas adsorption or mercury porosimetry to characterise porous solids, excepted in the case where the drying procedure that is needed for such experiments may change the structure of the materials. Then the use of thermoporometry to characterise polymeric membranes [5] or gels [6] can be interesting. Nevertheless, it must be kept in mind that the deformation of the porous structure may occur during melting–freezing cycles [7].

Many methods are associated with gas adsorption in order to use the capillary condensation phenomena to derive geometric information on the porous materials. Two types of methods can be considered. The first one consists in using equations that relate the pore size and the pressures of pore filling and emptying. The use of an equation can be replaced by regularisation methods that need a set of reference adsorption isotherms theoretically calculated (for example by DFT) [8]. The objective of this type of method is to derive a pore size distribution. The sample is modelled as an assembly of independent pores with a simple shape. The second type consists in studying the hysteric behaviour of the phenomenon to get information on the pore organisation (in terms of pore shape, connectivity and tortuosity). This can be simply done qualitatively by comparing the experimental adsorption–desorption isotherm to the IUPAC classification that proposes some typical behaviour [9,10]. This can be also achieved by trying to model the pore network in a way that allows the hysteresis of adsorption–desorption to be reproduced [11]. Such an approach needs to assume a mechanism for pore filling or emptying.

Thermoporometry has not been developed to this level. In the method proposed by Brun et al. [2], an equation was derived for solidification that is used in many subsequent studies. The value of the parameters were calibrated with the help of reference samples that were characterised by gas adsorption and application of the BJH equation [12]. The hysteretic behaviour were discussed in terms of pore shape factor but the interpretation they proposed has recently been shown to be not applicable to organised model mesoporous adsorbents [13]. It is still a challenge to find a correlation between the hysteretic behaviour of melting–solidification and pore spatial organisation. In order to better understand this phenomenon, which is a priori more complicated than the liquid–vapour phase change, the present paper proposes a qualitative comparison of the two types of phase change. In the first step the mechanisms of phase transition are compared in the case of a simple geometry on the basis of recent theoretical models. Then a method is proposed to plot a hysteresis loop from thermoporometry measurements. Finally this hysteresis loop is compared to that obtained for gas adsorption in the case of a few typical porous systems.

2. Experiments

A set of porous samples was selected that are typical of the IUPAC classification: Licrospheres Si60 and Si100 (provided by Merck, Germany), a controlled pore glass (CPG240), a montmorillonite and one MCM41-type sample (prepared in house and already characterised [14]). The main characteristics of these samples (BET surface area, pore volume, mean pore size calculated by 2V/A) are given in Table 1. The adsorption isotherms of nitrogen or argon were determined with an ASAP2010-Micromeritics apparatus after treatment of the samples under vacuum at 150 °C. The thermogrammes of melting and solidification of confined water were determined with a differential scanning calorimeter (DSC)92-Setaram differential scanning calorimeter. The following procedure was followed: (i) fast cooling of the sample until 180 K, (ii) heating at 1 K min^{-1} until 272 K to study melting and (iii) cooling at -1 K min^{-1} to study freezing.

Table 1
Main characteristics of studied samples

Sample	MCM41	CPG240	Si60	Si100	Montmorillonite
BET surface area ($\mathrm{m}^2\,\mathrm{g}^{-1}$)	439	123	721	380	50
Pore volume ($\mathrm{cm}^3\,\mathrm{g}^{-1}$)	0.5	0.63	1	1.26	
Mean pore radius (nm)	4.5	20	5.6	13	

3. Results and discussion

In the case of an infinite cylindrical pore, it is now admitted that condensation of the liquid occurs at a pressure that ranges between the equilibrium transition pressure and the pressure that corresponds to the end of the metastable range (spinodal) [15]. For narrow mesopores the adsorption occurs at equilibrium (reversible adsorption isotherm), whereas, for large pores the adsorption will occur close to the spinodal limit. This mechanism is applicable to real solids provided the pore length is long enough. Desorption is assumed to be observed at equilibrium because the barrier to vapour nucleation is eliminated by the presence of the liquid–vapour interface at the open end of the pore. The same vision was recently proposed for melting and solidification [13]. By using a simple phenomenological model, melting was supposed to occur at the end of the metastable range: the only condition is that of surface melting, which means that the pore wall is preferentially wetted by the liquid rather than by the solid phase. There is then a layer of a liquid-like phase between the solid and the pore walls (the so-called bound layer that has been evidenced by many different methods [16–18]). Melting occurs through the growth of this layer as capillary condensation does through the growth of the adsorbed film. Solidification is then supposed to occur at equilibrium. Experimentally, the way to overcome the nucleation barrier that may delay the freezing is to follow the procedure suggested by Brun et al. [2]. An excess of liquid is used and the system is first frozen at a very low temperature in order to obtain the solid phase throughout. The temperature is then increased to study the melting inside the pores until a value that is lower than the bulk melting temperature. The temperature is then decreased for studying solidification. By this procedure the solid phase always exists at the entrance of the pores, which can act as nuclei for solidification inside the pores. In the case of cylindrical pores, the relationship between pore size and temperature is then derived from the thermodynamic equilibrium condition for a hemispherical liquid–solid interface and from the thickness of the bound layer. For example, to integrate Eq. (1), Quinson and co-workers [2] have done a careful analysis of the temperature influence on the various parameters. An equation of the type $R = A + B/\Delta T$ is obtained that relates pore size and temperature shift.

The first conclusion of this analysis is that the mechanisms for condensation and vaporisation parallel those of melting and solidification, respectively. It means that if a porous medium is built of independent cylinders, both methods should give the same pore size distribution and hysteresis loop (that will be later defined for thermoporometry), provided the suitable parameters are used. Type H1 hysteresis are expected.

Independently of pore shape, the two main features that distinguish a real pore system from an assembly of cylinders is the presence of connections between pores and the existence of pores whose size is larger than that of their entrance (bottle neck effect). The simplest way to consider such a situation is to study the case of a sphere connected to the exterior through two cylinders [18]. As discussed recently from both experimental and theoretical results [19,20], the filling of the spherical part, after filling of cylinders, will occur at a pressure between the equilibrium transition pressure and the end of the metastable range pressure, whereas, desorption is a competition between the cavitation inside the spherical part and the emptying through the cylinders (pore blocking effect) that are connected to outside. The result depends on the relative radius of spheres and cylinders. The discussion can be found in the quoted references [19–21]. Here the aim is only to stress that the same behaviour can be expected from melting and solidification. Melting should occur first in cylinders then within the cavity. The transition temperatures could be calculated by the same phenomenological model (the equilibrium transition temperature was already calculated) [13]. Solidification should be a competition between the solid phase advancing through the cylinder and the nucleation of the solid phase inside the cavity. It must be stressed that the interpretations given here about the hysteresis are totally different from that of Quinson and co-workers [2] which is used by many other authors. Indeed, they assumed that the hysteresis width is mainly due to pore shape and they deduce a pore shape factor from experimental data. At the opposite it was shown recently [13] that even for a simple cylinder the pore width depends on pore size. These authors also often argued that thermoporometry gives the size of the cavities, whereas, gas desorption gives that of their opening. This is also different from our interpretation that proposes the same type of competition between pore blocking effects and nucleation for the two phenomena.

If the developed arguments are correct, one can imagine that for any porous material, the hysteretic behaviour could be the same for the two types of phenomena. The hysteretic behaviour of capillary condensation is evidenced by the hysteresis loop that is the reflection of how the system is filled or emptied with gas molecules. Usually calorimetric peaks are obtained from DSC measurement. By using a simple integration procedure described in Fig. 1, it is possible to get a hysteresis loop defined by melting and solidification branches (the other possibility would have been to derive the adsorption isotherm to compare with calorimetric peaks).

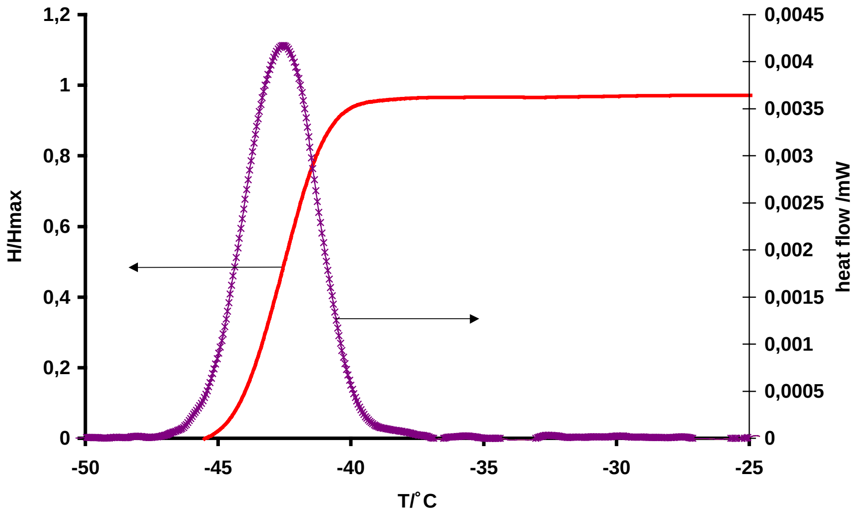

Fig. 1. Integration procedure of a solidification peak obtained in thermoporometry. It is transformed in the solidification branch of the melting–solidification hysteresis. H, the integrated value at a given temperature is divided by the total enthalpy of solidification $H_{\max}$. The same type of figure would be obtained with melting.

The calorimetric peak is integrated as a function of time, which allows the integral enthalpy of the transformation to be calculated and plotted as a function of temperature. The same integration can be done for both melting and solidification. The peaks are then transformed in two-step curves that are normalised in order to join each other at the beginning and the end of the processes, thus, forming a hysteresis loop as shown in subsequent figures. Because the enthalpy is proportional at a given temperature to the amount of fluid that has changed state, these curves parallel those of adsorption and desorption, which are directly related to the volume of pore filling. One problem specific to thermoporometry is the temperature dependence of the melting enthalpy. It means that the proportionality between integral enthalpy and pore volume is more temperature dependent than the proportionality between amount adsorbed and pore volume is pressure dependent. Nevertheless, one can qualitatively compare the two types of hysteresis despite the fact that the information reported on the X-axis, which is the temperature shift for the phase change in the porous medium with reference to the bulk, looks very different from the relative pressure reported in gas adsorption experiments. This temperature shift is directly related to the variation of chemical potential of the fluid on solidification or melting inside the confined space. At a given temperature T, it can indeed be written as follows [13]:

$$\mu_s - \mu_l = \overline{\Delta_{\text{fus}} h}\left(\frac{T - T_0}{T_0}\right)$$

where, μ_l and μ_s are the chemical potentials of the non-confined liquid and solid phases at temperature T, respectively, and where, T_0 is the bulk melting temperature. $\overline{\Delta_{\text{fus}} h}$ is the mean melting enthalpy of the considered fluid in the (T, T_0) temperature range. This difference of chemical potential is the driving force for solidification. It means that the temperature shift ($T_0 - T$) is proportional to this chemical potential difference. As a consequence this X-scale of thermoporometry is comparable to the

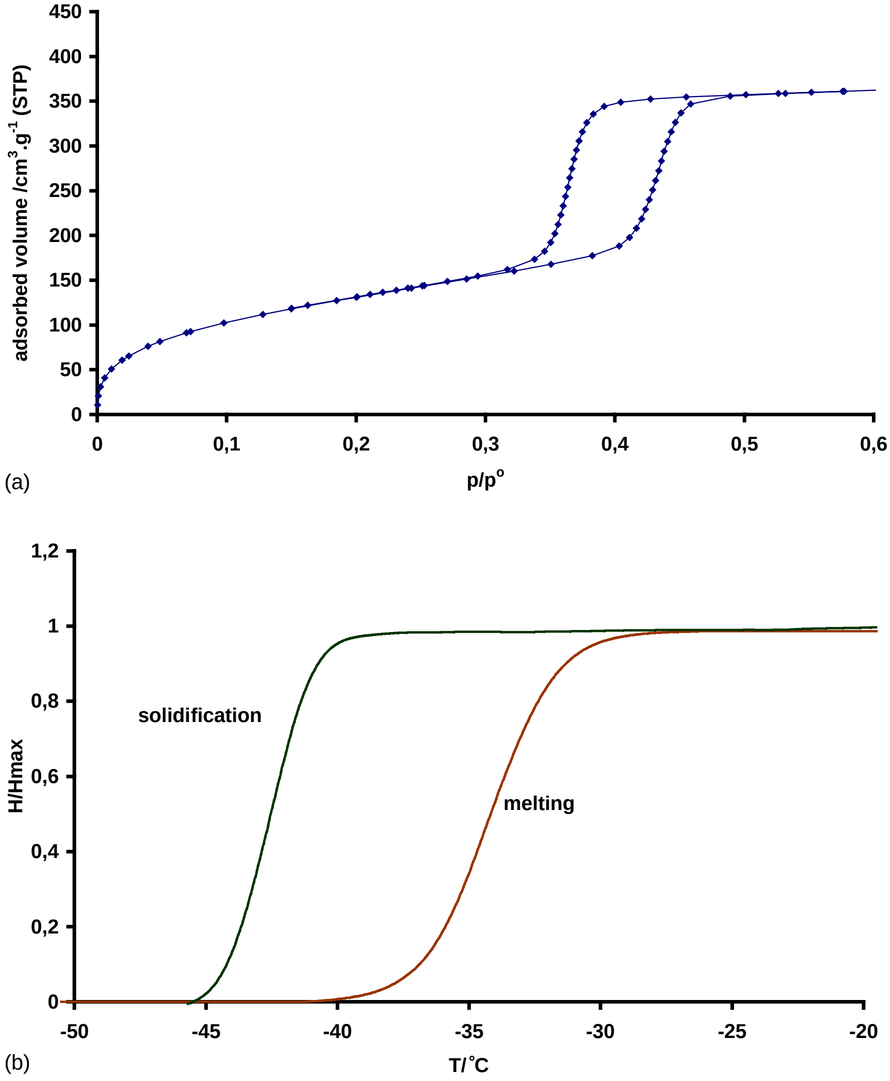

Fig. 2. Adsorption–desorption isotherm of argon at 77 K (a) and melting–solidification integrated curves (b) for MCM41.

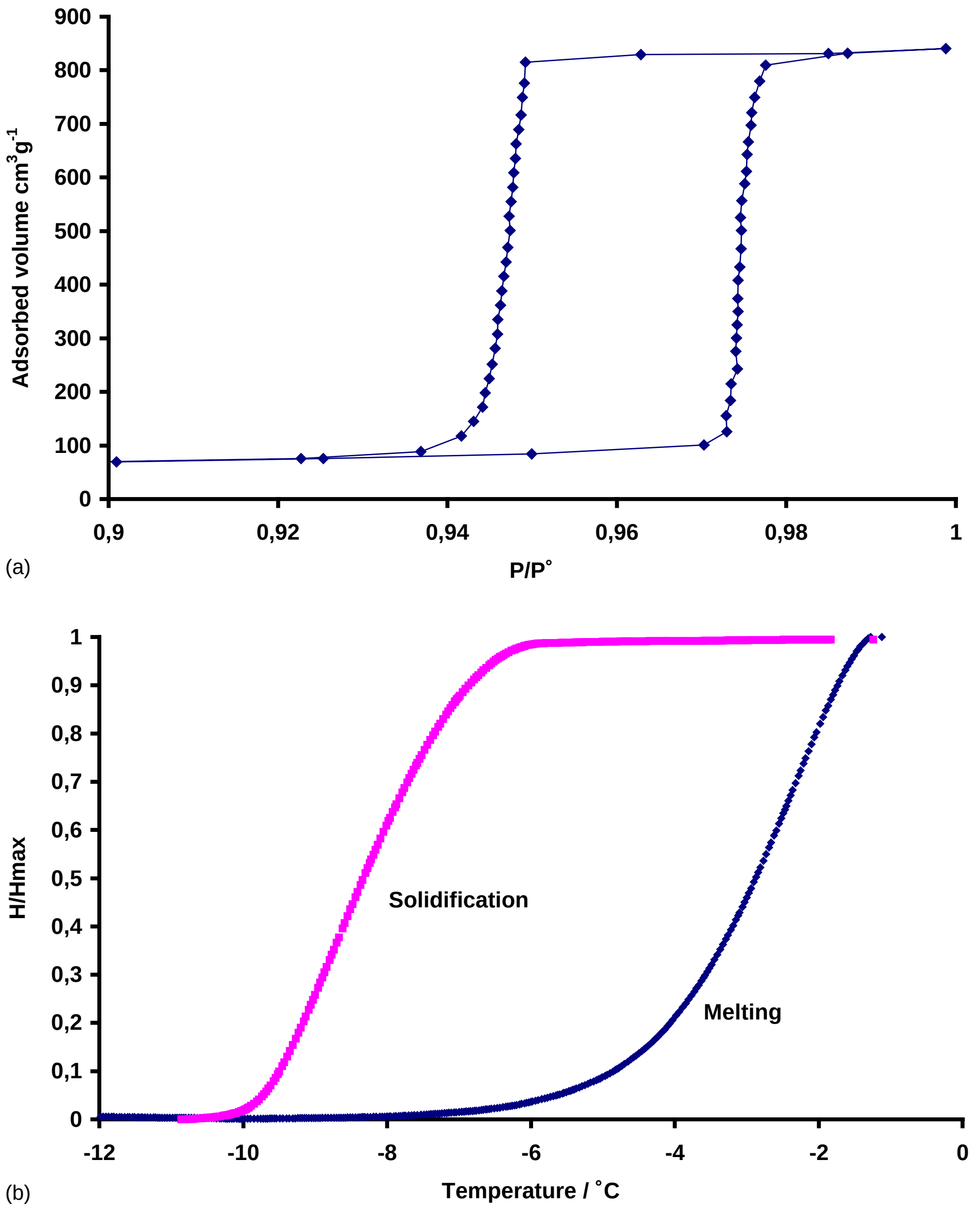

Fig. 3. Adsorption–desorption isotherm of argon at 87 K (a) and melting–solidification integrated curves (b) for CPG240. Only the hysteresis part is presented.

relative pressure scale of gas adsorption since one may write:

$$\mu_l - \mu_g = -RT\ln\frac{P}{P_0}$$

where, μ_l is the chemical potential of the liquid at P_0 and μ_g is the chemical potential of the gas at pressure P (the difference here is the driving force for liquefaction).

A first comparison is done in Figs. 2 and 3 that presents type H1 hysteresis loops for capillary condensation. Fig. 2 corresponds to a MCM-41 type sample (the structure has been controlled by X-ray diffraction), which mean that the sample is made of non-interconnected pores with a narrow pore size distribution. The gas adsorption–desorption isotherm (Fig. 2a) shows a hysteresis loop with parallel branches and a well-defined saturation plateau. The calculated hysteresis loop for melting–solidification that is presented in Fig. 2b presents exactly the same characteristics. Fig. 3 corresponds also to the case of a type H1 system, but it is a controlled pore glass (CPG240) that presents also a type H1 hysteresis loop despite the fact that it is a highly connected porous material [22]. The good agreement between the two type of hysteresis (Fig. 3a and b for adsorption and calorimetric experiments, respectively) is nevertheless again observed. Two examples of type H2 isotherm are given in Fig. 4a. They correspond to silica porous solids that are used in chromatography. The synthesis procedure of such silica leads in general to an assembly of spheres that constitutes a

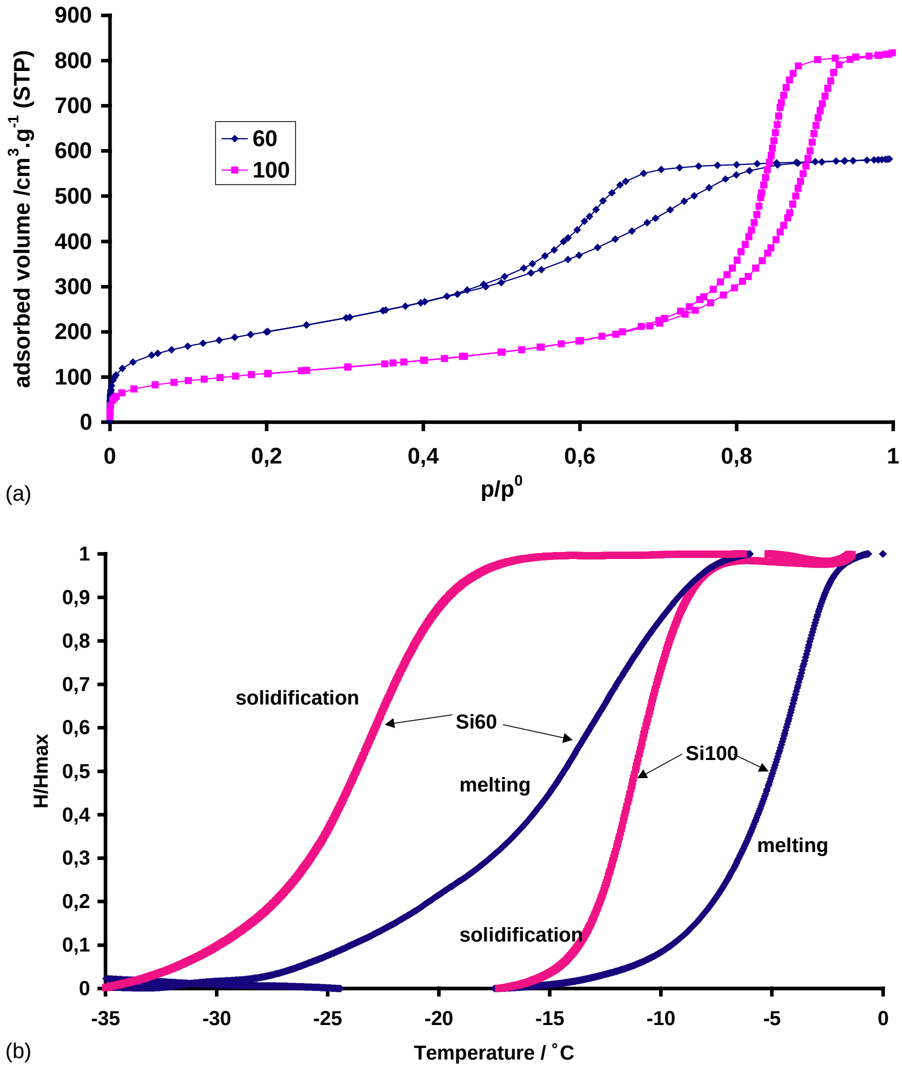

Fig. 4. Adsorption–desorption isotherm of nitrogen at 77 K (a) and melting–solidification integrated curves (b) for lichrospheres Si60 and Si100.

highly connected system. Again the hysteresis loop obtained by thermoporometry (Fig. 4b) is very similar to that of gas adsorption. A similar result was obtained recently by Soprunyuk et al. [23] who calculated the amount of liquid argon in the pores of Vycor as a function of temperature from heat capacity measurements during melting–solidification cycles. They did not discuss their results in the same manner as here but the similarity of the hysteresis loop they obtained with their adsorption isotherm of argon is striking. Another interesting result they showed is that the hysteresis loop is only reproducible if the porous system is full of liquid. When it is not full, one can also observe that there is a delay for solidification but with a lower limit temperature that is the same for many of the partially filled samples. This behaviour reminds that of many desorption isotherms that show a sharp return on the adsorption branch when the pressure of the end of hysteresis is reached (around 0.42 for nitrogen). This phenomenon is probably related to the cavitation that occurs in pores that are connected to the exterior by very small pores. In the case of Soprunyuk et al. [23] results, it may be due to the existence of domains that solidify when a sufficiently low temperature is reached even if solidification has not yet occurred in the neighbouring pores that are narrower. Like capillary condensation, the phenomena of melting–solidification is indeed reversible below a given size.

A class of samples that give an adsorption–desorption isotherm with a sharp return of the desorption branch on the adsorption branch at the end of the hysteresis is that defined by H3 type loops. Experimentally, clay samples and other lamellar solids give rise to such behaviour. As an example, the adsorption–desorption of nitrogen on a montmorillonite sample is given in Fig. 5a. This sample was also tested by thermoporometry using the proposed integration method. Again there are common points between the hysteresis loop such obtained (Fig. 5b) and that of Fig. 5a. Notably, the shape of the hysteresis at the closure point at low temperature is the same as that of gas adsorption, with a sharp return of the solidification branch on the melting curve. The behaviour

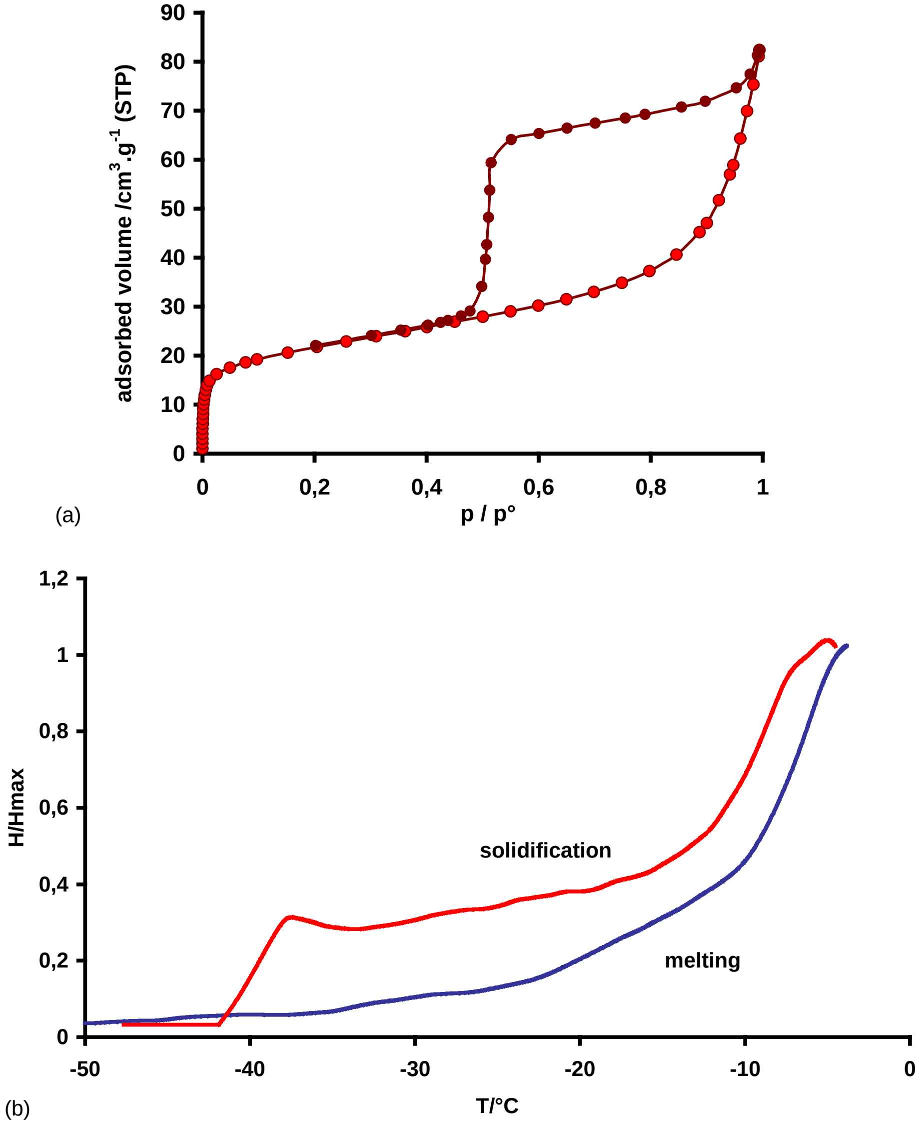

Fig. 5. Adsorption–desorption isotherm of nitrogen at 77 K (a) and melting–solidification integrated curves (b) for montmorillonite.

seems different at high temperature, which corresponds to high relative pressure. The reason may be that the state of the montmorillonite in water cannot be exactly the same as its dry state due to the swelling of the structure.

4. Conclusions

The general conclusion of this work is that the mechanism of melting and solidification in complex pore systems parallels that of adsorption and desorption, respectively. It means that when a phase replaces the other (liquid > gas or liquid > solid) the way followed by the advancing front, defined by the interface between the considered phases, is the same. For independent pores with a simple shape, the mechanism of melting proceeds through the increase of the liquid surface layer thickness until a sufficiently unstable state is reached in the same way as capillary condensation proceeds through the increase of the adsorbed layer thickness. In the same way, provided a suitable experimental procedure is used, solidification corresponds to the advancing of the solid–liquid interface from outside to inside the pore in the same way as capillary evaporation corresponds to the advancing of the vapour–liquid interface. In the case of complex shape and connectivity of the pore system, the mechanism of phase change depends also on the nucleation of one phase in the other. Under the conditions of surface melting that prevents heterogeneous nucleation, solidification may occur through the homogeneous nucleation of solid nucleus inside the pore in the same way as the nucleation of a small bubble may occur along the desorption branch. This is the similarity between the microscopic mechanisms that leads to the similarities between the shapes of the measured hysteresis loops. A classification could be defined in thermoporometry with the same meaning (but also the same limits) as gas adsorption classification. These conclusions are applicable to porous systems that are not deformed or damaged during freezing–melting cycles.

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