THREE-DIMENSIONAL RECONSTRUCTION OF LIQUID PHASES CONFINED IN DISORDERED POROUS MEDIA: AN IN SITU SYNCHROTRON SAS ANALYSIS

Gommes, C. J.[1], Hermida Merino, D.[2]

[1] *Department of Chemical Engineering, University of Liège, B6A, 3 allée du 6 Août, B-4000 Liège, Belgium*
[2] *Dutch-Belgian Beamline, European Synchrotron Radiation Facility, 6 rue Jules Horowitz BP220, 38043 Grenoble Cedex 9, France*

SUMMARY

We use Synchrotron Small-Angle X-ray Scattering to investigate temperature-induced morphological changes in binary hexane/nitrobenzene solutions confined in the pores of disordered mesoporous solids. The scattering data is analyzed with a plurigaussian model, which enables us to reconstruct the 3D morphology of the phases with a nanometer resolution. The reconstructions bring to light wetting transitions whereby the morphology of the nitrobenzene passes from a nanometer-thin layer that uniformly covers the solid surface to plugs that locally occlude the pore space. Our analysis enables us to quantitatively analyze the SAS data in terms of changing interface areas and wetting angles. The present contribution offers unprecedented insight into nanometer-scale wetting transitions. It also presents a novel SAS data analysis methodology that is applicable to a host of experimental situations involving disordered mesoporous materials.

INTRODUCTION

Numerous technologies and chemical processes exploit physicochemical phenomena that take place inside nanopores. Heterogeneous catalysis, adsorption separation processes, kinetically selective membrane processes are but a few examples. To fully understand the performance of nanoporous materials for specific applications and to develop new ones, it is therefore key to develop methodologies for the in situ analyses of matter confined in nanopores with *a resolution comparable to the pore size*. In the case of mesoporous materials (pore sizes from 2 nm to 50 nm) Small-Angle Scattering is close to being the only option.

Recently, many in situ SAS studies have been conducted with ordered mesoporous materials, which considerably simplifies the data analysis compared to disordered materials (e.g. Hofmann et al, 2005). However, this type of approach suffers from two drawbacks. First, there is increasing evidence that disorder plays a crucial role in determining the phase equilibria inside nanopores (Wallacher, 2004). Slight deviations from geometrical ideality can play the role of nucleation sites, and trigger phenomena that would otherwise not happen (Gommes, 2012). Second, the choice of a particular material for any engineering application results from a difficult compromise between several properties, and being ordered in never one of them (Rolison, 2003).

In the present contribution, we present a general SAS methodology to analyze in situ phenomena in disordered nanoporous materials. In particular, we propose a novel data analysis methodology, based on plurigaussian models (Armstrong et al, 2003), that enables one to reconstruct the morphology of the pore-filling phases. We illustrate its potential by applying it to the analysis of temperature-induced morphological transitions in near-critical hexane/nitrobenzene solutions imbibed in the pores of a resorcinol/formaldehyde gel (Gelb et al, 1999).

EXPERIMENTAL

Resorcinol/formaldehyde (RF) gels were synthesized as described elsewhere (Job et al, 2004). The gels were aged for 3 days at 70 °C, and their mother liquor was then exchanged to nitrobenzene/hexane solutions of various concentrations. The solvent exchange was performed in two steps with acetone as an intermediate.

In situ Small-Angle and Wide-Angle X-ray Scattering was then measured on the samples, while the temperature was progressively decreased from +30°C to -30°C at the rate of 1°C per minute. All the measurements were conducted at the Dutch-Belgian beamline (BM26) at the European Synchrotron Radiation Facility in Grenoble, France, on a setup fully described elsewhere (Bras et al, 2003). The data are expressed in terms of the scattering vector q.

RESULTS AND DISCUSSION

Figure 1 displays typical Small-Angle (SAXS) and Wide-Angle (WAXS) scattering patterns measured on a RF gel imbibed with near-critical nitrobenzene/hexane solution (about 42 mol. % nitrobenzene) when the temperature is decreased from 30°C down to -30°C.

The SAXS patterns are initially qualitatively similar to those measured on the gel imbibed with a pure nitrobenzene solution. Some extra scattering appears at low angles below +15°C, which points to some structural changes in the system at the nanometer scale. It is interesting to note that the WAXS patterns exhibit no change before the temperature of -15°C is reached. Below that temperature some Bragg peaks appear which are typical of solid nitrobenzene.
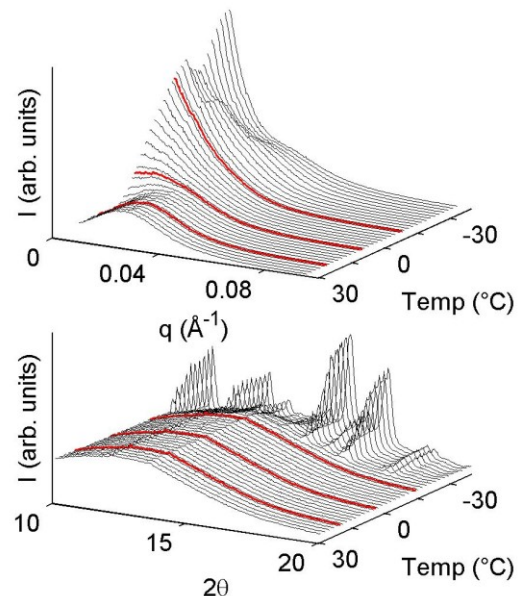

Figure1. Small-Angle (top) and Wide-Angle X-ray (bottom) scattering of a RF gel imbibed with critical nitrobenzene/hexane solution, measured while cooling from +30°C to -30°C. The three highlighted profiles are analysed further in Fig. 2.

An interesting feature of the SAXS data is that the total scattered intensity Q (Porod's invariant) is a constant above -15°C. This means that the extra scattering that appears at low angles is almost compensated by a simultaneous decrease at large angles which is not visible on the scale of Figure 1. The absence of WAXS signal, and the constancy of Q, proves that the evolution of the SAXS pattern above -15°C has to be analyzed in terms of a nanometer-scale reorganization of existing liquid phases.

The SAXS data was analyzed using a plurigaussian model (Armstrong et al, 2003), which is a generalization of the clipped Gaussian field model that we used previously to analyze the structure of RF gels (Gommes and Roberts, 2008). The detailed analysis will be published elsewhere (Gommes and Hermida Merino, in preparation); we only briefly discuss here the main steps of the analysis and the results.

The systems analyzed here are three-phasic: they comprise the solid phase of the RF gel and the two pore-filling liquid phases. The SAXS patterns have therefore to be analyzed in terms of a linear combination of three correlation functions, one for each phase, with the coefficients depending on the electron density of all phases. The basic assumption of our analysis is that the solid phase remains unchanged during the process. The correlation function of the solid phase of the RF gel was determined once and for all from a SAXS pattern measured on a gel imbibed with pure nitrobenzene. The evolution of the SAXS in Figure 1 was subsequently analyzed in terms of the morphology of the pore-filling phases alone. Typical reconstructions obtained through this approach are reported in Figure 2, for the same temperatures as highlighted in Figure 1.
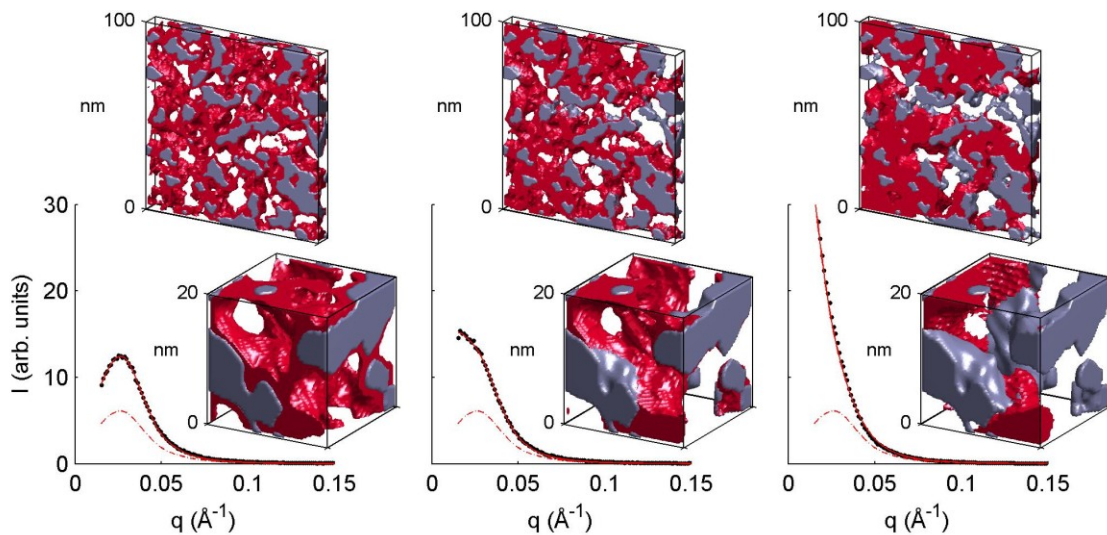

Figure 2. Reconstructed nanostructure of the nitrobenzene/hexane phases confined in the pores of a RF gel at T=20°C, 5°C and -14°C (from left to right) corresponding to the temperatures highlighted in Figure 1. The solid phase is grey, the red phase is the nitrobenzene, and the remainder of the pore is the hexane phase that is not represented. Two reconstructions are shown at each temperature, corresponding to two different length scales. The experimental SAXS patterns are shown (•) together with the SAXS curves of the reconstructions (red line). The theoretical SAXS curves of the gel filled with a homogeneous hexane/nitrobenzene solution is shown for comparison (dashed red line)

The reconstructions bring to light a wetting transition, whereby the morphology of the nitrobenzene passes from a layer that covers uniformly the solid surface (Figure 2, left) to plugs that locally occlude the pore space (Figure 2, right). It is interesting to note that in the layer configuration, there is no contact between the hexane and the solid. However, upon cooling some patches appear on the solid surface, which are in contact with hexane (Figure 2, middle).

The use of a plurigaussian model enables us to derive sophisticated parameters to describe the contact between the various phases: interface areas, specific length of the triple line, and contact angles (Gommes and Hermida Merino, in preparation). Figure 3 plots the temperature-dependence of the hexane/nitrobenzene interface area and of the nitrobenzene/solid contact angle.

Figure 3. Two structural parameters derived from the SAXS data as a function of temperature: hexane/nitrobenzene interface area $S_{H/N}$ (Δ), and nitrobenzene/solid contact angle $\theta_{N/S}$ ($\square$).

This figure provides insight into the driving force of the process. A macroscopic hexane/nitrobenzene solution has an upper critical temperature at 20.3 °C. Accordingly, the surface tension of the hexane/nitrobenzene interface vanishes above that temperature and increases when the temperature is lowered. Therefore, low interface areas are favored at lower temperature. This is in agreement with the SAXS data (Figure 3) that shows that the dewetting process leads to a more than twofold decrease of the hexane/nitrobenzene interface area.
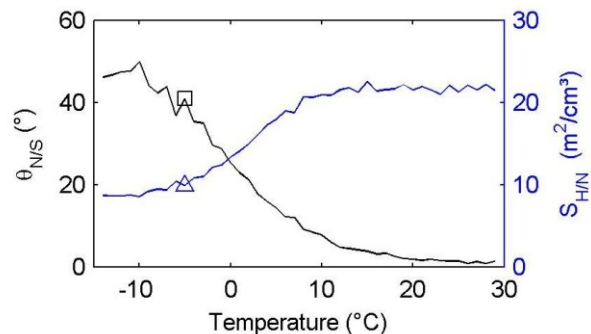
CONCLUSIONS

Plurigaussian models are extremely convenient to analyze in situ SAS data measured on disordered mesoporous solids. We have illustrated this by applying them to synchrotron SAXS data obtained on RF gels imbibed with hexane/nitrobenzene solutions.

The data analysis method that we developed enables us to reconstruct the morphology of the various phases present in the system, and to characterize them though sophisticated parameters such as interface areas, specific length of the triple line, and contact angles. Our analysis shows that the observed nanometer-scale changes result form an increase of the surface tension of the hexane/nitrobenzene interface.

Our SAS data analysis methodology is applicable to a host of experimental situations involving disordered mesoporous materials, notably capillary condensation, and to any three-phase system in general.

ACKNOWLEDGMENTS

REFERENCES

Armstrong, M., Galli, A.G., Beucher, H., Loch, G., Renard, D., Doligez, B., Eschard, R., Geffroy, F. Plurigaussian Simulations in Geosciences. Berlin: Springer, 2003.

Bras, W., Dolbnya, I. P., Detollenaere, D., van Tol, R., Malfois, M., Greaves, G. N., Ryan, A. J. and Heeley, E. Journal of Applied Crystallography 36**,** 2003, 791-794.

Gelb, L.D., Gubbins, K.E., Radhakrishnan, R., Sliwinska-Bartkowiak, M. Reports on Progress in Physics, 62, 1999, 1573-1659.

Gommes, C.J. and Roberts, A.P. Physical Review E, 77, 2008, 041409.

Gommes, C.J. Langmuir, 28, 2012, 5101-5115.

Gommes, C.J, Hermida Merino, D. in preparation.

Hofmann, T., Wallacher, D., Huber, P., Birringer, R., Knorr, K., Schreiber, A. and Findenegg, G.H. Physical Review B, 72, 2005, 064122.

Job, N., Pirard, R., Marien, J., Pirard, J.-P. Carbon, 42, 2004, 619-628.

Rolison, D.R. Science, 299, 2003, 1698-1701.

Wallacher, D., Künzner, N., Kovalev, D., Knorr, N., Knorr, K. Physical Review Letters, 92, 2004, 195704.